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# WORKSHOP

ON

# CO-PRODUCTS AND BY-PRODUCTS OF THE BAYER ALUMINA PRODUCTION

**Budapest, Hungary**

**2̶5̶ November - 6 December 1991.**

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ON

# CO-PRODUCTS AND BY-PRODUCTS OF THE BAYER ALUMINA PRODUCTION

Budapest, Hungary

25 November - 6 December 1991.

# CO-PRODUCTS AND BY-PRODUCTS OF THE BAYER ALUMINA PRODUCTION

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# CHAPTER 1

## APPLICATIONS AND DEVELOPMENT OF PRODUCTS CONTAINING ALUMINA AND/OR ALUMINIUM TRIHIDROXIDE

# 1.1 MAIN TRENDS OF THE FURTHER DEVELOPMENT OF THE ALUMINA PRODUCTION: GEOGRAPHICAL AND PRODUCT RESTRUCTURING

K. Solymár

After some very attractive years of the world aluminium industry characterized by extremely good market situation for aluminium and alumina, great efforts are required again in order to maintain the profitability of the metal grade alumina production, especially relating to the alumina refineries of smaller capacity and located far from the bauxite deposits.

The main ideas of the keynote speech of Mr Jacques Bougie (ALCAN) held at the Light Metals Luncheon in Anaheim, USA in February 1990 are world-wide actual for the whole verticum of the aluminium industry:

"... what I regard as the four key issues: better management of our manufacturing operations, the development of new products and markets, rising environmental expectations and, last but not least, recycling."

As far as the main tasks of the European aluminium industry are concerned, Mr. Th. M. Tschopp (EAA Chairman and Executive Vice-president) emphasized the following [1]:

1. "We must optimize and speed up technical development. We must increase the quality of our products, must create more products designed for customers needs, must modernize our plants and intensify the search for new materials.

2. We must optimize the economics of our businesses. We must concentrate our investments accordingly and be prepared for new partnerships that give us strength under new market conditions such as the "United Europe".

All these mentioned points of view are referring to the alumina production, too. The main trends of the world-wide development of Bayer process are nowadays the reduction of the production costs of alumina and the increase of the efficiency of the equipment [2].

The metal grade alumina production is determined by the large alumina plants located close to the huge bauxite deposits. Consequently, rearrangement of aluminium industry is already in course, the new capacities are built mainly in Australia, Brazil, India, Venezuela and China where raw materials, energy and market are simultaneously available. This is the geographical restructuring of the world alumina production.

The importance of the production of chemical grade alumina and
valuable by-products, e.g. zeolites and gallium, is increasing,
first of all in the smaller alumina refineries. This product
restructuring between the metal grade and chemical grade alumina
production is the most significant actual trend to remain
competitive with the large capacity refineries focused on metal
grade alumina production.

It should be mentioned, however, that the production of co-
products and by products of the Bayer alumina production can be
also more economic when it is combined with the economic
production of metal grade alumina, that is low-price hydrate,
alumina and process liquor is available for further special
manufacturing.

Furthermore, sometimes the erection of smaller capacities of
aluminium-hydroxide/alumina plants can also be justified in order
to produce mostly or only more valuable special products, first
of all where the market demand is existing already.

## 1.1.1 Geographical restructuring of the world alumina industry

The geographical restructuring of the primary world aluminium
industry can be evaluated by studying the changing alumina
refinery and aluminium smelter capacities (including both the
metal-grade and non-metal grade alumina production) in the
function of time.

Furthermore, the future trends of the territorial development of
the world alumina industry can be forecast by means of the
comparative evaluation of alumina production potential and costs
by region and by countries.

### 1.1.1.1 Changing of the alumina refining and smelter capacities
by region

The already mentioned geographical restructuring of the world
aluminium industry can be studied by means of the changing of the
alumina refining and smelter capacities by region in time. The
data published by Mr. R. R. Kalpoe [6] are plotted in Figure 1.11
and Figure 1.1-2, respectively.

It can be seen that the most attractive increase both in alumina
refining and smelter capacities in Latin America (Brazil and
Venezuela) and China is expected. The comparison of the smelter
capacity with the equivalent alumina refinery capacity by region
in Figure 1.1-2 indicate the world trade of the metallurgical
grade alumina.
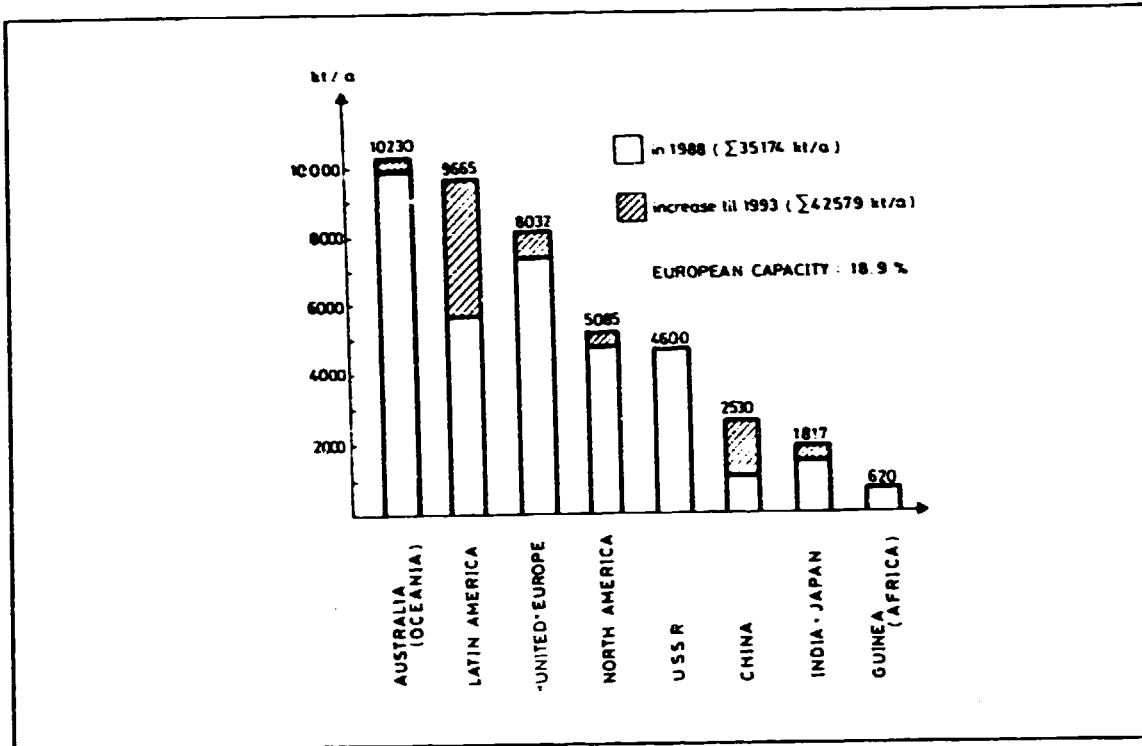
Figure 1.1-1
Alumina refining capacity by region [3]
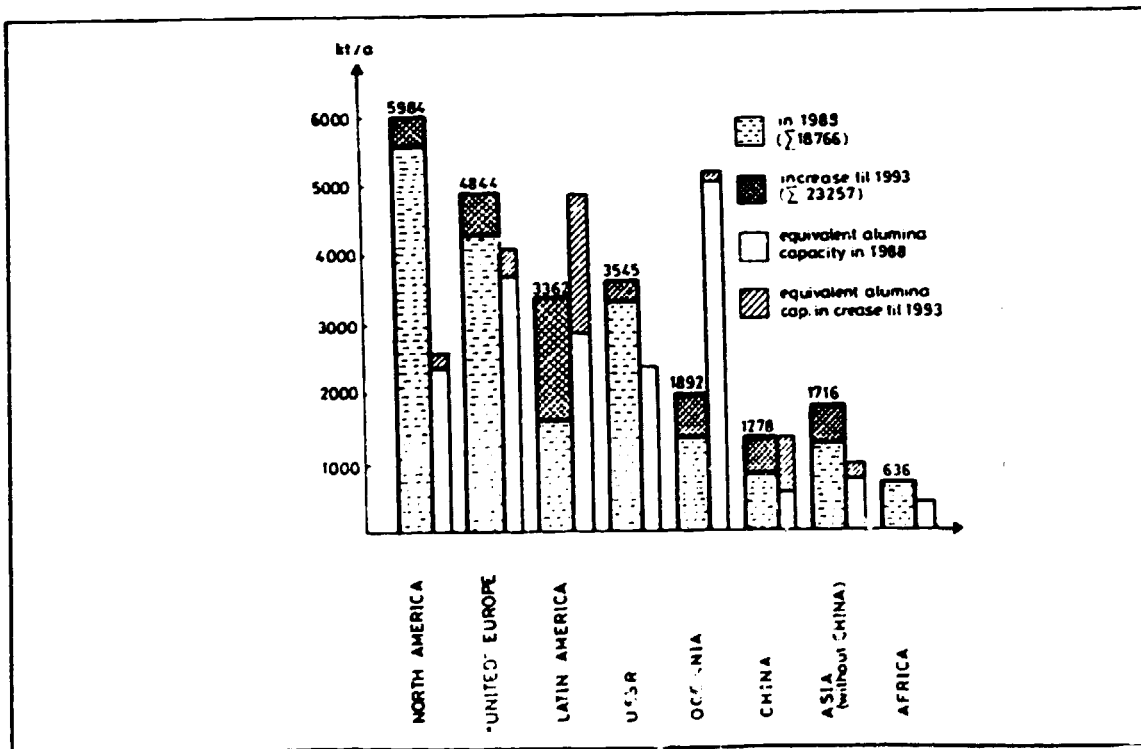


Figure 1.1-2
Primary aluminium smelter capacity by region[3]

The alumina plant closures 1980-88 are summarized in Table 1.1-1 [3].

**Table 1.1-1**
**Alumina plant closures 1980-1988 [3]**

| Region | Country/refinery | Closed capacity | |
|---|---|---|---|
| NORT AMERICA | USA, Mobile (Alcoa) | 800 | (1982) |
| | USA, Baton Rouge (Kaiser) | 730 | (1983) |
| | USA, Hurricane Creek (Reynolds) | 650 | (1983) |
| | USA, Burnside (Ormet) | 635 | (1985)(1) |
| | US Virgin Island (M.Marietta) | 550 | (1985) |
| EUROPE | Italy, Porto Marghera | 200 | (1981) |
| | Yugoslavia, Obrovac | 300 | (1982) |
| | France, Salindres (Pechiney) | 270 | (1984) |
| | W.Germany, Lünen (VAW) | 450 | (1987) |
| | W.Germany, Ludwigshafen (ALCOA) | 140 | (1988) |
| CARIBBEAN | Guyana, Linden (Bidco) | 300 | (1982)(2) |
| | Jamaica, Alpart (Kaiser, Reynolds) | 1180 | (1985)(3) |
| ASIA | Taiwan, Talxo | 140 | (1981) |
| | Japan, Yokohama (Showa) | 200 | (1983) |
| | Japan, Kikumoto (Sumitomo) | 740 | (1984) |
| | Japan, Wakamatsu (Mitsui) | 300 | (1985) |
| | Japan, Tomakomai (NLM) | 360 | (1987) |
| TOTAL CLOSURES | | 7945 ktg | |

(1) Recommissioned in October 1988.
(2) To be reopened in the short to medium term.
(3) Reopened early 1989.
SOURCE: IBA SECRETARIAT

Major increases of alumina capacity can be seen in Table 1.1-2 based on the data published by D. Wilks, IBA secretariat [4].

According to G. Bárdossy [5] the world bauxite reserves can cover the needs of humanity for at least 250 to 300 years because the total amount of the known bauxite reserves amounts to 38.8 billion tons and additional 23 to 30 billion tons of bauxite resources are indicated. Fortunately, 81% of the global reserves occur in surface deposits and further 14 % can be mined in open pits after stripping of the overburden. In consequence, the perspectives of the underground mining are very limited.

**Table 1.1-2**
**Major instances of alumina capacity increases 1985-1989 (kty) [4]**

| Country | Refinery | Capacity | Remarks |
|---------|----------|----------|---------|
| USA | Ormet | 565 | Re-start |
| Australia | Gove | 250 | Expansion |
| Australia | Wagerup | 200 | Expansion |
| Australia | QAL | 160 | Expansion |
| Jamaica | Alpart | 600 | Re-start |
| Jamaica | CAP | 100 | Expansion |
| Venezuela | Interalumina | 250 | Expansion |
| Brazil | Sao Luis | 200 | Expansion |
| Suriname | Paranam | 250 | Expansion |
| India | Nalco | 800 | New Refinery |
| | TOTAL | 3.375 | |

The distribution of alumina capacity of the "Western World" by size in 1970 and 1988 is compared in Figure 1.1-3. It can be seen, that 50% of the total alumina production in 1988 was made by the refineries of above 1000 kt/a capacity and that of 14 % only in the relatively small refineries (under 500 kt/a capacity). The plant capacity is a determining factor in the competitiveness.
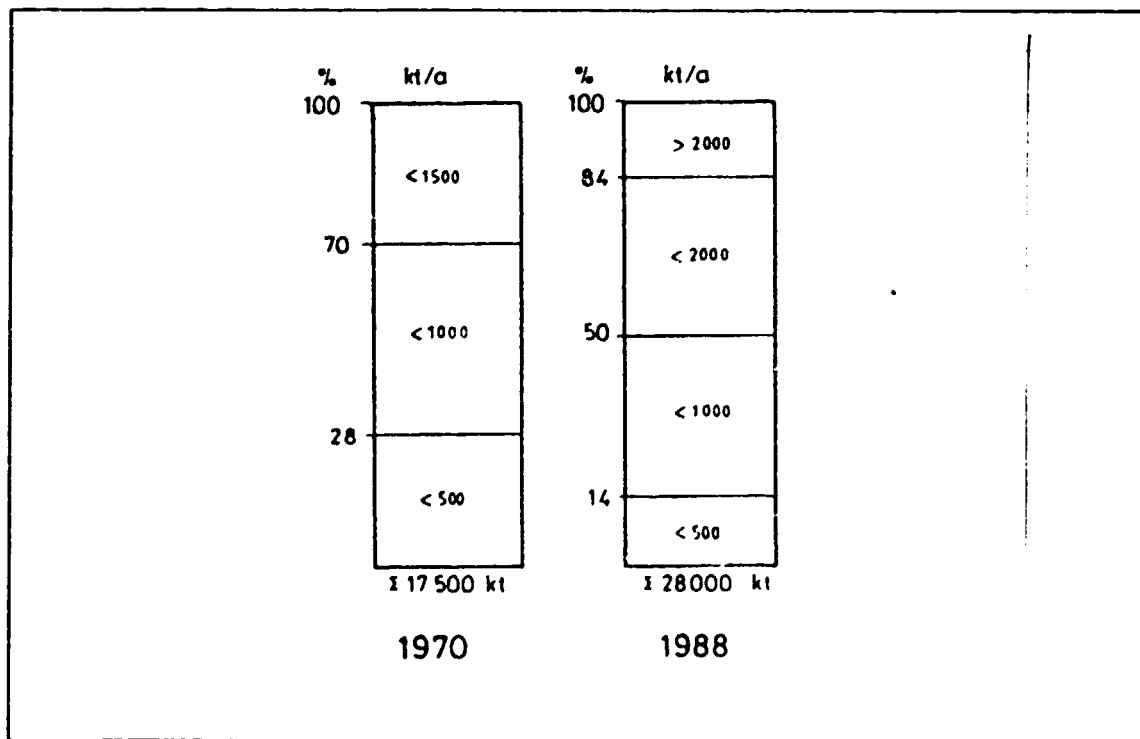


**Figure 1.1-3**
**Distribution of alumina plant by size in "Western World"**

The expected non-metal grade alumina producing capacity by country in 1993 is plotted in Figure 1.1-4.
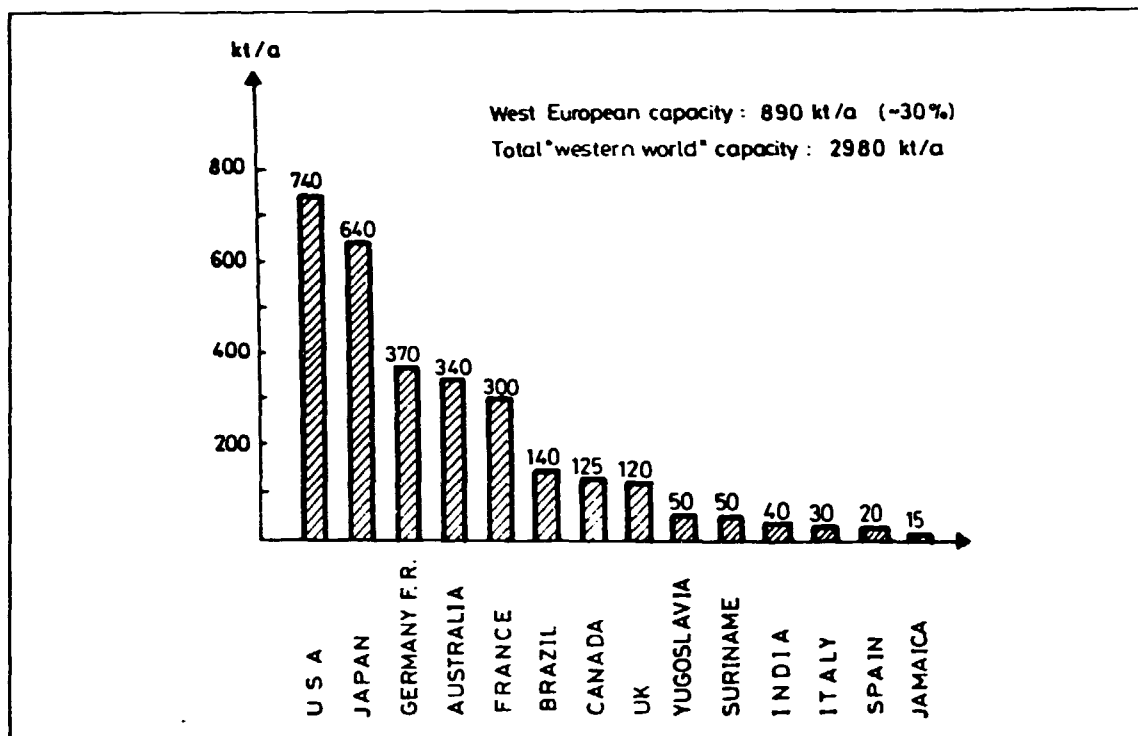


**Figure 1.1-4**
**Non-metal grade alumina producing capacity by country in 1993[3]**

Naturally, the developed countries with significant chemical industry are determining producers in this field. It is remarkable that the share of Europe amounts to 30% in chemical grade alumina production of the world in comparison with 18.9% share in the world production capacity of the metallurgical grade one. The total world production of only 3 million t/a gives a good chance to increase significantly the amount of the special products in the next future already.

It is to be mentioned, however, that a relatively rash increase of the demand for alumina-hydrate (as filling and fire retarding material), aluminium-sulphate, some kinds of ceramic aluminas can be expected in the developing countries, too. Considering the limited transportability of these products from economic points of view and the relatively good conditions for local production in the existing or future alumina refineries, the domestic manufacturing of such products can be highly recommended in the developing countries in the next future.

## 1.1.1.2 Alumina production potential and costs

In order to see a realistic picture concerning the future trends of the world alumina industry the alumina production potential

and costs should be studied and evaluated very thoroughly on a comparative basis. For this purpose the basic data of the study prepared by D. R. Wilburn and D. A. Buckingham [6] is available. In this report the costs for alumina refining for selected MEC (market economy country) countries have been subdivided into operating costs (i.e. labour, supplies and energy), overhead (averaged at 15 percent of operating cost), transportation, recovery of capital, taxes and royalties at 0 and 15 percent discounted cash flow rate of returns (DCFRORs) and return on investment /at 15 % DCFROR/). At the analysis refineries were assumed to operate at full capacity for a 30 year period. All costs were considered in January 1989 USD/t of alumina on a weighted average basis. The annual production was calculated on the basis of the total recovered alumina divided by life of refinery. The potential total production of alumina was approximately 916 million tonnes, from MEC operations.

The results are summarized in Figure 1.1-5. The estimated weighted-average net operating cost for all refineries evaluated (including Canada, France, Greece, Guinea, Guyana, Ireland, Japan, Spain, Suriname, Turkey and Venezuela, too) is  158 USD/t of alumina, the total production costs 182.50 USD/t at a 0 percent DCFROR and 220.80 USD/t at 15 percent.

It can be stated that not only Australia and USA, but also Brazil, Venezuela and Jamaica (and some other developing countries) have very good potential for economic production of metal grade alumina. The non-metal grade alumina production combined with the metal-grade one can increase the profitability and competitiveness of the given alumina refineries even more.

It is clear, that the European alumina refineries can not be competitive with the Brazilian and giant Australian or Venezuelian refineries in long term, especially by processing costly imported bauxite. The only favourable condition in Europe is the existing demand on metal grade alumina of the smelters in the vicinity. This fact makes possible the further operation of some refineries at least in short or medium term. The main task is here to increase the efficiency by means of technical development with very effective and low-cost investment and to produce more and more valuable special products.
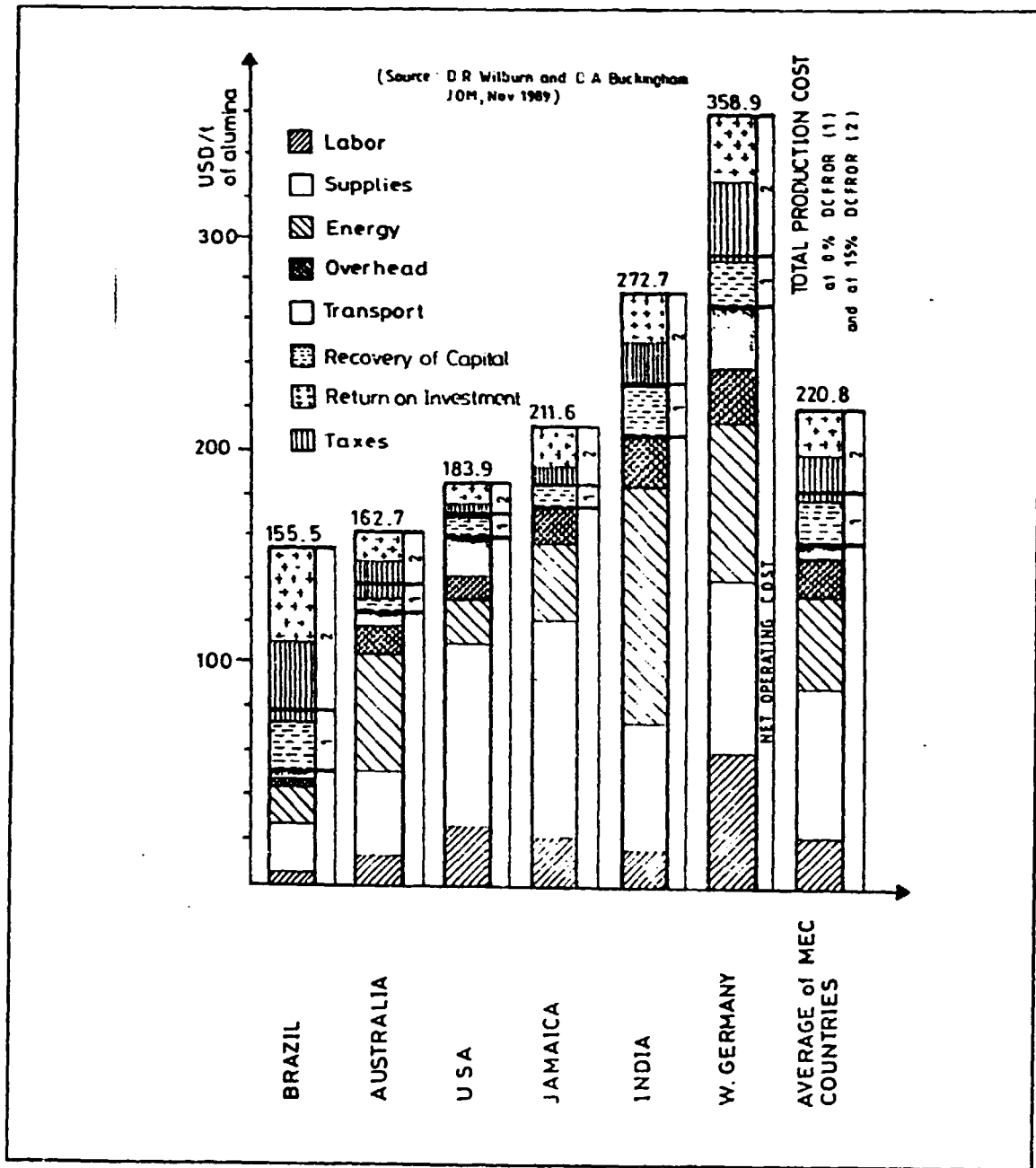
**Figure 1.1-5**
**Alumina production costs**
(at production pontential) [6]

In agreement with the above cost analysis the major expansions of alumina capacity projected to 1995 are given in Table 1.1-3 [4].

It can be seen that beside Brazil, Australia, Jamaica and Venezuela only China, India, US Virgin Island and Greece can be found on the list. All countries mentioned in Table 1.1-3 have (mostly high grade) local bauxite and/or extending domestic market (e.g. China and India).

Table 1.1-3
Major expansions of alumina capacity projected to 1995 (kty) [4]

| Country | Refinery | Capacity | Remarks |
|---------|----------|----------|---------|
| Brazil | Alunorte | 1.100 | Greenfield |
| Greece | Elva | 600 | Greenfield |
| China | Heijin/Shanxi | 650 | Greenfield |
| China | Zheng Zhou/Henan | 250 | Greenfield |
| China | Pingguo/Guanxi/ Zhuang | 300 | Greenfield |
| Jamaica | CAW | 200 | Brownfield |
| Jamaica | Alpart | 580 * | Re-start |
| Jamaica | Alpart | 320 | Brownfield |
| Venezuela | Interalumina | 600 | Brownfield |
| Australia | Gove | 150 * | Brownfield |
| Australia | QAL | 300 * | Brownfield |
| Australia | Wagerup | 650 * | Brownfield |
| Australia | USSR/Comalco | 1.000 | Greenfield |
| Australia | Worsley | 500 * | Brownfield |
| US Virgin Islands | Vialco | 640 * | Re-start |
| India | Nalco | 200 | Brownfield |
| | TOTAL | 8.040 | |

* Capacity expected to come on stream before 1992.

The changing of the world alumina refining capacity between 1985 and 1995 is given in Table 1.1-4 [4].

Although the expected increase of the alumina capacity between 1989 and 1995 seems to be more or less overestimated, the further restructuring of the alumina industry is evident and as a consequence further closures of the highest cost (mostly small and old) refineries (first of all in Europe in the former CPE countries) can be forecast.

It should be mentioned here that sometimes a relatively small special alumina-hydrate/alumina oriented refinery can also be competitive. The first precondition is the availability of a high grade low cost bauxite which can be processed at a low cost (low demand on energy and caustic soda), that is gibbsitic (low temperature digestion) and low reactive silica bauxite is preferred for this purpose.

Table 1.1-4 [4]
Alumina refining capacity by region total world 1985-1995 (ktpy) [4]

| Region | 1985 | % of Total World | 1989 | % of Total World | 1995 | % of Total World |
|---|---|---|---|---|---|---|
| USA | 4.350 | 11.38 | 4.945 | 12.12 | 5.535 | 11.29 |
| Canada | 1.125 | 2.94 | 1.140 | 2.79 | 1.140 | 2.32 |
| W. Europe | 4.782 | 12.51 | 4.270 | 10.47 | 4.270 | 8.71 |
| Australia | 9.420 | 24.64 | 10.525 | 25.80 | 13.225 | 26.97 |
| Japan | 1.360 | 3.56 | 910 | 2.23 | 910 | 1.86 |
| Total Developed World | 21.037 | 55.03 | 21.790 | 53.42 | 25.080 | 51.15 |
| Africa | 620 | 1.62 | 620 | 1.52 | 670 | 1.37 |
| Latin America & Caribbean | 5.325 | 13.93 | 6.935 | 17.00 | 10.110 | 20.62 |
| Asia | 653 | 1.71 | 1.607 | 3.94 | 1.807 | 3.69 |
| Other1 | 2.320 | 6.07 | 2.520 | 6.18 | 2.396 | 4.89 |
| Total Developing | 8.918 | 23.33 | 11.682 | 28.64 | 14.983 | 30.37 |
| Total Western World | 29.955 | 78.36 | 33.472 | 82.06 | 40.063 | 81.71 |
| CPEs | 8.270 | 21.64 | 7.320 | 17.94 | 8.970 | 18.29 |
| Total World | 38.225 | 100.00 | 40.792 | 100.00 | 49.033 | 100.00 |

1 = Includes Spain, Yugoslavia and Turkey.

The increasing importance of the secondary aluminium industry should also be emphasized. This industry is becoming more and more important for the metal supply [7]. The recycled proportion of aluminium is about 32 per cent in world average nowadays. Considering the 12 years of average life time of aluminium containing products, a significant increase of this recycled proportion is very realistic in the next future and a well organized collecting and recycling system would be one of the most effective field for cooperation among the related countries. In this connection it has to be mentioned that the remelting of scrap requires only 5% of energy used for the extraction of primary aluminium from alumina [8].

Naturally, the increasing amount of the secondary, recycled aluminium decreases the demand for the primary metal and metal-grade alumina. In light of this trend the less economic alumina refineries should be closed step by step in the future, especially in Europe, in connection with the mentioned geographical restructuring of the world alumina/aluminium industry.

## 1.1.2. Technical development of the metal grade alumina production

The alumina production can be characterized as a material and energy-intensive process with considerable investment requirement. The basic trends of the development of the Bayer process are nowadays the reduction of the production costs of alumina, especially that of determining basic material and energy costs, furthermore the increasing of the efficiency of the equipment, [2] based on the cost-analysis of the alumina production.

### 1.1.2.1 Material saving

Costs of the bauxite, caustic soda and lime reach 40-50% of the total production costs. Price of bauxite and transportation is the decisive factor in plants processing imported bauxite.

The specific bauxite consumption to produce 1t of alumina is depending on the digestion yield of alumina and on the secondary losses determined by the autoprecipitation, the dissolved losses with red mud and the dust losses at calcination.

The means of the reduction of the alumina losses are therefore:

- elimination of the undigested losses (with high temperature tube digestion and with catalytic additives) [9...13]
- reduction of the autoprecipitation
- decrease of the dissolved losses (with higher solid concentrations in the underflow of the thickeners)
- decrease of the dust-formation at the calcining (with the production of coarser alumina).

The typical specifications for different grades of bauxite according to the consumers are given in Table 1.1-5 as published by Sehnke and Plunkert, US. Bureau of Mines [14].

The maximum value of $SiO_2$ in this Table is as high as 3.0 per cent only, however, this limit can not be assured in fact in a lot of alumina refineries.

Nevertheless, the processing of low-grade, high-silica bauxite can not be economic, first of all due to the costly caustic soda consumption.

Table 1.1-5
Typical specifications for grades of bauxite [14]

| Constituent | Metal grade (dried Jamaica type) | Refractory grade (calcined) | Abrasive grade (calcined) |
|---|---|---|---|
| $Al_2O_3$ min. | 47.0 | 86.5 | 83.0 |
| $SiO_2$ | 3.0 | 7.0 | 6.0 |
| $Fe_2O_3$ | 22.0 | 2.5 | 8.0 |
| $TiO_2$ | 3.0 | 3.75 | 3.0-4.5 |
| $K_2O+Na_2O$ | NS | 0.2 | 0.7 |
| $MgO+CaO$ | NS | 0.3 | NS |
| CaO | NS | NS | 0.2 |
| MgO | NS | NS | 0.4 |
| $MnO_2+Cr_2O_5+V_2O_5$ | 2.0 | 1.0 | 1.0 |
| $P_2O_5$ | 1.5 | NS | 0.5 |
| Loss on ignition | NS | 0.5 | 1.0 |

NS No specification

The specific consumption of caustic soda varies from 0.032 t NaOH/t alumina for Boké type bauxite to 0.093 for Weipa bauxite and even higher for some others. [15] The alumina industry consumes 7% of the world production of caustic soda.

The quantity of caustic soda circulating within the Bayer cycle amounts to about 1 t/t alumina produced. At a world production level of 40 million t/a alumina, the same amount of NaOH can be found circulating in alumina refineries. The silica neutralization (formation of Na-Al-hydrosilicates) requires 75% and the treatment of oxalic acid about 10 % of the total caustic soda consumption. The caustic soda spot prices reached 600 USD/tonne in 1988-89 and the current level is USD 300-350. Furthermore no significant reduction is expected reduction even in medium term. Therefore, the reduction of caustic soda losses (regeneration by causticization) by means of lime chemistry becomes more and more economic and actual all over the world (not only for the alumina refineries processing high silica bauxite) [12, 13].

The application (economy) of the lime chemistry is determined by the operational and technological aspects on the one hand and the price relations between NaOH and lime on the other hand.

## 1.1.2.2 Energy saving

The energy audit is the base of the conservation program, therefore material and energy balances are to be elaborated. It is advised to deal with the alumina hydrate production and the calcination of the hydrate separately. The heat flow diagram of the production of alumina hydrate by high temperature digestion 3ayer process plotted by Lang et al. [18] is shown in Figure 1.1-6. In this Figure the values of the radiation heat losses (signed by the numbers from 1 to 7) and the waste heat flows (signed by

the numbers from 8 to 10) of an alumina plant with a specific
heat consumption of 8500 MJ/t of alumina for the alumina hydrate
cycle are given, as well. The greatest waste heat occurs with the
discharge of cooling water from the condenser in the evaporation
plant. This hot well waste heat is in our example 2900 MJ/t of
alumina (in Figure 1.1-6 signed by No. 10). This enormous waste
heat can be eliminated by means of the evaporationless
technology.
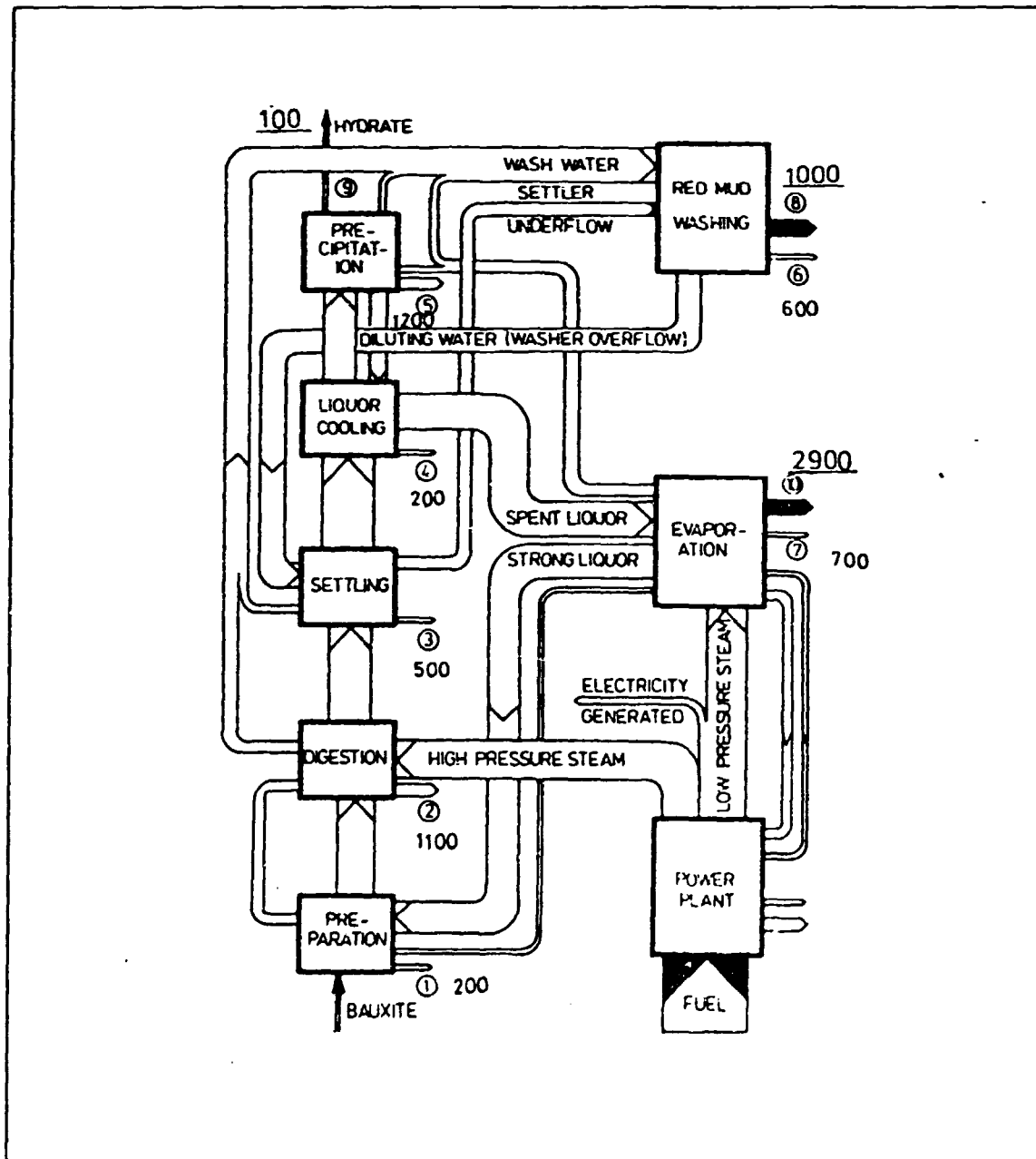


Figure 1.1-6
Heat flow diagram [18]

Bielfeldt and Winkhaus [19] showed that the minimum energy consumption in the Bayer cycle might be 7.88 GJ/t alumina in a modern refinery where evaporationless technology, high temperature digestion (tube digestion), efficient heat exchangers and up-to-date fluidized bed calcination are applied and the electric energy is partially produced locally by back pressure turbines. Donaldson [20] pointed out that the preferred ways of energy savings are modernization of existing refineries by installing supplementary heat recuperation equipment or enhancing their efficiency, switching over from oil or gas fuel to coal and modification of the operations in an energy conscious conception. Chin [21] emphasizes the importance of joint optimization of technology and energy supply, minimizing heat losses with red mud, elimination of heat for special evaporation and maximizing liquor productivity.

The main aim of the optimisation of the caustic soda concentration in the whole Bayer cycle is to reduce the quantity of the water to be evaporated. In this respect the high temperature digestion (by means of tube digester) has determining importance, because a less concentrated caustic soda liquor can be used at higher temperature digestion, consequently, the output of flash expansion in the extraction will be increased. Although more heat input is required for digestion stage but this is overcompensated by reduced evaporator losses.

The heat recuperation can be improved by increasing the average heat transfer coefficient at the digestion by means of an optimized cycle time between two cleaning operations and by increasing heating surface area in the heat exchangers and autoclaves.

The specific energy consumption for hydrate calcination has been reduced down to 3100 MJ/t of alumina in an up-to-date gas-suspension-calciner retrofitted from rotary kiln at 1500 t alumina per day production rate [22].

A further great potential for energy conservation is the intensification of the red mud settling and washing, which can reduce the waste heat flow with the mud. (in Figure 1.1-6 signed by No. 8.= 1000 MJ/t of alumina) and the dissolved caustic soda losses, as well. Evaporation can be reduced by decreasing the wash water demand.

The raising of efficiency in the cycle (liquor productivity,) careful fitting of technology to the properties of the bauxite processed and optimisation of the concentration relations seem to be less investment demanding ways of energy conservation.


### 1.1.2.3 Alumina quality and liquor productivity

The requirement relating to both the increasing chemical purity and given physical properties of metal grade alumina is more and more definite.

The typical level of impurities of the metal grade alumina can be seen in Table 1.1-6 [23].

**Table 1.1-6**
**Typical level of impurities in the metal grade alumina [23]**

| Impurity | Weight % |
|---|---|
| $Fe_2O_3$ | 0.015 |
| $SiO_2$ | 0.015 |
| $TiO_2$ | 0.003 |
| CaO | 0.015 |
| $P_2O_5$ | 0.001 |
| $V_2O_5$ | 0.002 |
| ZnO | 0.005 |
| $Na_2O$ | 0.5 |

The physical properties of the typical metal grade alumina suitable for feeding of the automated centre-worked pots with prebaked anodes are summarized in Table 1.1-7.

**Table 1.1-7**
**Physical properties of a typical sandy type alumina compared with a fluory type [23]**

| Properties | Alumina type | |
|---|---|---|
| | Sandy | Fluory |
| Spec.surface area (BET) $m^2/g$ | 50-80 | 5 |
| $\alpha$- $Al_2O_2$ % | 20-10 | 90 |
| Grains < 45 $\mu m$ % | 10-20 | 45 |
| >105 $\mu m$ % | 10 | |
| Apparent density $g/cm^3$ | 0.95 | 0.8 |
| Angle of repose | 35-30 | 45 |
| L.O.I.% | 0.6-0.9 | |
| $P_2O_5$ % | < 0.001 | |

The alumina refineries producing floury type alumina (mostly old and small capacity plants) are to be converted into sandy productions or to use them for manufacturing specialty alumina-hydrates and aluminas, eventually to be closed in the next future already.

Increasing the liquor productivity is a very important means to save energy. The actual characteristic liquor productivity in plants for sandy alumina is about 55 gpl and in plants for floury alumina 70-75 gpl. It is expected that alumina plants producing floury alumina will disappear. It is estimated that liquor productivity-values in the range of 80 to 90 gpl may soon become common [24]. This forecast can be justified by the results achieved at the Gove Alumina Plant by adapting the Alusuisse

precipitation process to convert floury alumina production into sandy [25].

The liquor productivity in function of time relating to both sandy and floury type alumina is plotted in Figure 1.1-7. It can be stated that no more floury metal grade alumina will be produced at the end of this decade.
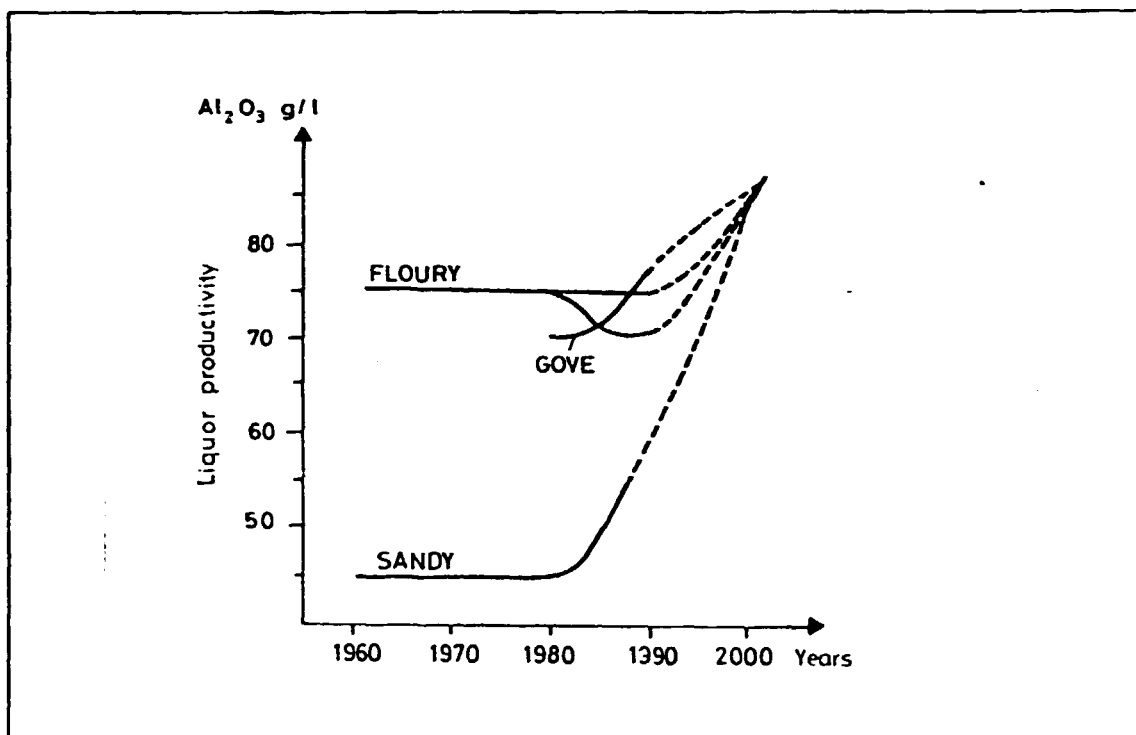


**Figure 1.1-7**
**Alumina quality and liquor productivity**

In connection with the liquor productivity the importance of the reduction of organic and inorganic impurities of the process liquor should be mentioned.

The increase of the liquor productivity is the most economic way to raise production capacity of the given alumina plants (brownfield expansion). This could result an additional world capacity of 4 million tonne/a of alumina.

## 1.1.3 Product restructuring

It has been emphasized already that one of the most effective means to increase the competitiveness of the alumina refineries seems to manufacture higher value, new products based on the alumina cycle. Gallium, vanadium-pentoxide, alumina-hydrate, special aluminas, fused corundum, mullite and special refractories, abrasive materials, $Al_2O_3$ based fibres (insulators), sodium-silicate (water glass), zeolites

(detergents) and aluminium-sulphate can be mentioned among these without completeness. According to Lester A.D. Chin the special products can be made in alumina plants are belonging to two main groups, namely to co-products and by-products [26, 27] Co-products include aluminium-hydroxide products, activated aluminas, industrial aluminium chemicals and ceramic aluminas, while gallium and cements are the two significant by-products.

The estimated quantity of the specialty alumina chemicals products amounts to 8 to lo per cent of all production of alumina plants.

Figure 1.1-8 shows the conceptual possibilities for producing chemicals in connection with the Bayer process, plotted by Mr Chin [26]. As a traditional product in this field the alumina trihydrate can be mentioned for non-metallurgical uses [28]. The demand is increasing to use it as flame retardant filler [29].
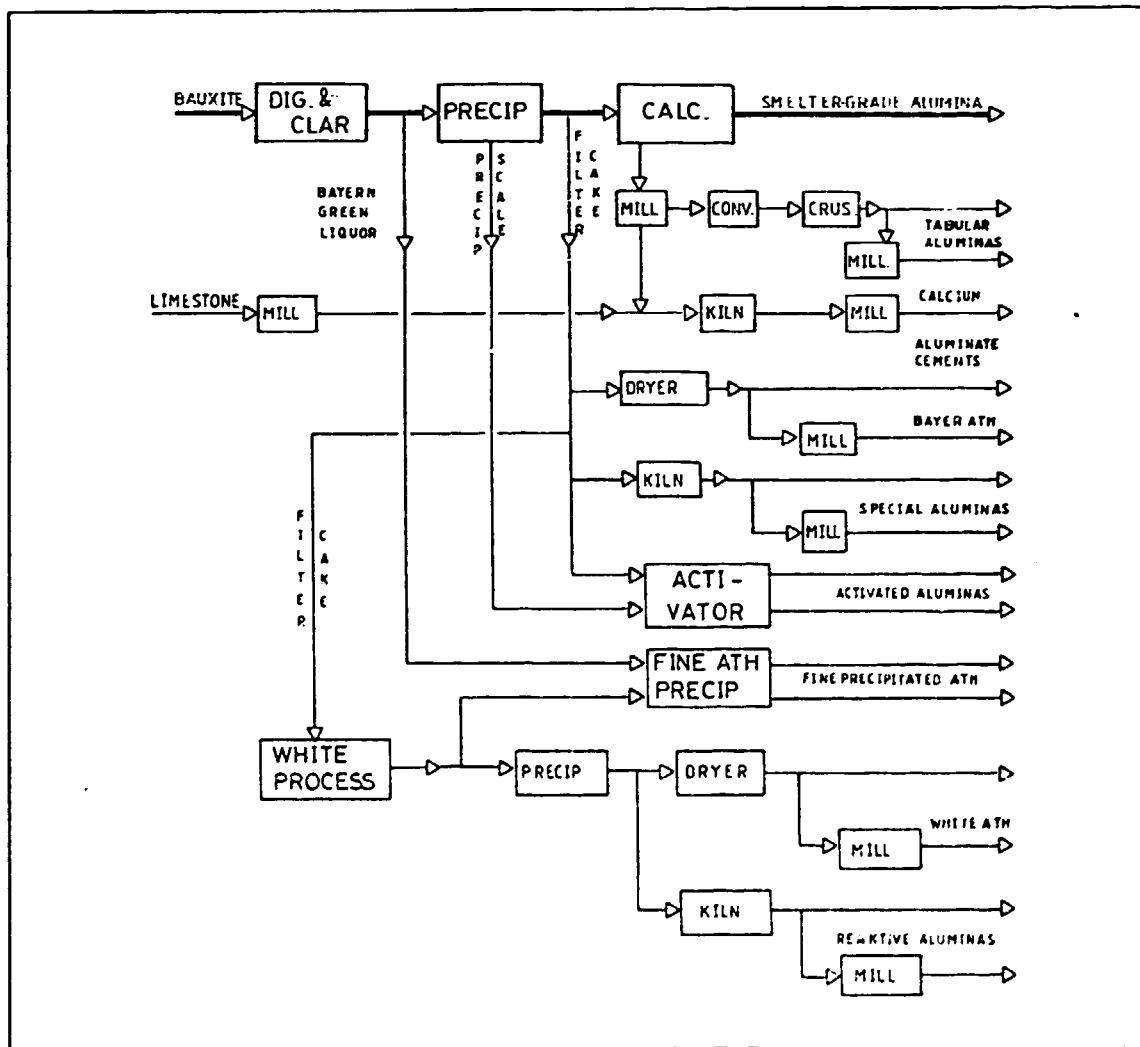


Figure 1.1-8
Bayer process with grafts of chemicals processes

### 1.1.3.1 Main strategies to produce specialty alumina chemicals

There are three main strategies:

1. Manufacturing specialty alumina chemicals in connection with the production of metal grade alumina in Bayer (or sinter) refinery. (See Figure 1.1-8).

2. Manufacturing only specialty alumina chemicals in the given alumina refinery based on bauxite processing.(e.g. Martinswerk in Bergheim (D), Burntisland (U.K.), Kidricevo (YU), Mosonmagyaróvár (H).)

3. Manufacturing specialty alumina chemicals from the alumina-trihydrate (or alumina) transported from alumina plant in a chemical plant /mostly focused on one or few selected products only) located in close vicinity to the market.

**The combined production of metal grade alumina and alumina chemicals** has both advantages and disadvantages

The main preferences are the availability of the relatively cheap raw material (hydrate, alumina or process liquor) for special alumina chemicals (without transportation and storage costs) the infrastructure and the trained personnel.

The main disadvantages may be the high production cost of the metal grade alumina or alumina hydrate (mostly small and old refineries are considered), the more complicated control of material and energy balances and harmonizing the operations of different nature and scale, difficulties in management, cost accounting and marketing.

It is clear, however, that some specialty alumina chemicals can be produced technically and/or economically only at the alumina refinery, where either the process liquor is used as raw material and/or mass production is required.

Such products are:
- gallium,
- zeolite,
- aluminium trihydrate,
- vanadium-salt,
- aluminium-sulphate,
- ceramic aluminas.

**Manufacturing specialty alumina chemicals only in a given alumina plant** is more and more characteristic nowadays in some small and old (sometimes reconstructed) alumina refineries. The process technology is mostly very flexible in these plants (lot of and small size equipments, batch precipitation, many tanks for different operations, etc.) and the experiences of the well trained personnel can be utilized very easily in the similar field.

More sophisticated and special products can also be produced in such plants (which can be considered as chemical plants and no longer as alumina refineries) where the added value of the products can be extremely high.

Establishment of such type cf greenfield chemical plants with relatively low capacity based on bauxite processing (trihydrate type, high grade bauxite is preferred) can be mentioned as a latest tendency. There are some projects under consideration and approval.

**Manufacturing of specialty alumina chemicals from imported alumina-trihydrate or alumina** is characteristic for the countries where alumina refinery does not exist yet, however, the chemical industry needs the related products. They can be market related chemical plants, specialized for given product(s) only. Very special products as composites, catalysts, integrated circuit subtrates can be manufactured in cooperation with end-user only and the establishment of such plants need cooperation (e.g. joint venture) with the companies disposing the proper license and know-how.

Any of the a.m. three possibilities of the production of co-products and by-products of the Bayer alumina production can be realised in developing countries, too. As first stage, however, the manufacturing of the products mentioned in connection with metal-grade alumina production should be preferred. In such way the expected economic result would be achieved by mass production of the valuable but less sophisticated alumina chemicals.

## 1.1.4 Forecast of the further development of the world alumina industry

1. The geographical and product restructuring of the world alumina industry is going on and will be continued.

2. The metal grade alumina production will be more and more concentrated in the close vicinity of the large and high grade bauxite deposits (significant part of them can be found in developing countries.)

3. The technical development of the metal grade alumina production will be focused on material and energy saving, process control and alumina quality. The tube digestion and caustic soda regeneration have special importance in the next future already.

4. The availability of the cheap metal grade alumina (and alumina hydrate) promotes the economic manufacturing of the specialty alumina chemicals.

5. The product restructuring means the production of increasing amount of specialty alumina chemicals partly in connection with metal grade alumina production, partly in independent chemical plants using either bauxite or alumina hydrate (alumina) as raw material.

--------------------------------------------------------------------

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# 1.2 PRODUCTION, USE AND MARKET FOR CO-PRODUCTS AND BY-PRODUCTS IN CONNECTION WITH BAYER ALUMINA PRODUCTION

T. Kálmán

## 1.2.1 Scope of co- and by-products

The aluminium containing compounds are one of the highest volume inorganic chemical products in the world. Most of these compounds are the originates of aluminium hydroxides or aluminas which are the direct products of the basic Bayer process for over 100 years.

Approximately 90 % of alumina resulting from Bayer process is used for the manufacture of aluminium - an end use specifically excluded from this study - and the remainder is converted into other commercial aluminium containing products. The names of these products are different from country to country, however the most commonly used names are specialty alumina products or alumina chemicals.

Beside of the above mentioned direct products of alumina refining by the Bayer process there are other closely related products, which can be obtained from the down streams of Bayer circuit. The production of these by-products - namely gallium and vanadium pentoxide - is important not because of their alumina content but because of their impact on the overall economy of the Bayer process.

The simplified flowchart - Figure 1.2-1 - shows all of the co- and by-products which are originating from or relating to alumina refining by the Bayer process.

According to the flowchart the following main groups of products can be distinguished.

```
                              ┌──────────┐      ┌──────────────────┐
                              │ BAUXITE  │──────│ Abrasive grade   │
                              └──────────┘      │ Chemical grade   │
                                                │ Chemical grade   │
                                                └──────────────────┘
              ┌─────────────┐
              │ METAL GRADE │
              └─────────────┘

 ┌──────────┐  ┌──────────┐   ┌──────────┐        ┌──────────────┐   ┌──────────────┐
 │ BY       │  │ BAYER    │   │ ALUMINATE│        │ PURIFICATION │   │ WHITE OR HP  │
 │ PRODUCTS │  │ PROCESS  │───│ SOLUTION │────────│              │   │ AL(OH)3      │
 └──────────┘  └──────────┘   └──────────┘        └──────────────┘   └──────────────┘

                                              ────CHEMICAL INDUSTRY────
 Gallium
 Vanadium-    ┌──────────┐   ┌──────────┐
 pentoxid     │ AL(OH)3  │───│ MILLING  │
              └──────────┘   │ GRADING  │
                             └──────────┘
                                              ────Pharmaceuticals────
                  ┌──────────────┐            ────Flame retardants────
                  │ DEHYDRATION  │            ────Fillers────
                  └──────────────┘            ────Pigments────
                                              ────Activated aluminas────

              ┌──────────┐                    ┌──────────┐
              │ CALCINED │                    │ MILLING  │
              │ ALUMINA  │────────────────────│ GRADING  │
              └──────────┘                    └──────────┘

 ┌──────────┐ ┌──────────┐   ┌──────────┐    ┌────────────────────────────────────┐
 │ FUSED    │ │ METAL    │   │ SINTERED │    │ LOW      MEDIUM       NORMAL        │
 │ AL2O3    │ │ GRADE    │   │ TABULAR  │    │ SODA     SODA         SODA          │
 │ ABRASIVES│ │ ALUMINA  │   │ ALUMINAS │    │          ALUMINAS                   │
 └──────────┘ │ SMELTER  │   └──────────┘    └────────────────────────────────────┘
              └──────────┘
```

**Figure 1.2-1**

**By- and co-products originating from or relating to the Bayer process**

## 1.2.2 Co-products

### 1.2.2.1 Bauxite

Bauxite is weathered rock consisting mainly of aluminium hydroxide minerals with variable amount of reactive and non-reactive silica, iron oxides and titanium oxides.

The world bauxite production of different qualities approaches 100 million metric tons a year, and the 90 % of this quantity is used for the production of aluminium hydroxides and oxides.

The residual - non-metallurgical grade bauxite - is used in abrasives, refractories, chemicals and other special products like proppants, sorbents, filter aids etc.

The non-metallurgical grade bauxites must meet much more rigid requirements with regard to iron oxide, silica and titanic

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contents than the metallurgical grade ones used in bauxite refining plants.


## 1.2.2.2 Aluminium trihydroxide

Aluminium trihydroxide (termed also gibbsite, hydrargillite, $\alpha$-, $\beta$-, $\Gamma$-Al(OH)$_3$, ATH) is one of the direct products in the Bayer process using bauxite refining plants and consists of both quasi spherical and irregular grains with sizes from a few microns to over 100 microns, however the individual crystals may be much smaller. It is a non-abrasive, off white or white stable, odourless, non-toxic, and chemically inert powder with Mohs hardness of 2.5 to 3.5, a specific gravity of 2.42. It should be also noted that ATH has quite few important end use oriented properties, namely:

i    ability of creating arc and track resistance in polymer
     systems

ii   thermal stability at processing temperatures of many organic
     matrix

iii  the ability to cool organic system on heating higher
     temperatures due to its endothermic decomposition.

ATH is manufactured in the precipitation step of the Bayer circuit and produced in a wide range of grades and particle sizes depending upon the precipitation technology applied. The colour of Bayer ATH is generally off white, due to its organics contamination. Currently, the whitest colour and highest purity commercial ATH products come from non-Bayer processes. The major uses of aluminium trihydroxide outside of the production of calcined metal grade alumina are shown in Figure 1.2-2.

It can be seen from Figure 1.2-2 that the end use applications of ATH for non-metallurgical purposes are extremely numerous, therefore the discussion here-below will cover only some of the most important areas of ATH manufactures and end-use applications.

```
                                    ┌──────Zeolites
                                    ├──────Al₂(SO₄)₃
                      ┌──────────┐  ├──────Aluminate cements
                      │ CHEMICAL │──┼──────Glass
                      │ INDUSTRY │  ├──────Ceramics
                      └──────────┘  ├──────AlF₃ & AlCl₃
                                    └──────Paper manufacture

                                       ┌──────Cosmetics
                      ┌──────────────┐ ├──────Toothpaste
                      │PHARMACEUTICALS│─┼──────Deodorants
                      └──────────────┘ └──────Antacids

   ┌──────────┐                          ┌──────Foam & solid plastics
   │BAYER ATH │  ┌───────────────┐       ├──────Carpet backing
   │   or     │──│FLAME RETARDANTS│──────┼──────Plastics wire insulation
   │ HIGH(ER) │  └───────────────┘       └──────Rubber
   │ GRADES   │
   └──────────┘                     ┌──────Paints
                      ┌─────────┐   ├──────Paper
                      │ FILLERS │───┼──────Rubber
                      └─────────┘   └──────Synthetic marble

                                     ┌──────Wallpaper
                      ┌──────────┐   ├──────Ink paint
                      │ PIGMENTS │───┼──────Paper
                      └──────────┘   └──────Rubber
```

**Figure 1.2-2**
**Non-metallurgical use of aluminium trihydroxide (ATH)**

## Aluminium trihydroxide as raw material for the production of co-products for non-metallurgical use

*Aluminium sulphate*

The aluminium sulphate $(Al_2(SO_4)_3 * nH_2O)$ is white, crystallized material which can be produced by the reaction of $Al(OH)_3$ and sulphuric acid. Aluminium sulphate is used in large quantities for municipal and industrial water treatment and for the paper industry. More details on Hungarian practice will be given in Chapter 2.4.

*Zeolites*

Generally, synthetic zeolites are white, porous, crystalline sodium alumina silicates with a regular structure. The range of zeolites are so versatile that it would be difficult even to list all the possible applications .

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Zeolites are used first of all as water softeners, detergents, sorption agents, ion-exchange resins, catalysts etc.

More details on zeolites in Hungarian practice will be given in Chapter 2.3.


*Aluminium fluoride*

Aluminium fluoride is a colourless or white, crystalline material which is used in large quantities for the production of cryolite as solvent for electrolyte reduction of alumina to aluminium in the Hall-Heroult process.

Basically, there are two processes - known as dry and wet processes - available for the production of aluminium fluoride. The dry process is based on the reaction below:

$$Al(OH)_3 + 3HF \xrightarrow{>500\ °C} AlF_3 + 3H_2O \qquad \{1\}$$

The resulting products contain $\approx$ 92 % of $AlF_3$ with $\approx$ 0.3 % silica.

The wet process resulting higher purity of $AlF_3$ than that of dry process is based on the following reaction:

$$Al(OH)_3 + H_2ClF_6 \xrightarrow{\hspace{1cm}} 2AlF_3 + SiO_2 + 4H_2O \qquad \{2\}$$

$AlF_3$ is than precipitated from the instable solution by heating/agitation and the product is subjected to calcination to remove crystalline water.

The calcined product contains $\approx$ 96 % $AlF_3$ with <0.1 % of silica. Beside the major use of $AlF_3$ for aluminium electrolyses there are other minor but important applications, too. For example it is used as a flux in brazing, and for removing the magnesium from aluminium scrap during the refining process. It is also used in ceramic refractory, glazes and fine glass industries.


### 1.2.2.3 Aluminium trihydroxide for direct applications

Since the application fields of ATH as additive are extremly large (see Figure 1.2-2) only its most important applications will be discussed in details here.


### Aluminium trihydroxide as filler/flame retardant filler

Aluminium trihydroxide originating from Bayer or non-Bayer processes has all the preconditions (large production background, availability in a wide range of qualities, non-toxicity, chemical inertness, outstanding fire-retardant and smoke-suppressant properties) to be an effective flame retardant filler [1].

When a polymer filled with ATH is exposed to fire ATH has two useful functions and acts as flame retardant both in condensed and flame phases. It endothermically decomposes above approx. 220 °C. By-products of this decomposition are water and anhydrous alumina, thus inhibiting the fire by acting as a heat sink and absorbing energy.

The second useful function is that during the reaction  water vapour is released which cools the fire on the one hand and helps to prevent the oxygen in the air from "fanning the flames" on the other hand.

Additionally - and perhaps more importantly - no toxic fumes are associated with the reaction unlike the halogenized hydrocarbon compounds which earlier were considered as suitable fire retardants .

While these materials are effective fire-retardants indeed , they decompose into corrosive and toxic by-products to the extent that often more damage is caused by the decomposition products than by the fire itself.

Apart from the favourable features of ATH, the main motivation for its steadily expanding use is the consumer safty-oriented government legislation according to which certain products (carpet backings, automobile and building furnishings etc.) should possess the specified flame retardancy.

Although there are many advantages of using ATH as a (flame retardant) filler, there is a few disadvantages limiting it's use, too [2]. These are the relatively low end-processing temperature (200 °C or below) and the considerable strength reduction in plastics when ATH charge is increased. The later can be partially diminished by using coupling agents like silanes which bond the ATH to the organic polymer with an increased physical strength result.

The most important fields of current use of aluminium trihydroxide in polymer systems are listed in Table 1.2-1.

**Table 1.2-1.**
**ATH containing polymers**

| POLYMER SYSTEMS | | |
|---|---|---|
| **Elastomers** | **Thermoplastics** | **Thermosets** |
| Ethylene-propylene terpolymer Styrene-butadiene copolymer Chloroprene polymer Polyisoprene, synthetic | Polyolefins and their copolymers Polyvinil chloride | Epoxy Phenolic Polyester Polyurethane |

**Manufacture of aluminium trihydroxide**

All the secondary processes aiming to produce specialty aluminium trihydroxide are generally based on a mechanical alteration of the Bayer gibbsite crystal size, shape and particle size distribution.

Wet or dry grinding and static or centrifugal classification systems are widely used to produce white or off white, ground and classified ATH products especially for the large range of polymer applications.

The relatively simple grinding and classification techniques can be used economically up to 2 micron median particle size of the ground product, however, below of 2 or even below 1 micron the chemical reactions (precipitation) return as the only technique by which the desired submicron size, narrow distribution products can be produced economically.

As to the grinding, many different mill types including hammer mills, roller mills, fluid-bed mills, air-jet mills etc. are used with varying success for the different applications.

In Hungary, air jet mill together with external, static classification units are used for the production of ground ATH products [2]. For more details see Chapter 2.1.

Some of the characteristics data of typical ground products by Hungalu Hungamola Ltd., and ALCOA Europe are listed in Table 1.2-2.

Table 1.2-2.
Characteristics data of typical ground products

| | HUNGAMOLA ALOLT | | | ALCOA M | | |
|---|---|---|---|---|---|---|
| | 2 | 8 | 30 | 15 | 10 | 6 |
| $d_{50}$ micron | 5-10 | 10-15 | 5-10 | 10-12 | 8-10 | 5-6 |
| white | off white or white | | | white | | |
| Whiteness* | 88-92 | 90-92 | 92-54 | 95-96 | 96-96 | 96-97 |
| Surface area, BET, $m^2$/g | ≈1 | >2 | >3 | 1-2 | 2-3 | 3-4 |
| Al(OH)$_3$ cont. % | >99.5 | | | >99.6 | | |

* Measured by different instruments

## Current and future market for aluminium trihydroxide

World trade [3] in aluminium trihydroxide increased from around 600 ktpy in 1984 to approx 1000 ktpy in 1988, and over 1500 ktpy in 1990.

The demand for ATH is buoyant and according to trends it is likely to be so in the future, too since the ATH products are finding increasing bulk of use in water and effluent treatment, and are called for as detergents and fire retardant fillers. All over the world, the government legislations are likely to ensure continued growth of their use for these important environment protective applications.

## 1.2.2.4 Transition aluminium oxides

The transition aluminas (commonly termed also as activated or sometimes active aluminas) are produced from aluminium trihydroxides by controlled heating to remove most of the water that is chemically bound as hydroxils.

Nowadays, the activated alumina term is applied for all the alumina crystal morphologies which are porous in structure and produced by thermal dehydration. Their crystal structure is chi, eta, gamma, and rho alumina in the temperature range of approx 200 to 900 °C. There is delta, kappa and theta alumina in the higher temperature range of approx 900 to 1100 °C.

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Activated aluminas are extensively used in adsorbtion and
catalysis where their large surface area, pore structure, and
unique surface properties play essential roles.

The change in specific surface area of ATH in function of
temperature is shown in Figure 1.2-3.
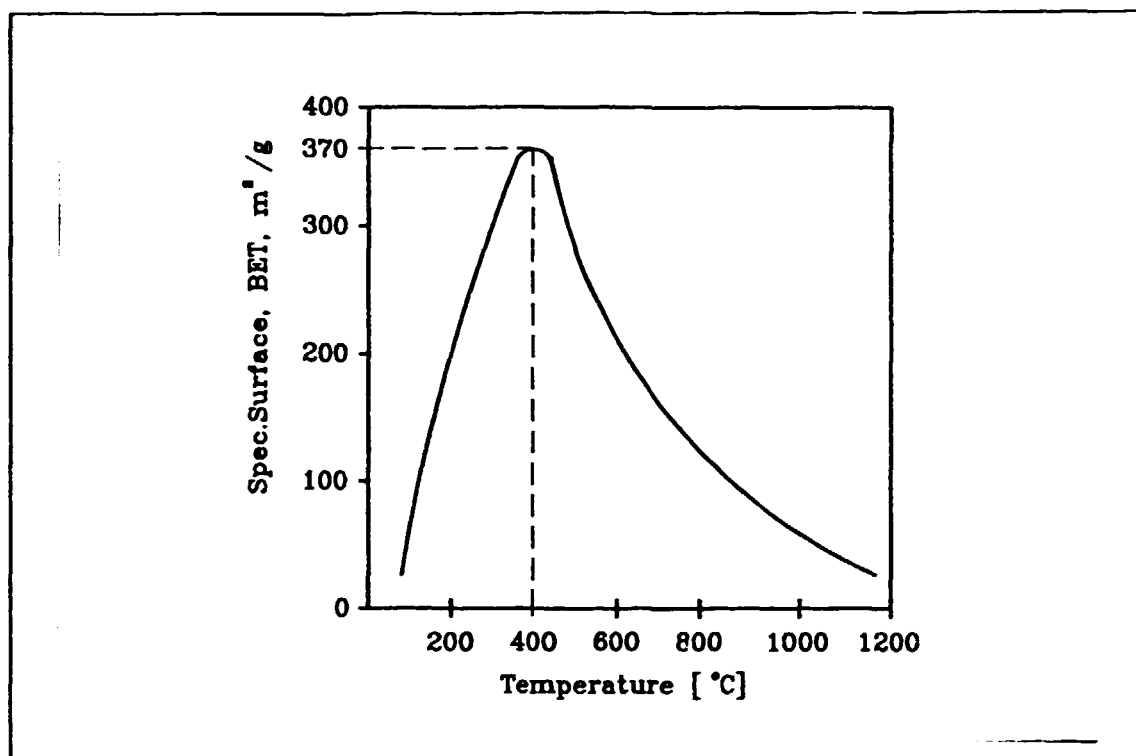


Figure 1.2-3
Specific surface area of ATH vs temperature

Figure 1.2-3 shows that the specific surface area of ATH is
growing in function of increasing temperature up to approx 400 °C
where the largest surface area of ATH can be obtained.

Beside the specific surface area, other important physical
parameters - particle sizes, shapes, and distributions, pore
volume and structure, abrasion resistance, the kind of formation
- are the main features of activated aluminas produced.

## Application of activated aluminas

Figure 1.2-4 is illustrating the main steps of producing
activated aluminas and their use.

```
                    ┌─────────────────┐
                    │   PURIFIED OR   │
                    │   NORMAL ATH    │
                    └─────────────────┘
                             │
                    ┌─────────────────┐
                    │     MILLING     │
                    │  CLASSIFICATION │
                    └─────────────────┘
                             │
                    ┌─────────────────┐
                    │    FORMATION    │
                    └─────────────────┘
                             │
                 ┌───────────────────────┐
                 │ CONTROLLED DEHYDRATION │
                 └───────────────────────┘
                             │
                 ┌───────────────────────┐
                 │  ACTIVATED ALUMINAS   │
                 │   FORMED OR POWDER    │
                 └───────────────────────┘
                             │
         ┌───────────────────┼───────────────────┐
   ┌───────────┐    ┌────────────────────┐    ┌───────────┐
   │ Dessicant │    │ Selective adsorbent│    │ Catalytic │
   └───────────┘    └────────────────────┘    └───────────┘
```

| Dessicant | Selective adsorbent | Catalytic |
|---|---|---|
| Air drying | Removal of P, F, As from | Claus process |
| Water removal | drinking water | -S recovery |
| from other | Cl- removal from | Hydro-treatment |
| gases and | petroleum streams | - increase H/C ratio |
| organic | Chromatography | - removal of S, N |
| liquid | | Reforming |
| | | Hydrocracking |
| | | Auto exhaust control |
| | | Catalyst substrate for |
| | | chemical reactions for |
| | | - ethylene oxide |
| | | - oxychlorination |
| | | - olefin izomerization |

Figure 1.2-4
Application of activated aluminas

## Market for activated aluminas

About 125 kt of activated aluminas are used each year as
catalysts, catalyst supports and several types of dehydration and
(selective) adsorbtion are also figuring on the list of
application.

Since the main fields of ATH applications cover the steadily
growing industrial branches, the increasing use of activated
aluminas is expected, too.


## 1.2.2.5 Calcined, fused and sintered aluminas


### Calcined alumina

This product is generally obtained from Bayer aluminium
trihydroxide by calcining in rotary - kilns and/or fluid-bed
calciners. The conversion to α-aluminium oxide is completed appro
within an hour and at the temperature of 1200 - 1300 °C.

The properties of the resulting product depend upon the quality
of feedstock retention time, and the use of mineralizers. The
products' alumina content ranges between 98 % and 99,8 % with a
proportion of approximately 80 % alpha form, and the surface
area is of 0.5 $m^2$/g - to 20 $m^2$/g.

They are used in the form of either unground, ground or super
ground products with normal, intermediate and low soda contents
for various non-metallurgical applications or are further
processing to sintered tabular or fused aluminas is foreseen.


*Use of normal soda grade alumina*

Normal soda grades of ground materials are produced in different
crystal sizes. Materials consisting of small - less than 1 micron
- crystals are used in the manufacture of abrasives for (metal)
polishing, and serve as additive to glasses and fibre glass.

Products of larger crystal size are used for the production of
electrical porcelain, kiln furniture and sanitary ware, and as a
feedstock to produce fused alumina.


*Use of intermediate soda grade aluminas*

These grades are more thermally reactive and possess better
dielectric properties. They are used for electrical insulators
and spark plugs.

As polishing material and high strength catalyst carriers they
are also used in the production of whiteware porcelains , .


*Use of low soda grade aluminas*

These grades provide good electrical properties and uniform
shrinkage during firing. Their applications are mainly in
electrical and electronic ceramics, high density wear parts, and
alumina involving advanced ceramics .

Development trends of the latter are:

i    improving mechanical properties of alumina ceramics by the
     improvement oftheir microstructure and composition

ii   production of transformation - toughened alumina ceramics

iii  producing very fine - grained bodies by using submicron
     powders in size

iv   producing alumina composites by direct oxidation of molten
     metal

v    development of fibre - reinforced alumina ceramics with
     outstanding mechanical properties

vi   development of alumina powder production by using flame,
     plasma and spray pyrolysis.

## Fused products

White fused alumina is produced from calcined Bayer alumina in
arc furnaces. The fused grain with alumina content of >99.5 % -
is crushed, ground and classified. The properties of fused
products can be modified by the addition of elements like
chromium, titania or zirconia. The fused alumina products are
mainly used for the production of abrasives and refractories.

## Sintered aluminas

Sintered tabular aluminas were developed in the 1930s by the
Aluminium Company of America (ALCOA) and its name has been
choosen because of its  large tablet like crystals of 50 - 400
micron in size. It is produced by heating calcined alpha alumina
to the fusion point and results in fine alpha form crystallites
converting into large hexagonal elongated crystals.

The sintered material is crushed and grounded (classified) to
cffer a wide range of particle sizes - from 6.4 mm to less than
44 microns.

The tabular alumina products are featured with excellent physical
and chemical properties (e.g. high chemical purity, extreme
hardness, high melting point, good thermal shock resistance,
chemical internes etc.) so they are extensively used as
refractory raw material. Generally, refractories made of tabular
alumina are needed in production processes where the temperature
are higher than approx. 600 °C with a number of uses in the range
of about 1400 to 1950 °C.

The greatest user of tabular alumina based refractories together
high quality aluminate cement is the iron and steel industry
consuming more than 50 % of the products.

--------------------------------------------------------------------

Tabular and other alumina based or involved refectories are used
for the following applications:

i    crude oil refineries and petrochemical processes
ii   aluminium production
iii  glass production
iv   casting of high-temperature steel alloys

### Calcium aluminate cement

For over a 100 years, calcium-aluminate cement (CAC) has been
used as  binder in refractory compositions.

These cements can be manufactured from bauxite and/or alumina and
limestone by sintering/fusing the raw material mixture. The
sinter or clinker in which the major hydrating phase is calcium
aluminate (CaO · $Al_2O_3$ and Cao · $Al_2O_3$) is ground to the required
fineness. Three different qualities of CAC - low-, intermediate-,
and high-purity (abbreviated as LP-, IP-, and HP-CAC resp) can be
distinguished depending upon the contamination of the row
material used for the production.

*Production of CAC*

Calcium aluminate cements of low- and intermediate purities can
be produced of high - iron bauxite and of $CaSO_4$ by sundering it
in rotary kilns at a temperature of approx. 1350 to 1450 °C.

As to the fusion method: limestone and bauxite are melted in
electric furnaces or in vertical kilns.

The properties of clinker are depending upon the type and the
rate of cooling.

High-purity CAC can be manufactured from high-purity limestone
and from calcined alumina by sintering them in rotary kilns.

HP clinker of good quality is containing 0.2 to 0.3 % of free CaO
and its L.O.I. is <0.5 % at 1100 °C.

*Market for calcined, fused and sintered alumina products*

The bulk markets for calcined alumina are relatively static -
varying mainly with the overall industrial activities - so no
important changes are expected in the future.

In 1989, the use of abrasives is estimated to be 300 kt,
consisting  of fused alumina grain, mainly. The overall market
for abrasives is declining partly because a better abrasive
product lasts longer and partly because parts are being made to
increasingly accurate tolerance and thus require less finishing.

As far as the refractories are concerned, they consumed 650 kt of calcined and tabular aluminas in 1989 [3].

Their use is declining since on one the hand developments on refractory saving technologies have proved to be successful and on the other hand the overall production of iron and steel industry has been decreased significantly.

On the market the demand for certain ceramics products - like spark plugs, insulators, white wares etc. - is stable (375 kt in 1989) and likely to be so in the future, too.

There are, however important, growing areas of specialty alumina application which are as follows:

- use as wear material for liners, chutes, cyclones, nozzles, mechanical seals, cutting tools, bearings etc. in many industrial branches
- potential growth is expected in the use of translucent alumina for gas discharge lamp envelopes
- increasing production of alumina silicate fibre insulation of which 195 kt were used in 1989 [3]
- fibres with higher (>72 %) alumina content
- use for higher grades of alumina and both for ceramic matrix and metal matrix composites.

## 1.2.3 By-products

### 1.2.3.1 Gallium

Gallium is a silvery-blue metal with similar chemical properties to those of aluminium and zinc and with several unusual physical properties. The main uses for gallium are in semiconducting compounds like GaAs, GaP, GaAlAs etc. These compounds have unusual and outstanding properties which are enabling the development of much higher speed, more compact computers, more efficient microwave receivers, amplifiers and transmitters for satellites and optoelectronic links.

Alloying or mixing of these compounds allows properties to be varied over a wide range for matching to specific needs in each application.

The most widely used techniques for the production of primary gallium are the direct electrolyses of the Bayer aluminate liquor and the selective separation [4, 5] process.

Further details on gallium production (Hungarian practice) will be given in Chapter 2.10.

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### 1.2.3.2 Vanadium pentoxide

Vanadium pentoxide is a reddish-yellow multi-component material in rhomboidal crystallinite form.

During bauxite refining by the Bayer process, vanadium containing sodium-vanadium multicomponent salt is formed consisting mainly of sodium, vanadium, fluoride, phosphorous and arsenic elements.

The salt separated out of Bayer circuit is subjected to further purification processes and the in pure sodium-vanadate solution resulted is processed into vanadium pentoxide by using sulphuric acid decomposition (Hungarian practice) or selective separation/extraction or electrolyses techniques.

Details on Hungarian process are given in Chapter 2.9.

## Reference

[1] W.C. Sleppy et al., Light Metals, pp. 117-124, 1991.

[2] T. Kalman et al., Light Metals, pp. 141-148, 1989.

[3] Mitchell Market Reports, Vol. 1, pp. 1-29, 1990.

[4] P. de la Bretaque et al., U.S.Pat. No. 3887681, June 3, 1975.

[5] J. Helgorsky and A. Leveque, U.S.Pat. No. 3971843, July 27, 1976.

# CHAPTER 2

# PRODUCTS AND THEIR TECHNOLOGIES

## 2.1 PRODUCTION OF ALUMINIUM TRIHYDROXIDE BASED PRODUCTS AT THE AJKA ALUMINIUMINDUSTRIAL CO., LTD.

T. Kálmán, B. Szabó

Changes that have taken place in the past years in world market placed more emphasis on the alteration of production mechanism at a rapid pace. The value added products are having special characteristics and representing high technical standards. According to our surveys, in the past years the demand both on national and - foreign markets increased towards classified aluminium trihydroxide products which are ground to micron grain size range, moreover, national industry consumes a significant quantity of micronized aluminium trihydroxide (ATH) purchased from western countries.

The world consumption of non-metallurgical ATH is very significant - more than two million tons at present - and is constantly increasing. Great amount of aluminium trihydroxide is used as flame retardant fillers in the synthetics, rubber and paper industry, furthermore, in the production of compounds for water treatment.

There is less, but not negligible demand for aluminium trihydroxide in other users' areas (e.g. glass enamel, ceramics coating, glass making, dye industry, cosmetics, etc).

The users' demands for aluminium trihydroxide going to be used as flame retardant fillers (still diminishing grain size possibly down to as small as some microns, narrow range of grain size along with sharp lower and upper limits) can no more be met by the Bayer-type aluminium trihydroxide. Therefore, the production of such kind of products can either be performed by adopting a proper technology, other than that of the Bayer process, or by grinding of Bayer aluminium trihydroxide.

In order to enlarge its product-structure and to meet the increasing users' demand the Ajka Aluminiumindustrial Co., Ltd. and the ALUTERV-FKI Ltd. developed the ALOLT product-family which contains an almost full variety of these products.

### 2.1.1 Application of ALOLT products

#### 2.1.1.1 Floor carpets

When ALOLT is mixed into the backside of floor carpets (which could be latex, rubber or foam) in a quantity of 0.5 to 1 kg/m², the flame propagation is arrested. Recommended compositions: ALOLT 2, ALOLT 8.

--------------------------------------------------------------------

### 2.1.1.2 Hard polyurethane foam

Mixing aluminium hydroxide in the quantity of 28 % total foam weight into any component before the foam producing reaction, the foam will be totally flame-resistant.

Recommended compositions: ALOLT 8, ALOLT 30.

### 2.1.1.3 Soft polyurethane foams

Such as furniture paddings. Flame resistance can be achieved by dipping into an aluminium trihydroxide suspension.

Recommended compositions: ALOLT 8, ALOLT 30.

### 2.1.1.4 Conveyor bands

Adding 14-20 weight % of aluminium trihydroxide into the rubber mixture, a flame resistance as required in the mining irdustry can be obtained, with the composition ALOLT 8.

### 2.1.1.5 PVC-coated tent-clothes

The amount of aluminium hydroxide should be about 20-25 weight % of the PVC coating. When the same textile is to be used for flat roof insulation, the amount of aluminium hydroxide to be added is about 30 weight %.

Recommended compositions: ALOLT 8.

### 2.1.1.6 Glass fibre reinforced polyester resin products

Such as containers, tubings, chairs, vehicle parts, sailing boats, etc.

Adding aluminium trihydroxide in a quantity of about 30 weight % of the laminate resin content, the flame is strongly suppressed, for higher aluminium trihydroxide concentration it is extinguished.

Recommended compositions: ALOLT 2, ALOLT 8, ALOLT 30.

Figure 2.1-1. illustrates the development of using flame suppression materials in USA in 1982 and 1987.

Description of production process:

Micronized aluminium trihydroxide is produced by two types of manufacturing processes. The ALOLT 1 and 1 F, 50 F and ALOLT 90 F products are produced by chemical reaction however the ALOLT 2 and 2 F, ALOLT 8 and 8 F, ALOLT 30 and 30 F are produced by grinding the ALOLT 1 and 1 F products. The filtered and washed

Al(OH)$_3$ is produced by chemical reaction which, considering its crystal structure, is a hydrargillite. Before grinding and marketing aluminium trihydroxide has to be dried which is carried out in an ATH-dryer of 12.000 tpy capacity, developed by Ajka Aluminiumindustrial Co., Ltd.
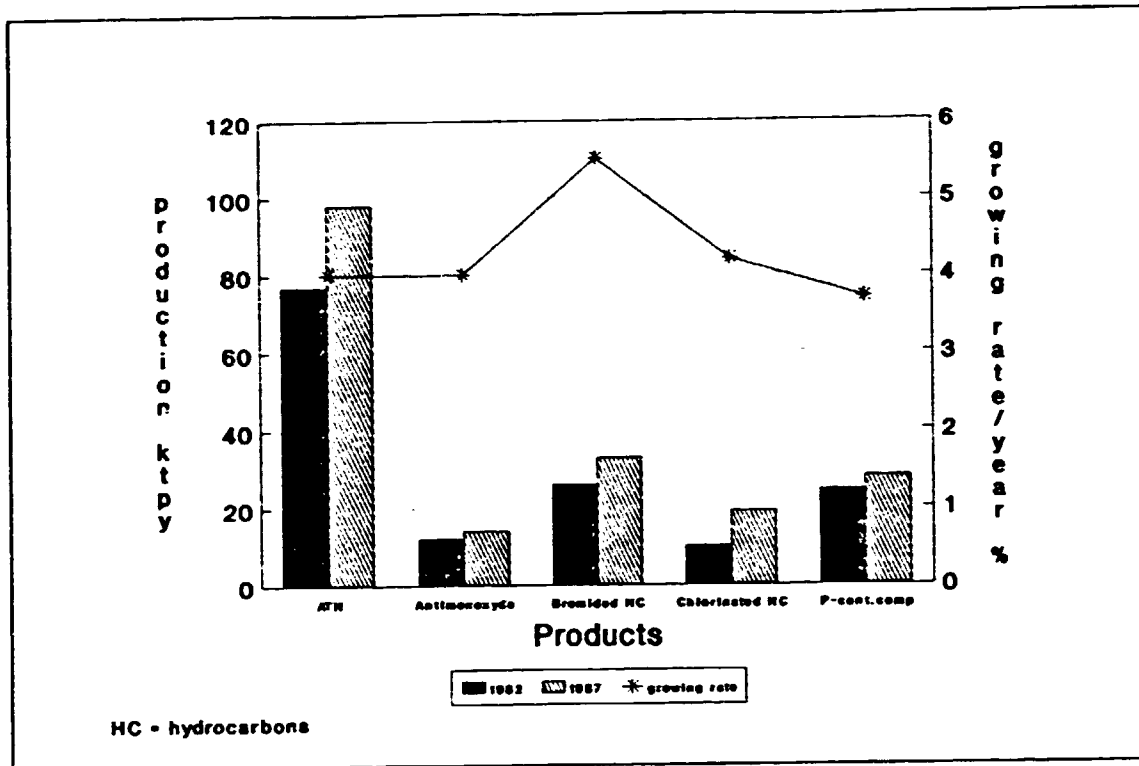


Figure 2.1-1
Flame retardant use in USA in year 1982 and 1987

## 2.1.2 Production by grinding

For grinding and separation of dried aluminium trihydroxide the Ajka Aluminiumindustrial Co., Ltd. together with the ALUTERV-FKI Ltd. has developed an air-jet mill along with separating and classification apparatus.

### 2.1.3.1 Principles of development of air-jet mill

The basic objective was to develop an equipment with lower operation costs than those of the units known and used at present.

It may be established in general that the specific grinding costs for a given material are affected by the following factors:

- grinding efficiency

- specific energy consumption
- abrasion resistance of materials used in the grinding
  chamber.

Grinding efficiency itself depends upon the following factors:

- structural solution
- material flow density applied
- free path and impact speed of particles
- pressure and velocity of grinding gas
- initial grain size of material to be ground
- feature of the grinding system (open or closed circuit)
- hardness of lining elements used in the grinding            c
  hamber.

On basis of detailed analysis of the above factors and the
solution of design of the air-jet mill known at present (Anvil-
mill, Majac, Micronizer, Jet-O-Mizer, Double-Impact-Mill,
Fluidized Bed Counter-Jet-Mill) and the investigation resulting
advantageous and disadvantageous characteristics, the conclusion
has been drawn that a new type air-jet mill could be developed by
eliminating the deficiency of the Micronizer-type mill thus
preserving its advantageous properties.

The following aspects have been taken into consideration:

Pressure of grinding gas must be kept at higher level than
usually in order to increase grinding efficiency.

Increasing pressure of grinding gas is justified by the
increasing speed of power impulse, innert tension of impacting
grains and at the same time they become also apparently more
brittle. Both factors affect positively the impact based crushing
process, however, the positive effect obtainable by increasing
the pressure is restricted by the fact that, at the moment, when
the inner stress attains the plastic yield stress the medium
starts coarsening due to agglomeration occurred.

Figure 2.1-2. visualizes the above standing and is based on
measuring data obtained from a model test unit.

Figure 2.1-2 (a) represents the specific work required to obtain
an identical grinding efficiency; (b) represents the specific
energy costs for equivalent work performed; (c) represents the
uniformity factor of the ground product of an RR-distribution;
(d) represents the 80 % grain-size of the ground product of ab
RR-distribution; (e) represents the specific consumption of
grinding gas; and (f) represents the specific working capability
of the grinding gas; all these features are plotted against the
pressure of $CO_2$ grinding gas.

It can be read off from the graph that increasing the pressure of
grinding gas increases the grinding efficiency (curve a) along
with diminishing grinding costs (curve b) and growing refinement
of the final product (curve c).
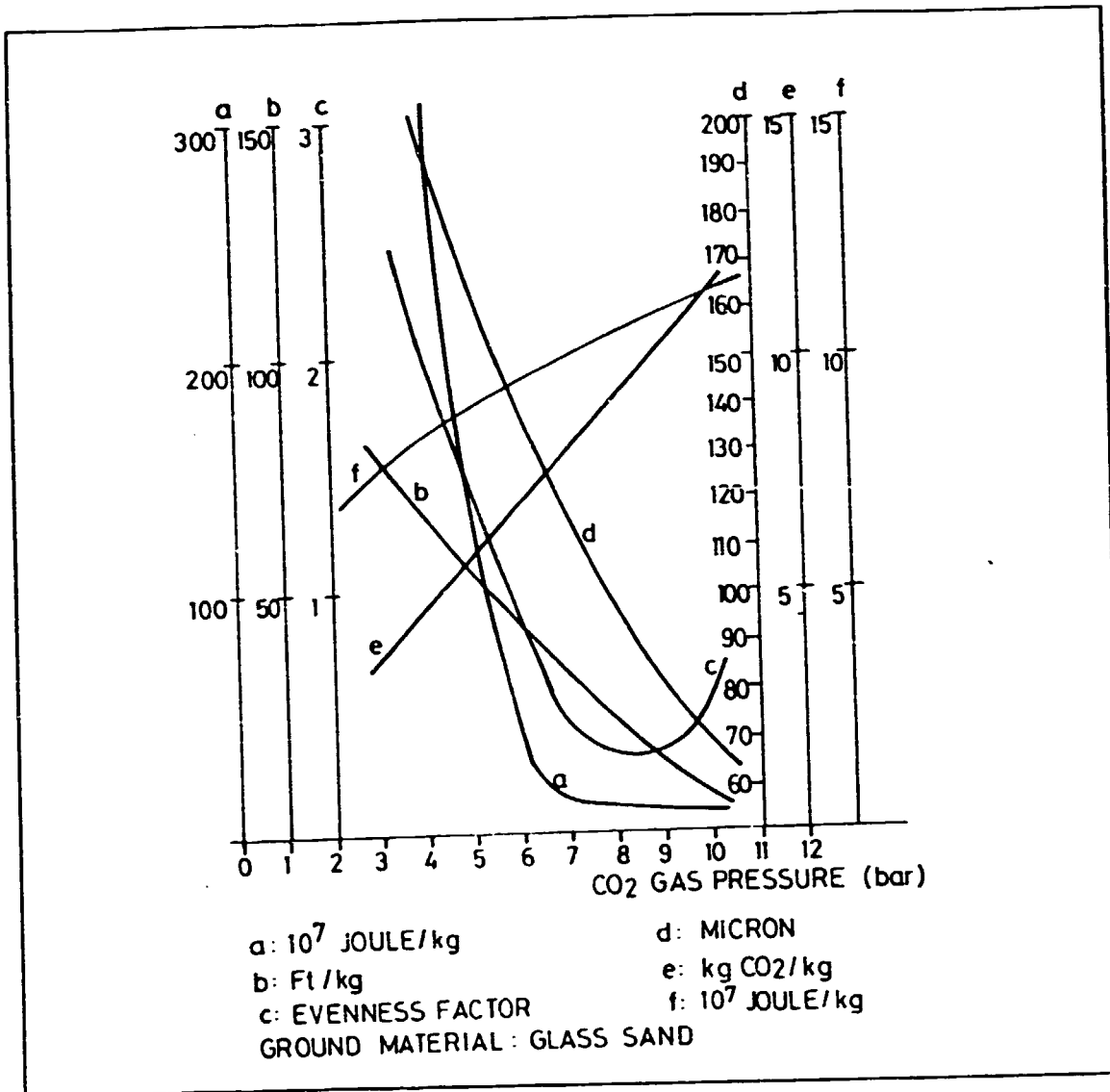
**Figure 2.1-2**
Characteristic curves of grinding

Figure 2.1-3. shows the essential relation according to which the useful grinding work increases hyperbolically in the function of speed (resp. pressure) of entering gas.

Calculating the rate of impact speed the value obtained is usually between one-third to twice the speed of sound, however, experimentally twice or three-times higher values can be obtained as optimum.

As to the structure of air-jet mill, the final conclusion can be drawn that grinding gas must leave the nozzle at the rate multiple of the sound velocity. In this case economical operation can be reached only if gases with the pressure of 10-25 bar are flown-out through nozzles of small diameter, because high outlet

velocities with little gas consumption can only be obtained with small diameters.
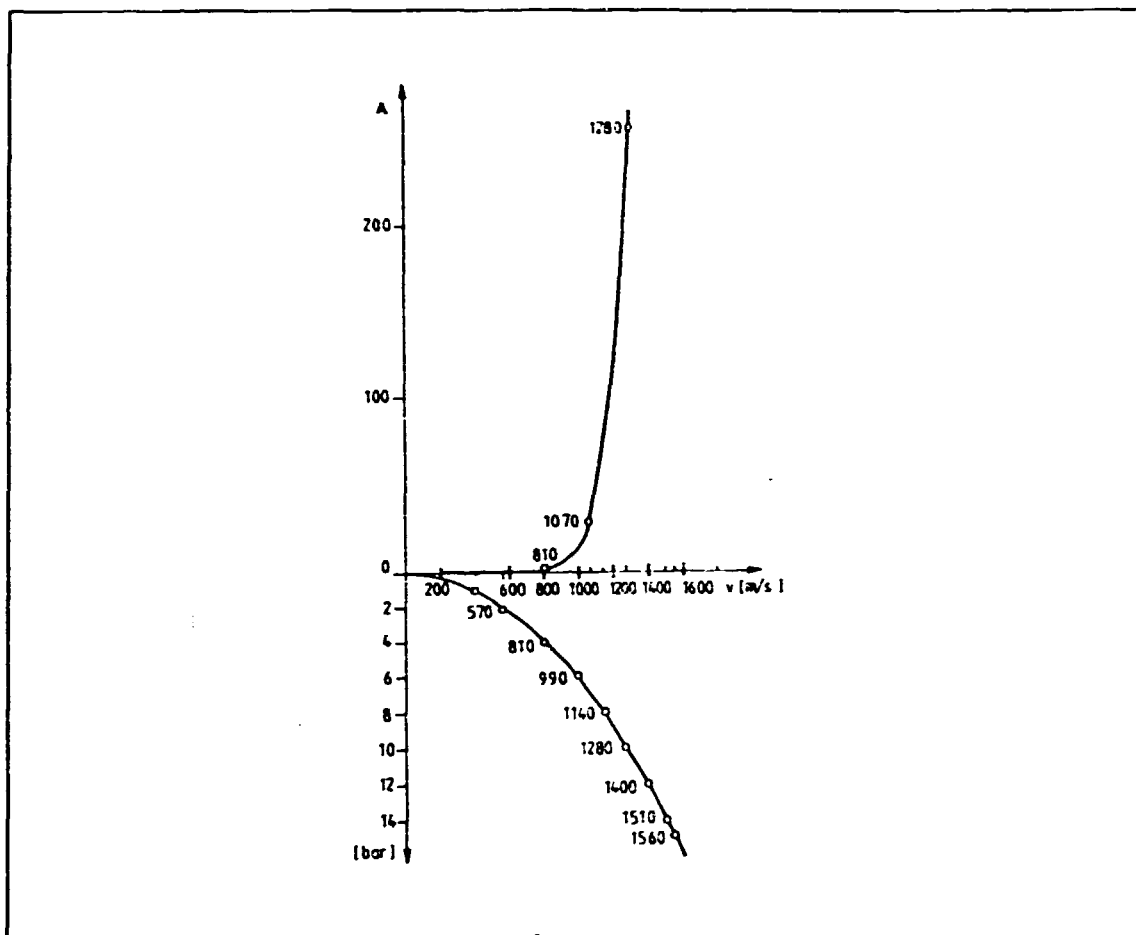


**Figure 2.1-3**
Effect of grinding gas pressure and velocity on useful grinding work

### 2.1.3.2 Air-jet mills in practice

Construction plans of the new air-jet mill and manufacturing of the apparatus were carried out on basis of the above principles .

Figure 2.1-4. shows the body of the air-jet mill along with 3 pregrinding chambers the feed direction being arranged tangentially to the former one. Wortex of the pregrinding chambers is generated by 4 nozzles each being arranged at 90° angles to each other and their axes are shifted in a way that they touch a theoretical circle. Two of the four nozzles serve to convey material the two others to reduce wear. The latter are operated at lower pressures and are capable of adding cooling medium or surface-treating reagents. The nozzles of the main grinding area are arranged before and behind the pregrinding chambers. The angle of direction of gas jets is adjustable. Optimization of operation of the mill is effected partly by the adjustment of the angles of nozzles, partly by setting the blade angles of the inner classifier in the main grinding area and by

changing the air pressure applied to the individual nozzles, as well.

The air-jet mill and the feeding system is located in a sound and dust proof cabinet. The sides of the cabinet are equipped with pneumatically operated folding doors to make assembly and operation easier. The control desk is in front of the cabinet, the feeding container is on its top, and the in- and outgoing pipelines are under it. An auxiliary injector is built into the pipeline, through which the granules leave, and it ensures the possibility of transportation to a greater distance, or a possible excess air supply of the separator.
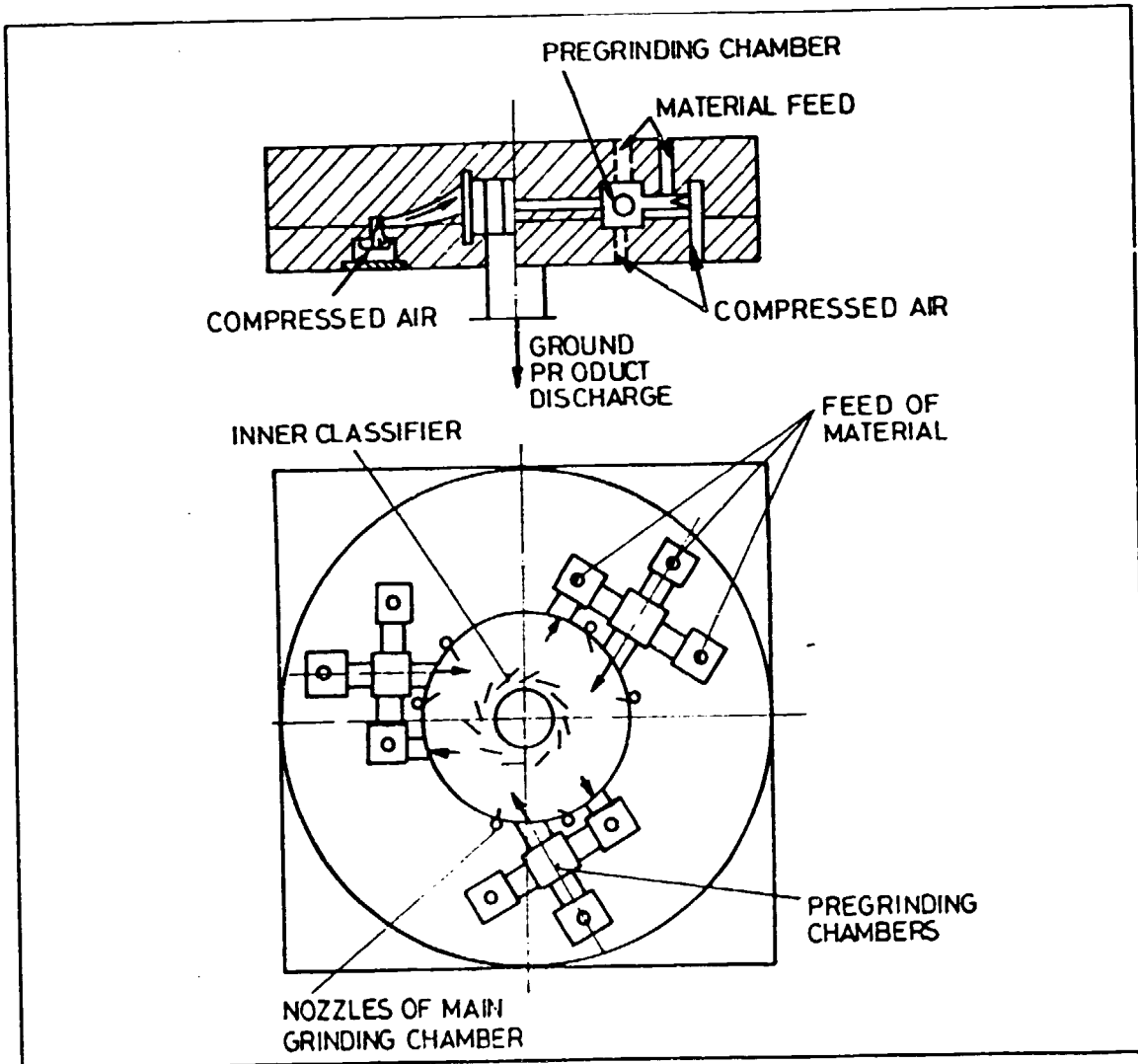


Figure 2.1-4
Air-jet mill

## 2.1.3.3 The external separator classifier, and cyclone

### Separator

When planning and manufacturing the apparatus it was a principle that the separator and cyclone to be developed should not contain mobile parts and the resistance should be minimal. These requirements can be satisfied by a cyclon-like apparatus in which material flow takes place on an optimum spiral course. In this case the grains are affected by a constant delivery force along the course. Its principle scheme can be seen on Figure 2.1-5.
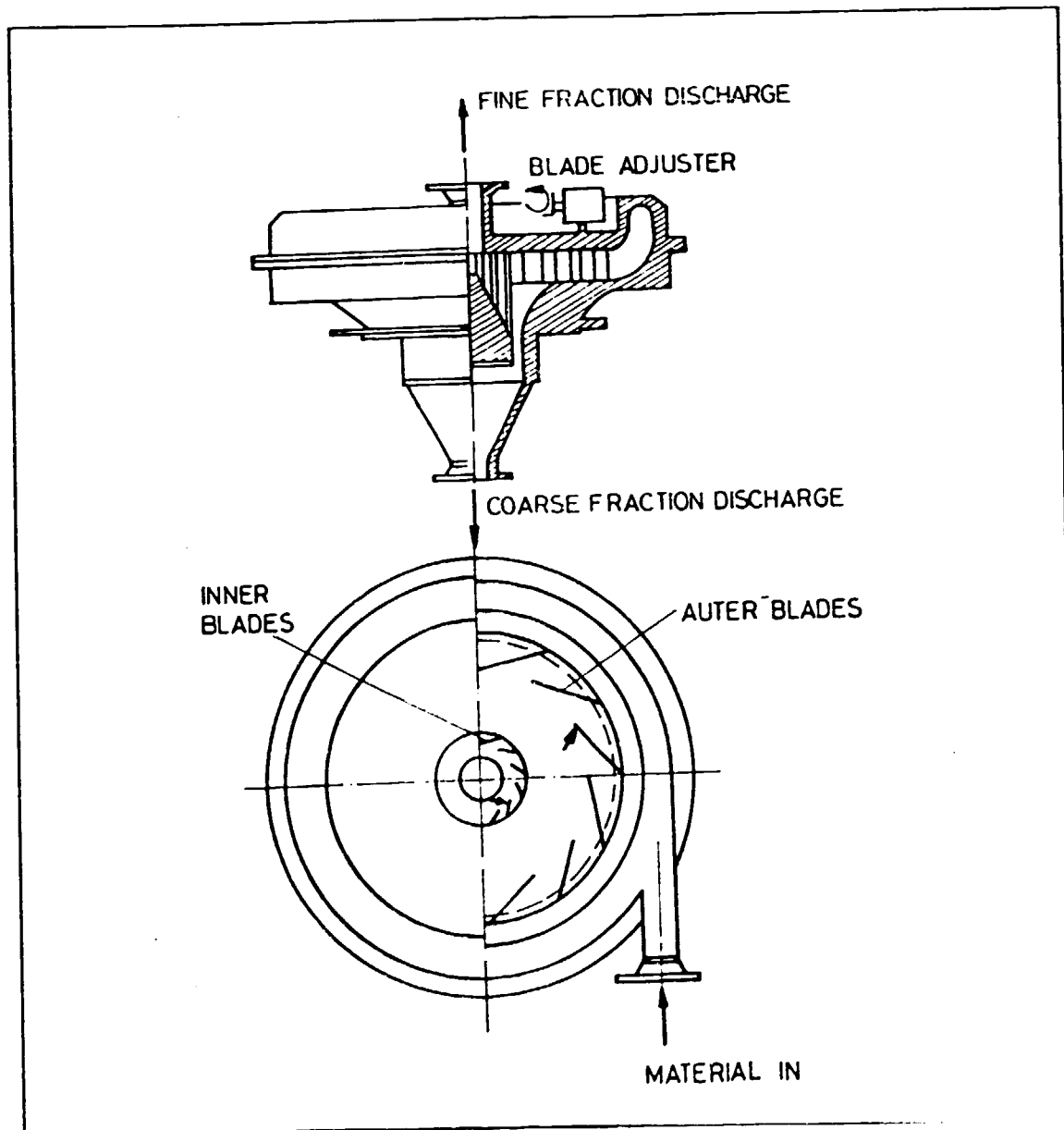


**Figure 2.1-5**
**Fine and coarse classifier**

This condition is fulfilled in a centrifugal field, if the radial acceleration, as well as the components of radial acceleration are constant. On the bases of development plans prepared at the ALUTERV-FKI Ltd. plant-scale apparatuses were made in two sizes (0.75 m and 1.5 m in diameter). The larger apparatus is suitable for fine, while the smaller one for rough separation. The blading of the separators, together with the mobile (blade-angle setting) mechanism can be lifted out from above, making their assembly and maintenance easier.

## Cyclone

The structure of the cyclones is very similar to that of the separators, but as to their size they are much smaller (their diameter is about half of that the diameterof the separators) to ensure the air speed required for good separation. Another difference is that the inlet pipe-end is the reverse of that of the separators to make better use of the course-alternating cyclone effect, and they have fixed blades.

## 2.1.3 Description of the technological system

According to the schematic diagram shown in Figure 2.1-6, a grinding and separation system was developed with the air-jet mill separators and cyclones introduced above.

Dry aluminium trihydroxide is transported pneumatically from the storage bin to the feeding container of the air-jet mill. Pneumatic transportation, compressed-air supply for the air-jet mill and separators are ensured by a screw-compressor which, at the final pressure of 20 bar can convey 1.180 $m^3$/h air. Separation is done in three stages, thus materials of various grain sizes can be obtained, according to the requirements of the customers. Products leaving with the air stream are recovered from the air in the cyclones. To recover the fine powder and to protect the environment, air leaving the cyclones is filtered by dust-separating bags. This is the very place where the finest, ALOLT 30 type product is obtained. Present capacity of the system is 1.500 - 1.6000 tpy. The contamination level, especially $Fe_2O_3$-contamination of ATH produced by the Ajka Aluminiumindustrial Co. Ltd. is comparatively high at present thus "white" ATH is purchased from the Magyarovar Alumina and Fused Alumina Mfg., Ltd. for the production of the chemically cleaner, F type ground products.
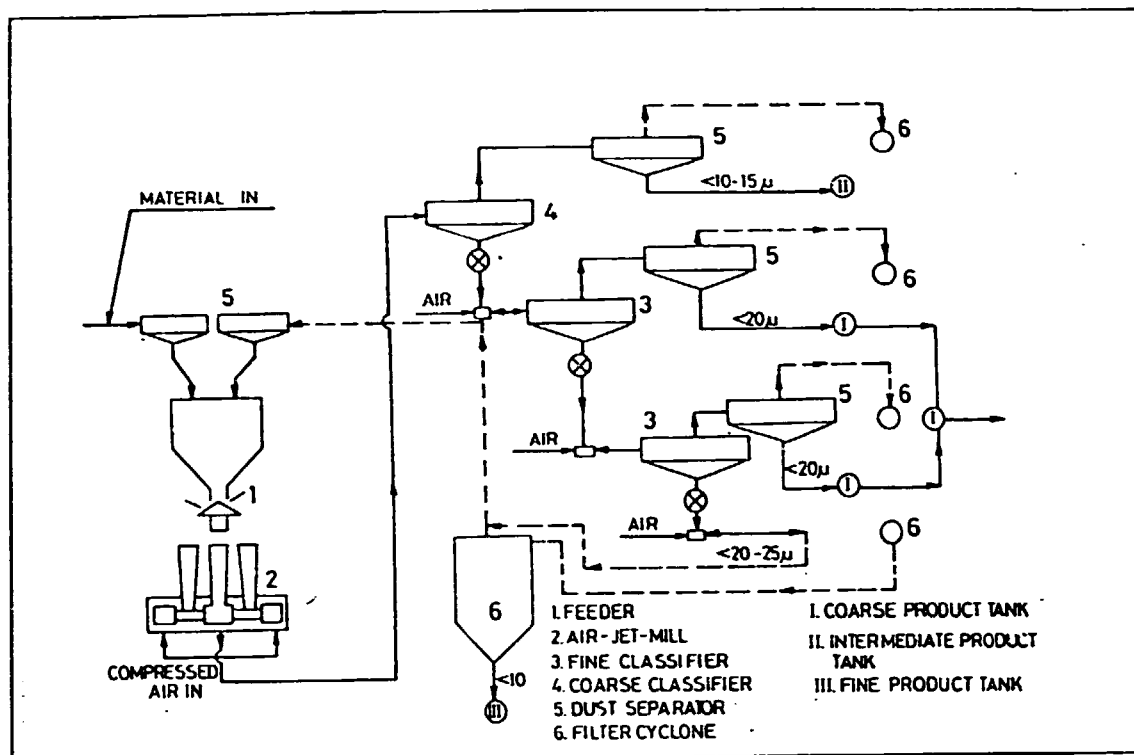
**Figure 2.1-6**
**Simplified scheme of ATH grinding plant**

Because of its crystal structure and larger average grain size
the grinding of ATH from Mosonmagyaróvár is harder, so it has to
be ground twice. Thus the capacity of the apparatuses decreases,
and the specific energy requirement is higher.

Specific energy consumption of producing ALOLT products when
grinding our own ATH is as follows:

- electric energy                800 kWh/t
- compressed air                5.200 Nm$^3$/t

## 2.1.4 Production by crystallization

ATH products like ALOLT 90 (average grain size 1.0 - 3.0 $\mu$m) and
ALOLT 50 (grain size   3.0 - 5.0 $\mu$m) are having   good sale
possibilities for special uses. The great energy demand would
make unprofitable the production of such grain size products by
grinding . The manufacture of these products are practically
obtained with special crystallization technology. The grain size
of the resulting ATH can be regulated by changing the
precipitation parameters, e.g. the cooling of seeding   rate
aluminium-sulfate additive. The great advantage of the process is
that the precipitation efficiency is not lower than the
efficiency which derives from the production of the normal Bayer
ATH, even it can be exceeded if parameters are well choosen.   We

succeeded in achieving 55 - 60 % precipitation efficiency during 48 hours retention time in our large-size laboratory. The grain size distribution of the originating ATH is homogeneous, and does not require any further procedures. The technological sketch of fine ATH production can be seen in Figure 2.1-7.
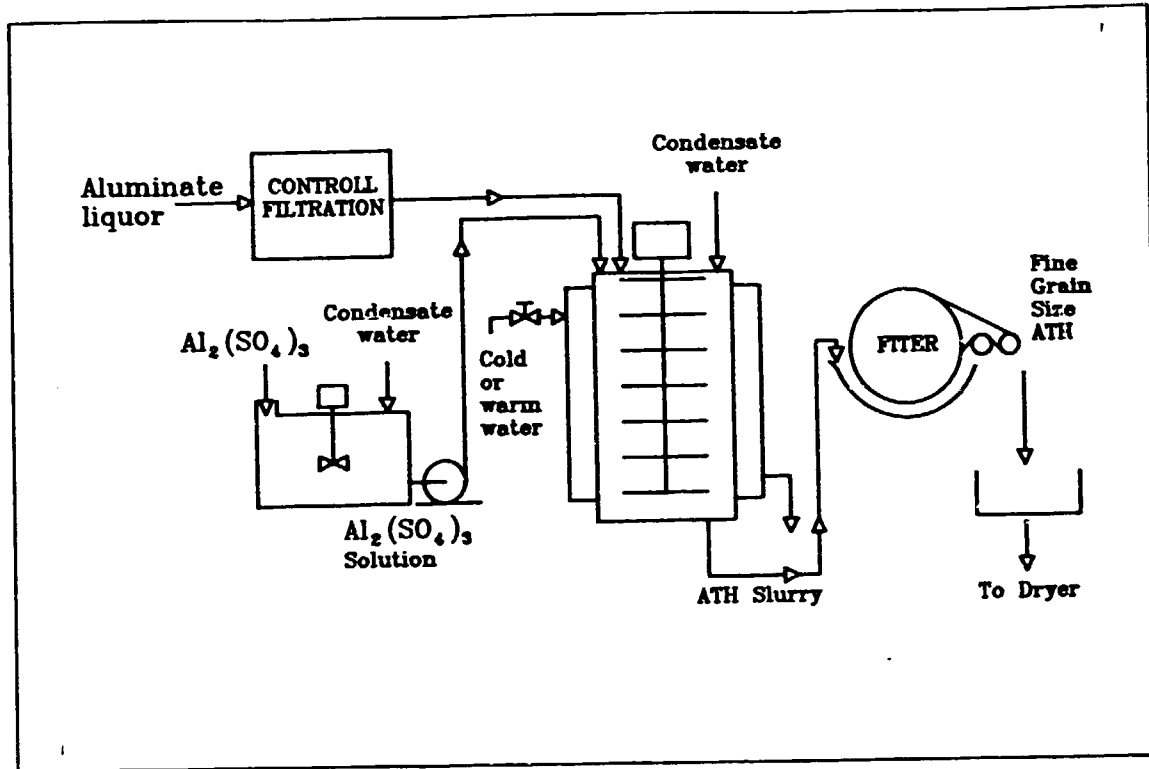


Figure 2.1-7
Technological sketch of fine ATH production

Figure 2.1-8. illustrates the grain size distribution of fine ATH produced by precipitation.
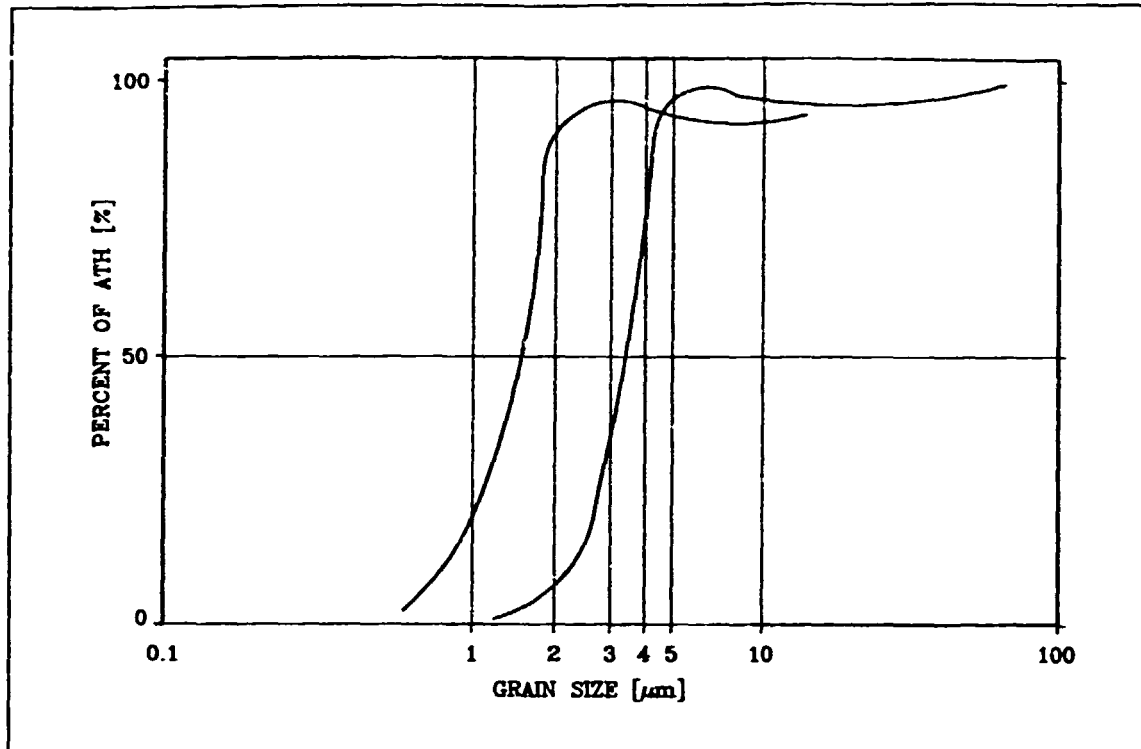
**Figure 2.1-8**
**Grain size distribution of fine ATH produced by precipitation**

The main parameters of our product can be seen in Tables 2.1-1 and 2.1-2

**Table 2.1-1.**
**Product manufactured by granulation**

| General characteristic parameters | |
|---|---|
| $Al(OH)_3$ | 99.5 % |
| $SiO_2$ | 0.01 - 0.02 % |
| $Fe_2O_3$ | 0.01 - 0.025 % |
| $Na_2O$ total | 0.3 % |
| $Na_2O$ water soluble | 0.03 % |
| Moisture content | 0.2 % |
| Combustion loss | 34.5 % |

Table 2.1-2
Caracteristics of ALOLT products

|                 | Litre weight kg/$m^3$ | Density g/$cm^3$ | $D_{50}$ $\mu m$ | Spec. surface $m^2/g$ |
|-----------------|-----------------------|------------------|------------------|-----------------------|
| ALOLT 1, 1 F    | 1.200                 | 2.4              | 40-60            | 0.01                  |
| ALOLT 2, 2 F    | 600                   | 2.4              | 20-25            | 0.2-1                 |
| ALOLT 8, 8 F    | 400                   | 2.4              | 10-15            | 1-2                   |
| ALOLT 30, 30 F  | 300                   | 2.4              | 5-10             | 2-4                   |
| ALOLT 50 F      | 250-350               | 2.4              | 2.5              | 3.5                   |
| ALOLT 90 F      | 250-300               | 2.4              | 1-3              | 6-9                   |

The colour of product F is white since its iron and organics
content is low.

## 2.2 PRODUCTION OF SPECIAL ALUMINIUM-HYDROXIDES AND ALUMINAS BASED ON THE BAYER CYCLE

J. Zöldi, M. Altrichter

### 2.2.1 Basic materials of specialty alumina-hydrate and alumina products

Most of the special alumina-hydrates and aluminas are produced using intermediate products of Bayer refineries as basic materials. Requirements of different users for physical and chemical properties of the special products are extremely varied.

The objective of this lecture is to show the most important properties of the main product lines of special aluminas, comparing to that of smelting grade alumina and showing the main technological modifications used for producing these special products.

In the last two decades due to development of electrolysis technology and environmental protection the requirements of aluminium smelters for chemical and physical properties of alumina became more and more strict. The main characteristic properties (chemical impurities, particle size, calcination degree, and handling properties) of the smelting grade (sandy type) alumina are summarized in Table 2.2-1.

**Table 2.2-1**
**Chemical and Physical Properties of Smelting Grade Alumina (Sandy Type)**

| Chemical impurities: | % |
|---|---|
| total $Na_2O$ | 0.3-0.4 |
| $SiO_2$ | 0.010-0.015 |
| $Fe_2O_3$ | 0.010-0.015 |
| $V_2O_5$ | 0.0024-0.0028 |
| $P_2O_5$ | 0.0010-0.0015 |
| MnO | 0.0005-0.0008 |
| Zn | 0.0006-0.0012 |
| **Particle size:** | **%** |
| - 45 $\mu$m | 5 - 7 |
| - 20 $\mu$m | 0.5 - 1.5 |
| - 10 $\mu$m | 0.2 - 0.7 |
| Median particle size | 60 - 70 $\mu$m |
| **Calcination degree:** | |
| L.O.I. (300-1000 $^{\circ}$C) | 0.6 - 0.8 % |
| $\alpha - Al_2O_3$ content | 7 - 20 % |
| Specific surface area (B.E.T.) | 50 - 75 $m^2$/g |
| **Handling properties:** | |
| Bulk density ("loose") | 920 - 1000 $g/dm^3$ |
| Bulk density ("tapped") | 1120 - 1160 $g/dm^3$ |
| Angle of repose | 30 - 34 grade |
| Attrition index | 15 - 20 % |
| Dust index | 1 - 2 kg/t |

Special alumina products differ from smelting grade alumina in purity, particle size, calcination degree, density, surface properties, hardness, shape of crystals, colour etc. On the basis of minerologycal composition the special products can be classified as follows:

- alumina hydroxides,
- activated aluminas,
- specialty calcined aluminas,
- high purity aluminas.

The connection between Bayer-cycle and special alumina-hydrate and alumina producing technologies is shown in Figure 2.2-1. Most important technological modifications used for producing above mentioned product lines will be discussed one by one.
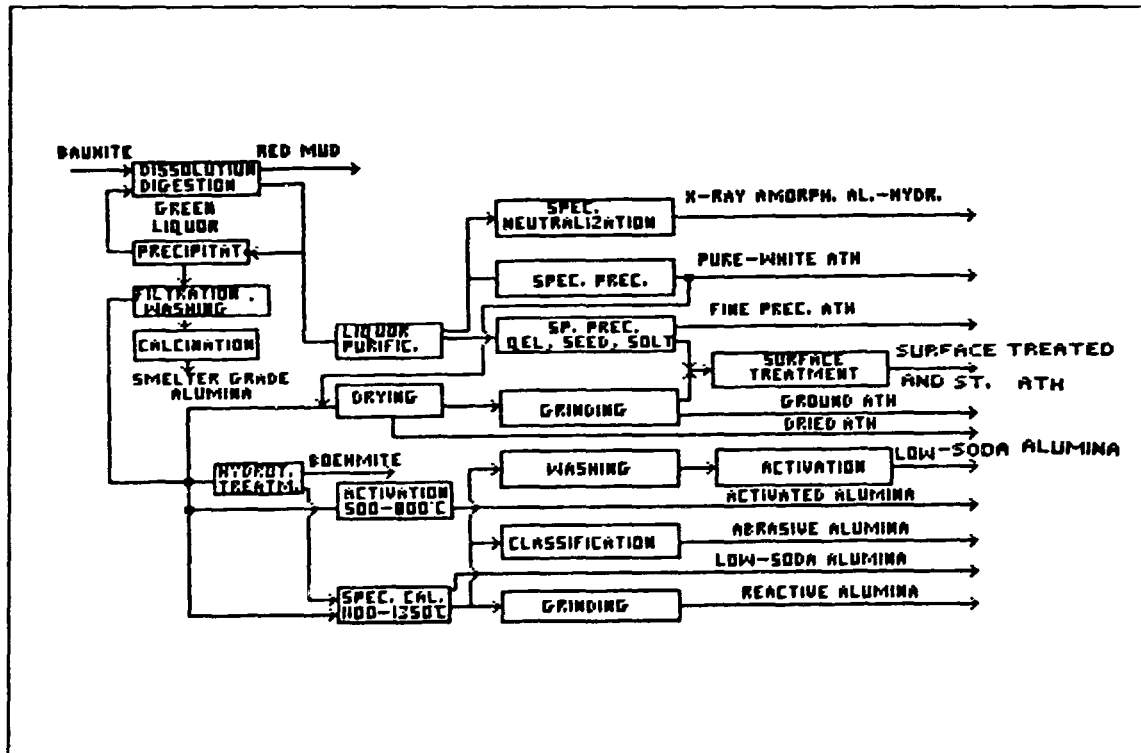


Figure 2.2-1
Connection beetwen Bayer-cycle and special alumina technologies

## 2.2.2 Aluminium hydroxides

The commonly used term, alumina-hydrate covers several different cristalline and amorphous aluminium hydroxides [1]. Minerological classification of different aluminium hydroxides is shown in Figure 2.2-2.
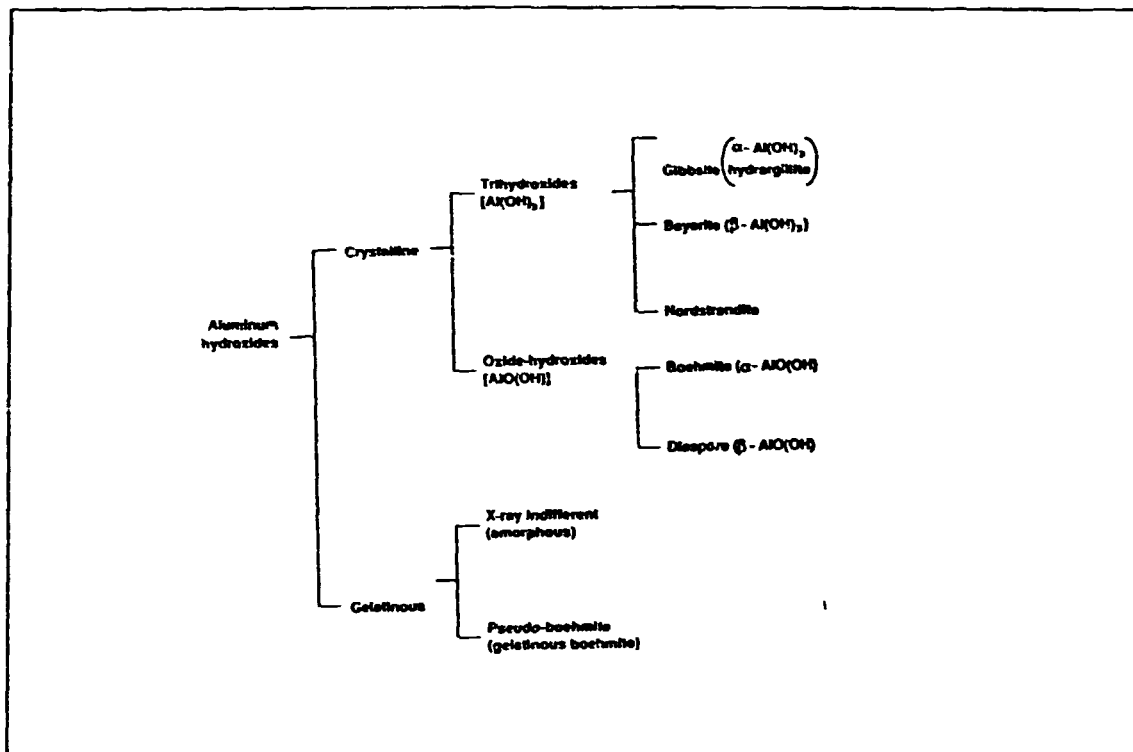
**Figure 2.2-2**
**Classification of aluminium hydroxides**

All of the aluminium-hydroxides shown in Figure 2.2-2. are true
hydroxides and do not contain water or hydration. Green liquor
and filtered, washed alumina-hydrate from Bayer-cycle can be used
as basic material for producing special aluminium hydroxide
products (see Figure 2.2-1).

Aluminium-hydroxid products used in several field of industry (as
filler material, flame retardant, pigment, basic material of
synthetic marble and onyx etc.) can be characterized by the main
properties summarized in Table 2.2-2. To reach the special
properties (whiteness, chemical purity, grain size, specific
surface properties etc.) the following technological solution are
applied:

- liquor purification,
- grinding and classification,
- special, fine precipitation,
- surface treatment.

Table 2.2-2
Chemical an Physical Properties of Special Alumina Hydrate Products

| Chemical impurities | Normal products | Pure products | |
|---|---|---|---|
| total $Na_2O$      % | 0.3-0.4 | max 0.1 | |
| washable $Na_2O$ % | 0.2-0.06 | 0.01 | |
| $Fe_2O_3$          % | ≈ 0.015 | < 0.01 | |
| $SiO_2$            % | ≈ 0.015 | < 0.01 | |
| $Al_2O_3$          % | ≈ 65 | ≈65.3 | |
| Physical properties | | | |
| | Unground | Ground | Fine precipitated |
| Median grain size $\mu m$: | 50-80 | 3-50 | 0.5-3.0 |
| BET surface area $m^2/g$: | <0.1 | <2 | 12-2 |
| Bulk density $g/dm^3$: | ≈1200 | 500-1000 | 160-400 |
| Whiteness (Elrepho 457 nm): | <80 | 80-95 | >95 |
| Surface treatment: | without | with and without | |
| Oil adsorption $cm^3/g$: | ≈ 25 | 15-60 * | |
| DOP. adsorption $cm^3/g$: | ≈ 10 | 15-70 * | |

* = depending on surface treatment


## 2.2.2.1 Liquor purification


### Decreasing of the colouring organics

Alumina hydrate obtained from the Bayer-cycle usually has rose-yellowish colour because of colouring organic compounds originated from bauxite and enriched in the Bayer cycle. Iron oxide content of bauxite residue built in a small quantity into the alumina-hydrate imparts a rose-like colour to the hydroxide, too. The soda-sinter process produces a hydroxide that is practically completely free from organic colouring matter and is white. Very few sinter plants are, however, in operation today. A lot of efforts have been made for liquor purification to satisfy the market demand for white aluminium hydroxide. The following methods can be used for decreasing the colouring organic contents of Bayer-liquor:

- Kieserite ($MgSO_4.H_2O$) and other magnesium compounds are proposed by ALCOA Chemie (former Giulini) [2] for humate removal. According to the procedure kieserite ($MgSO_4.H_2O$) is added into the bauxite digester or clean pregnant liquor prior to security filtration. In aluminate liquor there is a co-precipitation of $Mg(OH)_2$ and $Al(OH)_3$ which adsorb the high molecular weight humates. The method is effective in reduction of iron content of the liquor as well. Quantity of the kieserite added is 6-10 kg/t alumina.

- Wet oxidation by oxygen or air at different temperatures (200-260 $^\circ C$) is proposed by others [3, 4 - 6]. During the wet oxidation of aluminate liquor first the colouring high

molecular weight humates are decomposed. Humate destruction in a caustic liquor of 225 gpl caustic $Na_2CO_3$ concentration at 200 $^{\circ}C$ in the presence of 0.5 gpl $O_2$ is shown in Figure 2.2-3.
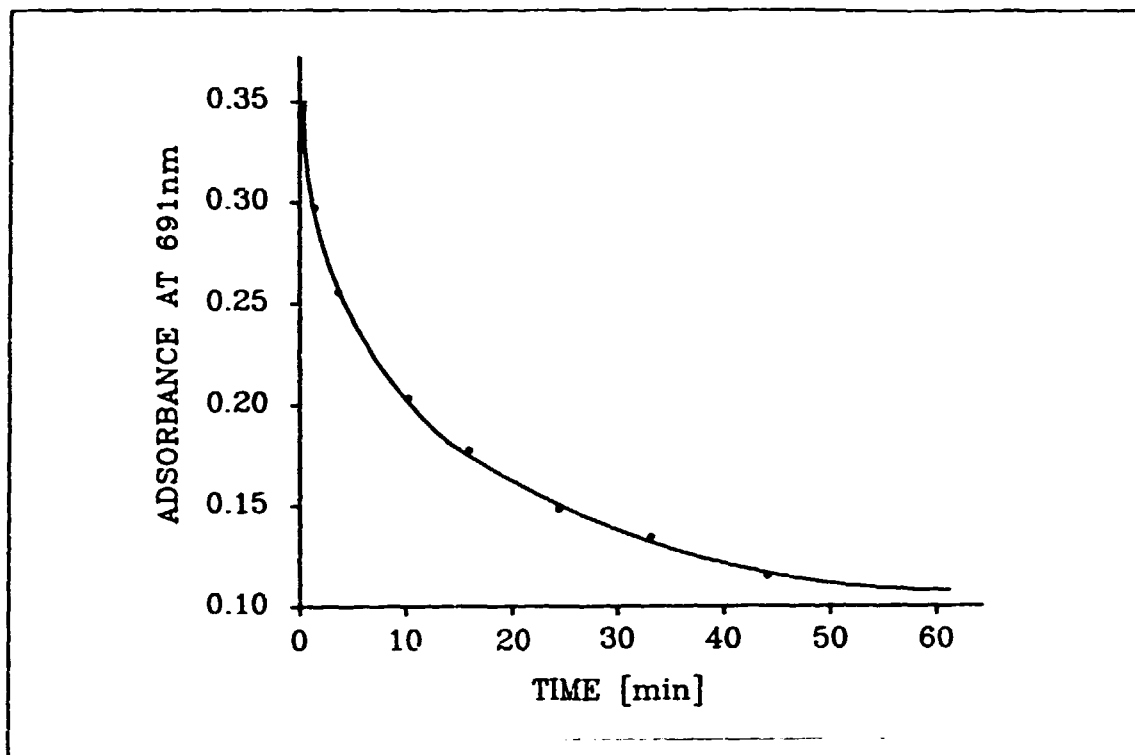


**Figure 2.2-3**
**Wet oxidation of organic compounds**

- Decomposition of the organic compounds by so called "liquor burning". Showa Aluminium has developed a new process [7, 8]. According to the process alumina trihydrate and the Bayer liquor is mixed together and the resultant mixture is calcined, sodium organates in the Bayer liquor are decomposed and, reacting with the alumina component forms sodium aluminate solid. Process flow diagram of the liquor burning is shown in Figure 2.2-4.
- Humate removal by synthetic cationic polymer additives. KAISER and NALCO suggested dosage of special cationic polymer to the pregnant liquor before security filtration for precipitation of colouring humates [9]. Quantity of the polymer added in plant practice is 15 - 50 $g/m^3$ aluminate liquor.
- Redissolving of Bayer-hydrate in fresh caustic solution. Clean aluminate liquor can be gained by dissolving Bayer hydrate in caustic liquor at 100-105 $^{\circ}C$ temperature or at higher temperature under pressure.
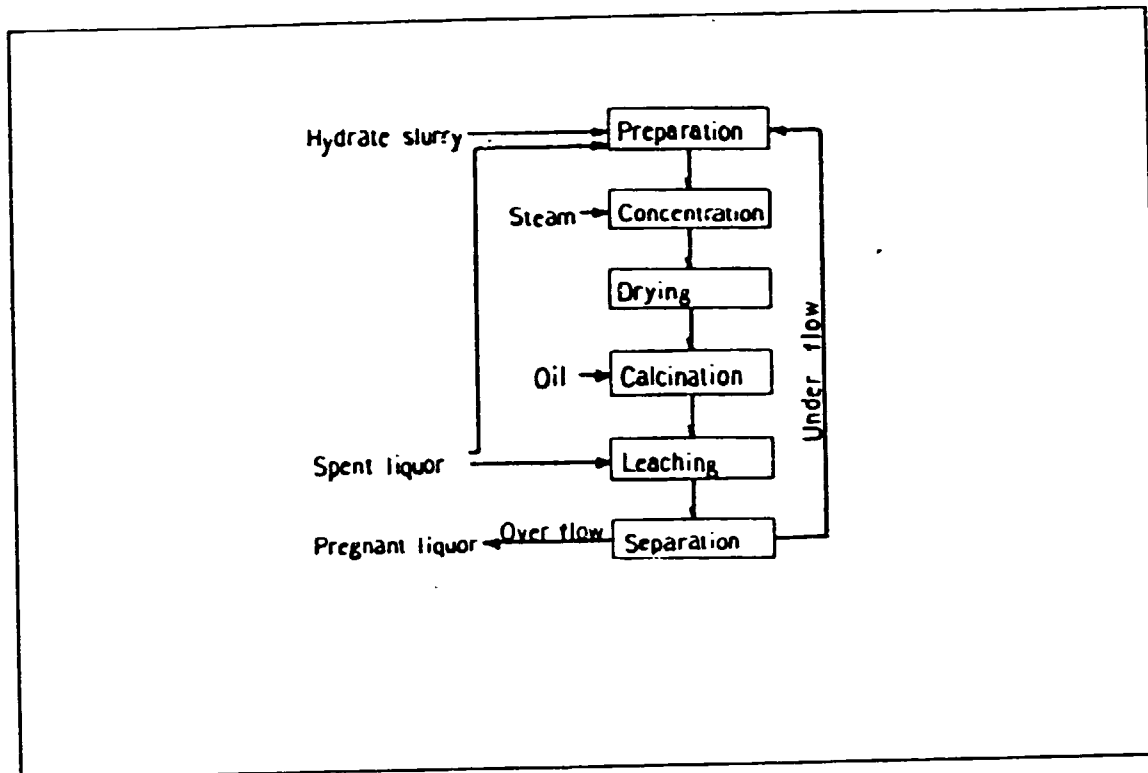
**Figure 2.2-4**
**Process flow diagram of the liquor burning**

## Decreasing of the iron content

Different processes are used for decreasing the iron content of the aluminate liquors.

- Security (or control) filtration of the aluminate liquor using lime or calcium-aluminate as filtering aid.
- Some special synthetic flocculents can be added to the red mud settling to decrease the so-called colloidal iron content of the aluminate liquor.
- Soluble iron in green liquor can be reduced by the addition of tertiary polyamines, which chelate the soluble iron and allows it to be scavenged from the liquor by the settled red mud and during security filtration of the green liquor [10].
- Iron content of the green liquor can be decreased effectively by the so-called "scalping precipitation". By mixing of green liquor in presence of 100-200 gpl alumina hydrate during 20-30 minutes iron content of the liquor can be decreased to 2-3 mg/l.

## 2.2.2.2 Grinding and classification

Separate paper (Chapter 2.1) deals with this topic.

--------------------------------------------------------------

### 2.2.2.3 Special precipitation methods for producing super-fine aluminium hydroxides and low $Na_2O$ containing hydrate products

Special precipitation processes are applied for producing amorphous hydroxides, pseudo-boehmite and super-fine (median size 0.5-3 $\mu$m) gibbsite. The main variants of special precipitation are as follows:

A./ Precipitation of amorphous gel by neutralization of the aluminate liquor and recrystallization into gibbsite, bayerite or pseudo-boehmite.

Neutralization can be made by water solution of aluminium salts, acids or $CO_2$, $SO_3$, $NO_2$ gases. Properties of the precipitated amorphous phases and crystalline phases developed after recrystallization are determined by parameters of precipitation (concentration of the reagents, temperature, velocity of the precipitation, pH of the liquor at the end of precipitation, anions present in the liquor etc.) Different phases can be formed depending on the $OH^-$/$Al_3^+$ ratio in initial amorphous phase. For example:

$OH^-$/$Al^{3+}$ molar ratio: 3.0-3.3
               gibbsite, boehmite, bayerite can be
               developed during few hours
               depending on other parameters.

$OH^-$/$Al^{3+}$ molar ratio: 2.1-2.75
               series of basic aluminium salts
               with composition of $Al(OH)_{2,2} \cdot X_{0.8}$
                        $Al(OH)_{2.75} \cdot X_{0.75}$
         $X = Cl^-$, $SO_4^{2-}$, $CO_3^{2-}$,..

$OH^-$/$Al^{3+}$ molar ratio: <2.1 $Al(OH)_{2.2} \cdot X_{0.8}$.

In plant practice $CO_2$ gas is used for neutralization of aluminate liquor. Amorphous and cristalline phases precipitated at the different parameters of carbonization are shown in Figure 2.2-5 [12].

B./ Precipitation of fine-disperse aluminium-hydroxide (gibbsite) by using amorphous seed material.

Aluminium-hydroxid gel can be precipitated directly from the initial pregnant liquor by addition of aluminium or ammonium salts ($AlF_3$, $Al_2(SO_4)_3$, $NH_4HCO_3$ etc.) or separately by neutralization of aluminate liquor with acids. Homodisperse product of 0.5-3 $\mu$m grain size can be produced by these special precipitations [13-15].

C./ Precipitation of fine disperse aluminium-hydroxid using Bayer alumina hydrate ground to 3-5 $\mu$m as seed material [16].

GEL REACTOR PRODUCT PHASE DIAGRAM—
SYNTHETIC SODIUM ALUMINATE LIQUOR
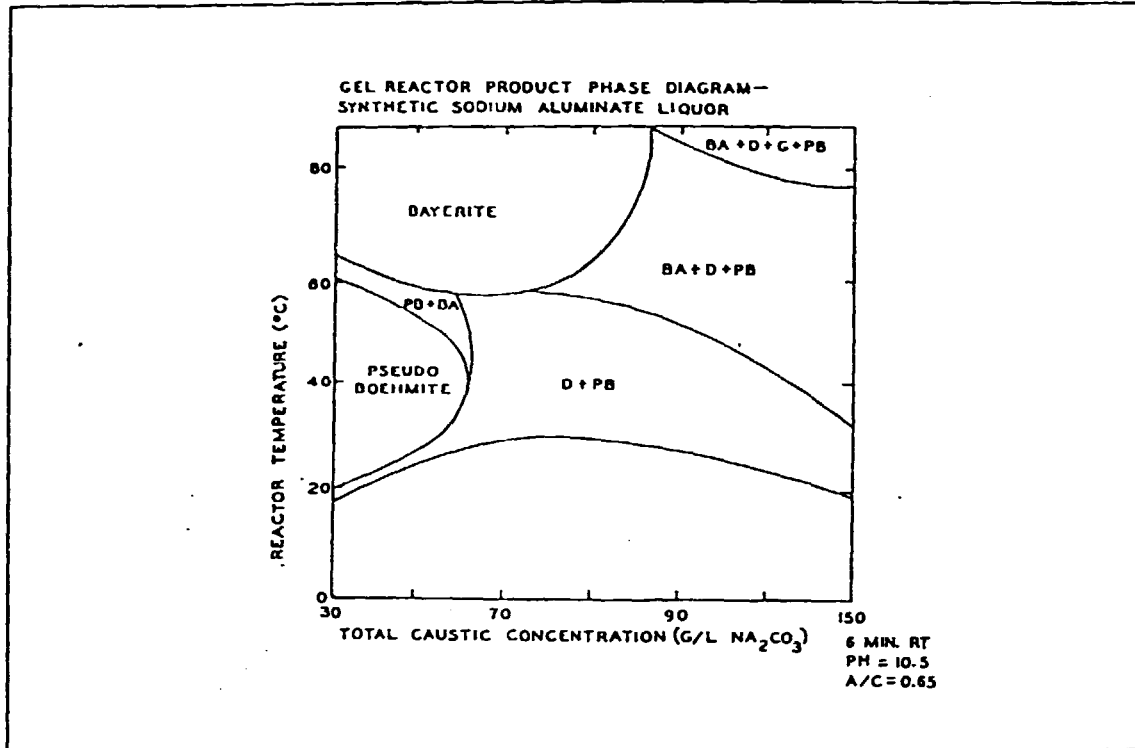
**Figure 2.2-5**
**Cristalline phases precipitated at the different parameters of carbonization**
**(D = DAWSONITE)**

New, so-called "white-pure" aluminium hydroxide was developed in Japan, which is used as filler material at the production of onyx and synthetic marble [17]. This type of alumina hydrate can be characterized by special shape of crystals, whiteness and low $Na_2O$ content (Table 2.2-3 and Figure 2.2-6 Sample A).

**Table 2.2-3**
**Analyses of standard particle size ATH samples (Samples A, B and C)**

|  | Chemical Analysis | | | | Sieve Analysis | | | Average | Spec. | White- |
|  | $H_2O$ | $SiO_2$ | $Fe_2O_3$ | $Na_2O$ | +74 $\mu m$ | 74-44 $\mu m$ | -44 $\mu m$ | die.($d_{50}$) | surface area | ness |
|  | (%) | | | | | (%) | | $\mu m$ | $(m^2/g)$ | (%) |
| Sample A | 0.02 | 0.01 | 0.008 | 0.13 | 45 | 42 | 13 | 70 | 0.20 | 92.5 |
| Sample B | 0.02 | 0.01 | 0.007 | 0.14 | 45 | 42 | 13 | 70 | 0.20 | 94.0 |
| Sample C | 0.02 | 0.03 | 0.006 | 0.23 | 52 | 40 | 8 | 75 | 0.44 | 92.5 |
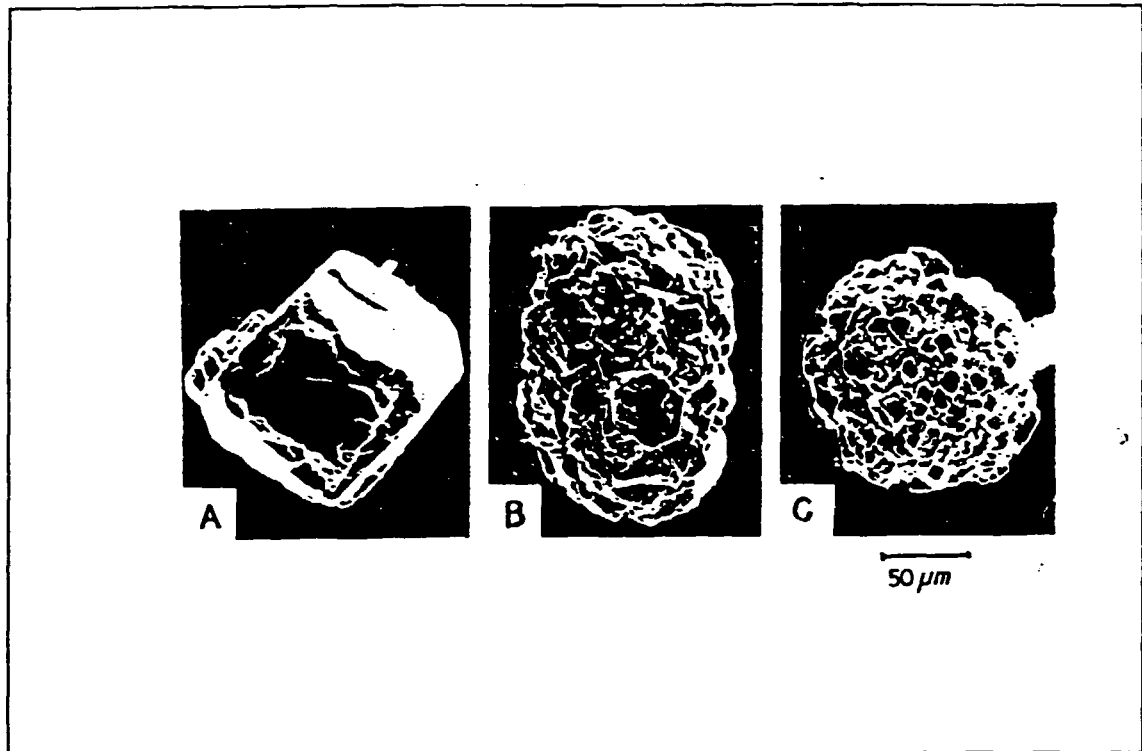
**Figure 2.2-6**
**SEM image of ATH samples**

Alumina hydrate signed by Sample "A" was produced by special precipitation process in which crystal growth was the main process when nucleation, and agglomeration were suppressed.

### 2.2.2.4 Surface treatment

The main goal of the surface treatment is to increase the adhesion between the surface of the filler material and polymer, to develop organophilic (hydrophobic) surface on the filler for reaching optimum rheological properties in the mixture of polymer and filler. Two sorts of agents can be used for surface treatment:

- Coupling agents developing molecular bridges between the surface of inorganic filler and organic polymer.
- Wetting agents and surface active additives.
  Application of surface treatment has a complex influence on the properties of composite materials. The interface between polymer and filler involves a complex interplay of physical and chemical factors related to the composite performance as indicated in Figure 2.2-7.

- Surface modification of the fillers affects the rheology of the polymer mix by changing wet-put, dispersion of particles, viscosity, thixotropy, and flow during plastic formation. The

adhesion determines the mechanical strength and chemical resistance of a composite.

- The filler surface interacts with the polymer through catalytic activity, orientation of molecular segments and other modifications of polymer morphology.

- The initial surface treatment should protect the mineral surface against abrasion and fracture during handling operation [18, 19].
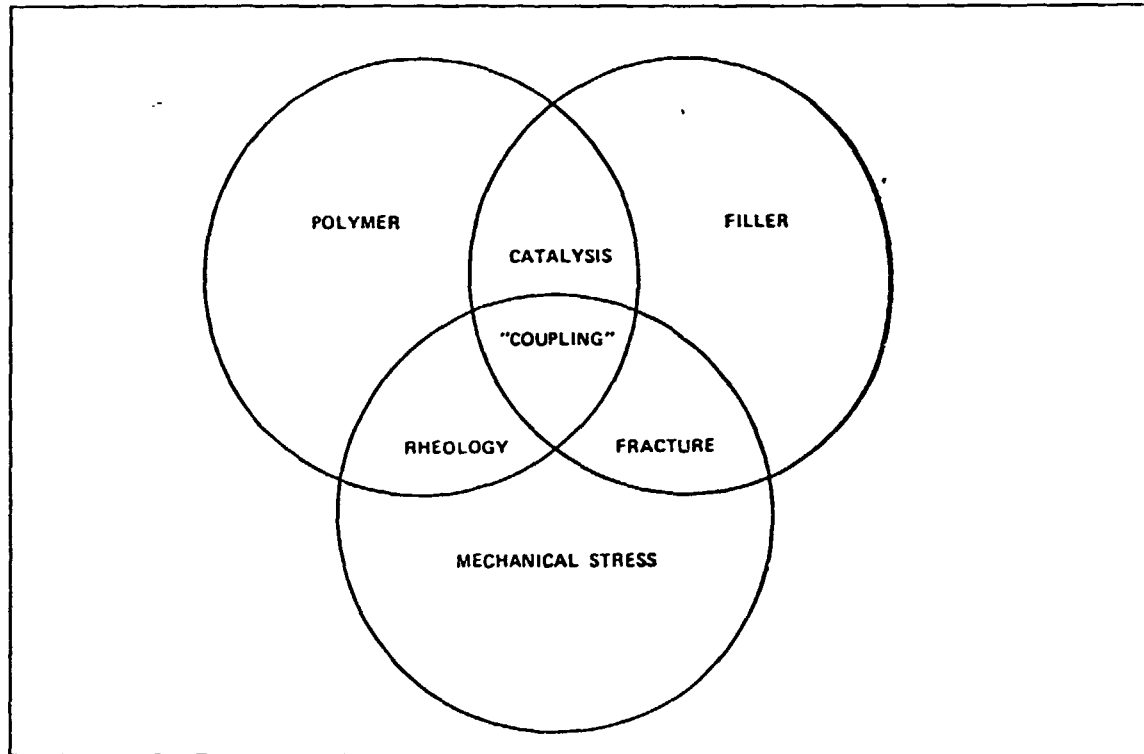


Figure 2.2-7
Inter-relationships of polymer, filler and mechanical stresses in composites

## Coupling agents

Silane coupling agents, $R'Si(OR)_3$ are characterized by dual functionality: R' represents an organo-functional group (such as amino, mercapto, vinyl, epoxi or methacrylate) and OR represents a hydrolysable alkoxy group attached to silicon.

R'is usually bonded to the silicon atom by a short alkyl chain. In use, the alkoxy groups hydrolyse to form silanols ( Si-O-) that react with OH⁻ groups being on the surface of aluminium hydroxide. [20]

It is unlikely that any surface treatment can perform in all
filler-plastic combination, but it would be impractical to supply
a different treated filler for each filler-plastic combination. A
cationic vinylbenzilsilane (silane "A" of Table 2.2-4.) is known
to be an effective adhesion promoter for virtually all polymers
to most mineral fillers.

It is also modified quite readily by simple addition of surface-
active agents such as fatty acids, and phosphate surfactants. It
is possible, therefore, that a single filler treatment based on
"A" may be combined with commercial surface-active additives to
impart the desired interface modification for almost all systems.

**Table 2.2-4**
**Typical Commercial Silane Coupling Agents**

| Silane identification | | | Organo-functional group on Silicon | End-use polymers |
|---|---|---|---|---|
| UCC | D.C. | Name | | |
| "A" | Z-6032 | Vinylbenzyl cationic silane | $HCl$ $VB-NH-CH_2CH_2NH(CH_2)_3-*$ | Polyesthers DAP, alkyds, polyethylene, cross-linked polyethylene, thermoset polybutadienes, polypropylene, EPDM, EPM |
| "B" A-172 | Z-6082 | Vinyl-tris(2-methoxy-ethoxy)silane | $CH_2=CH-$ | |
| "C" A-174 | Z-6030 | γ-Methacryloxypropyl-trimethoxy | $CH_3$ $CH_2=C-COOCH_2CH_2CH_2-$ | Phenolic, epoxy, melamine, polyamide, polyimide, polycarbonate |
| "D" A-1100 | Z-6011 | γ-Mainopropyltriethoxy-silane | $H_2NCH_2CH_2CH-$ | polybenzimadazole, urethane, EPDM, poly-cloroprens, nitrile |
| "E" A-1120 | Z-6020 | N-β-(Aminoethyl-γ-amino-propyltrimethoxysilane | $H_2NCH_2CH_2NHCH_2CH_2CH_2-$ | |
| "F" A-186 | | β-(3.4-Epoxycyclohexyl)ethyltrimethoxysilane | $O$ $CH_2CH_2-$ | Epoxy, phenolic, poly-vinylchloride, cycloaliphatic, epoxy, urethane, epichloro-hydrin |
| "G" A-187 | Z-6040 | γ-Glycidoxpropyltrimethoxy-silane | $O$ $CH_2CHCH_2OCH_2CH_2CH_2-$ | |
| "H" A-189 | Z-6062 | γ-Mercaptopropyltrimethoxy-silane | $HSCH_2CH_2CH_2-$ | EPDM, SBR, NR, poly-chloroprene, poly- |
| "I" A-143 | Z-6076 | γ-Chloropropyltrimethoxy-silane | $ClCH_2CH_2CH_2-$ | sulfides, polyvinyl-chloride, epichloro-hydrin |

* = $CH_2=CH$

The typical commercial silane coupl... ...... are shown in Table
2.2-4.

The following agents are used for surface treatment of aluminium hydroxide and alumina products:

- DSC-20, DSC-40,   in Polyesther resin system
- A-186, A-187      in Epoxy resin system
- A-172             in Styrene-Butadiene system
- Y-9868 or Y-9870 in Polyethylene resin system

There are two general classes of silanes, and requirements for optimum application

a./ neutral, volatile silanes that may require additional catalysts, ("C" in Table 2.2-4) and

b./ cationic, non-volatile silanes that are self-catalysed for reaction with surfaces, but may require solvent modification to aid dispersion in dry mixes. ("A" in Table 2.2-4).

There are two methods of the treatment of fillers with silane. The one is the "aqueous treatment" of filler when the filler is treated with diluted aqueous dispersion of silanes at the proper pH to get alignment of the silanes for maximum availability of the organo-functional group. Aqueous silane bath are generally applied to the filler within a few hours after precipitation. In general, cationic silanes are best, applied to fillers from aqueous media at a pH corresponding to the isoelectric point (IEPS) of the surface.

The second method of the treatment is the "dry blending" silanes with fillers. Silane may also be dry blended with fillers at room or at elevated temperature. A small amount of suitable solvent may be beneficial in aiding dispersion of a trace of silane over a large surface area of filler. High molecular weight amine-functional silanes, such as "A" do not diffuse readily when dry-blended with fillers at room temperature. Dilution of the silane with about 10 times its volume of a medium alcohol or glycol-ether before mixing with fillers seems to be rather effective in obtaining dispersion through the filler. The treated filler must than be dried before it is used in polymer mixes.

Other coupling-type materials for surface treatment of ATH are the zirconium-aluminates investigated by Cavedon Chemical Co. (CAVCO MOD M1) [21-22]. They may be put "in-situ" to the organic-systems. They decrease the viscosity of the filled epoxy and polyester resins.

## Non-coupling-materials

Lubricants and dispersion aids may be valuable in improving mixing at lower shear, but they will have no coupling action. Lubricants may allow a higher filler loading and promote improved impact strength of composites, but they do not improve flexural strength of resistance to moisture degradation of mechanical and electrical properties. Commonly used materials in this group are

lauric   acids,   oleic   acids,   octylbenzene   sulphonic   acids,
dodecylbenzene  sulphonic  acids,  sulpho-succinate.  ALCOA  has  a
material (LUBRAL) for surface treatment of its own fine hydrates,
such as Hydral-710 and Hydral 705 for polypropylene resins.

## 2.2.3 Activated aluminas

Activated  aluminas  display  high  specific  surface  areas,  large
pore  volume  with  defined  pore  size  distribution,  which  are  the
main  properties  that  have   bearing  on  catalytic   and  adsorption
behaviour.  The  activated  aluminas  are  used  mainly  in  adsorbent
and catalytic processes.

They   can   adsorb   a   great   number   of   pollutants   (fluoride,
phosphates,  organic  acids,  humic  acids  etc.)  from  liquids  and
vapours.  The  degree  of  adsorption  relies  on  the  polarity  of  the
substance  to  be  adsorb.  Polar  substances  are  bound  stronger  than
non  polar  ones.  On  the  basis  of  selective  adsorption  they  have
long been used in the chromatography too.

Activated  aluminas  are  available  with  a  variety  of  physical
properties  and  purity  required  for  different  applications.  Main
types  of  activated  aluminas,  classified  on  the  basis  of  purity
are shown in Table 2.2-5.

Table 2.2-5
Chemical and physical properties of activated aluminas

| Chemical Composition | Normal | Low soda type | High purity |
|---|---|---|---|
| $Al_2O_3$ % | Approx. 92 | Approx. 99.9 | >99.95 |
| $SiO_2$ % | =0.015 | 0.01-0.005 | max. 0.005 |
| $Fe_2O_3$ % | =0.015 | 0.01-0.005 | max. 0.005 |
| Total $Na_2O$ % | 0.3-0.5 | Approx. 0.01 | Approx. 0.001 |
| Physical Parameters | | | |
| BET surface area ($m^2$/g) | 130-180 | 250-350 | 250-350 |
| Water adsorption (static.) | | | |
| at 10 % rel.humidity (%) | 2-4 | 5-8(1) | – |
| at 60% rel.humidity (%) | 7-11 | – | – |
| at 90% rel.humidity (%) | 17-22 | 25-40(1) 40-50(2) | – |
| Crystal structure | | | |
| (1) drying at 110 °C | – | pseudo-boehmite | – |
| (2) activation at 550-650 °C | gamma-$Al_2O_3$ | amorphous, eta-$Al_2O_3$ or/and rho-$Al_2O_3$ | Pseudo-boehmite |
| Pore volume ($cm^3$/g) | | | |
| (1) drying at 110 °C | – | 0.1-0.8 | – |
| (2) activation at 550-650 °C | Approx.0.1-0.2 | 0.8-1.1 | 0.5-1.5 |

Bayer alumina hydrate and/or pregnant liquor are used as basic materials of the first two groups (normal and low soda quality) but for high purity products usually purer raw materials (aluminium, aluminium salts etc.) are needed.

The following main technological processes are used for developing the above mentioned special properties:

- special calcination,
- decrease of the impurities,
- precipitation of amorphous aluminium hydroxides,
- shaping of the products.


## 2.2.3.1 Special calcination

During calcination of different aluminium - hydroxides so-called "transitional" phases are formed depending on the temperature, other process conditions and the initial structure of the hydroxides (Figure 2.2-8).
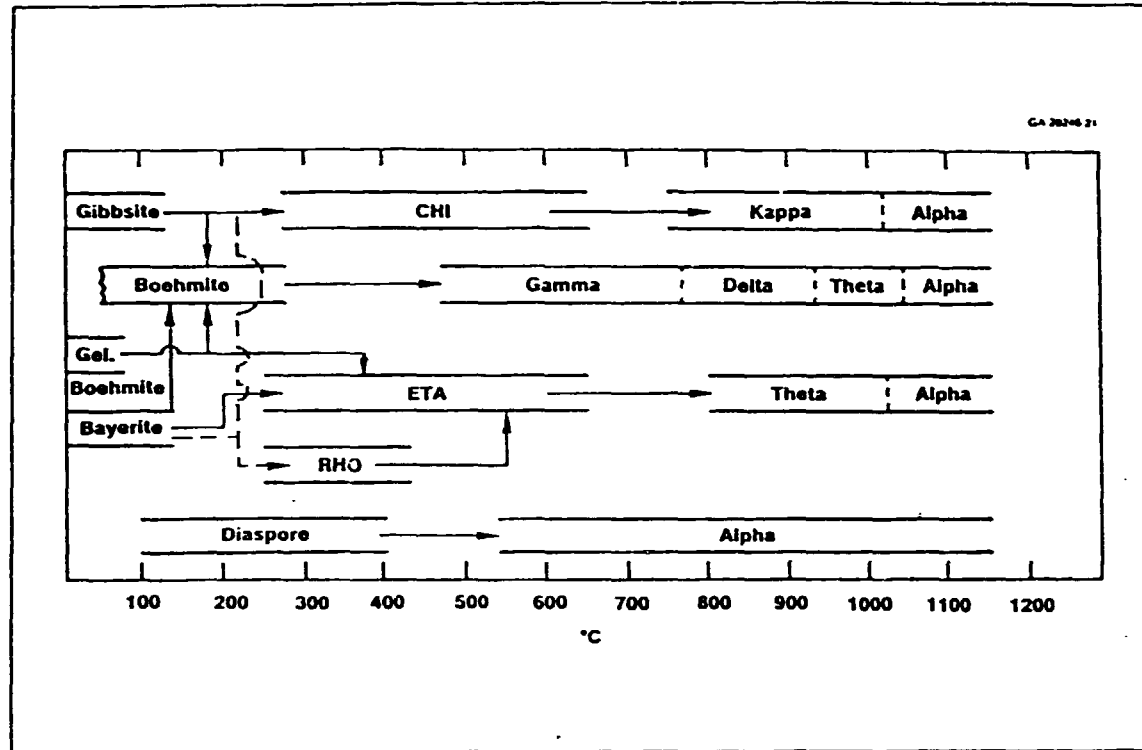
**Figure 2.2-8**
**Transformation sequence Al(OH)$_3$ ----> Al$_2$O$_3$**

These phase-transformation processes are irreversible. The crystal structure of these transitional phases affects both surface area and surface chemistry (distribution of acid and basic sites) of the products [23]. Specific surface area L.O.I. and density is registrated in function of the calcination temperature in case of gibbsite calcination on Figure 2.2-9.

The calcination temperature of development of different phases depends on many parameters for instance:

- initial crystal structure,
- impurities of the initial hydroxide,
- grain size,
- velocity of the heating,
- atmosphere of the calcination etc.
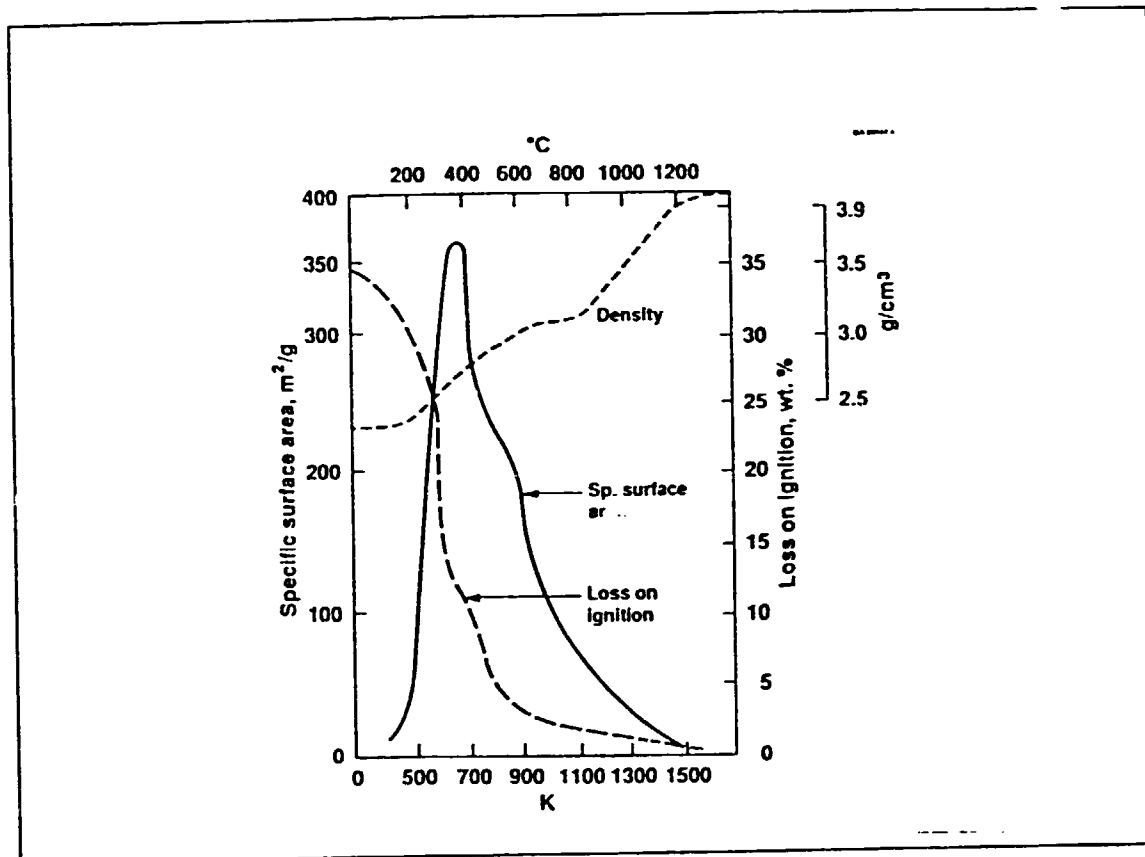
**Figure 2.2-9**
**Properties of activated gibbsite**

X-ray diffractograms of different transitional phases developed at the calcination of amorphous hydroxide(A), bayerite(B), pseudoboehmite(C) and boehmite(D) are shown in Figure 2.2-10 [24].
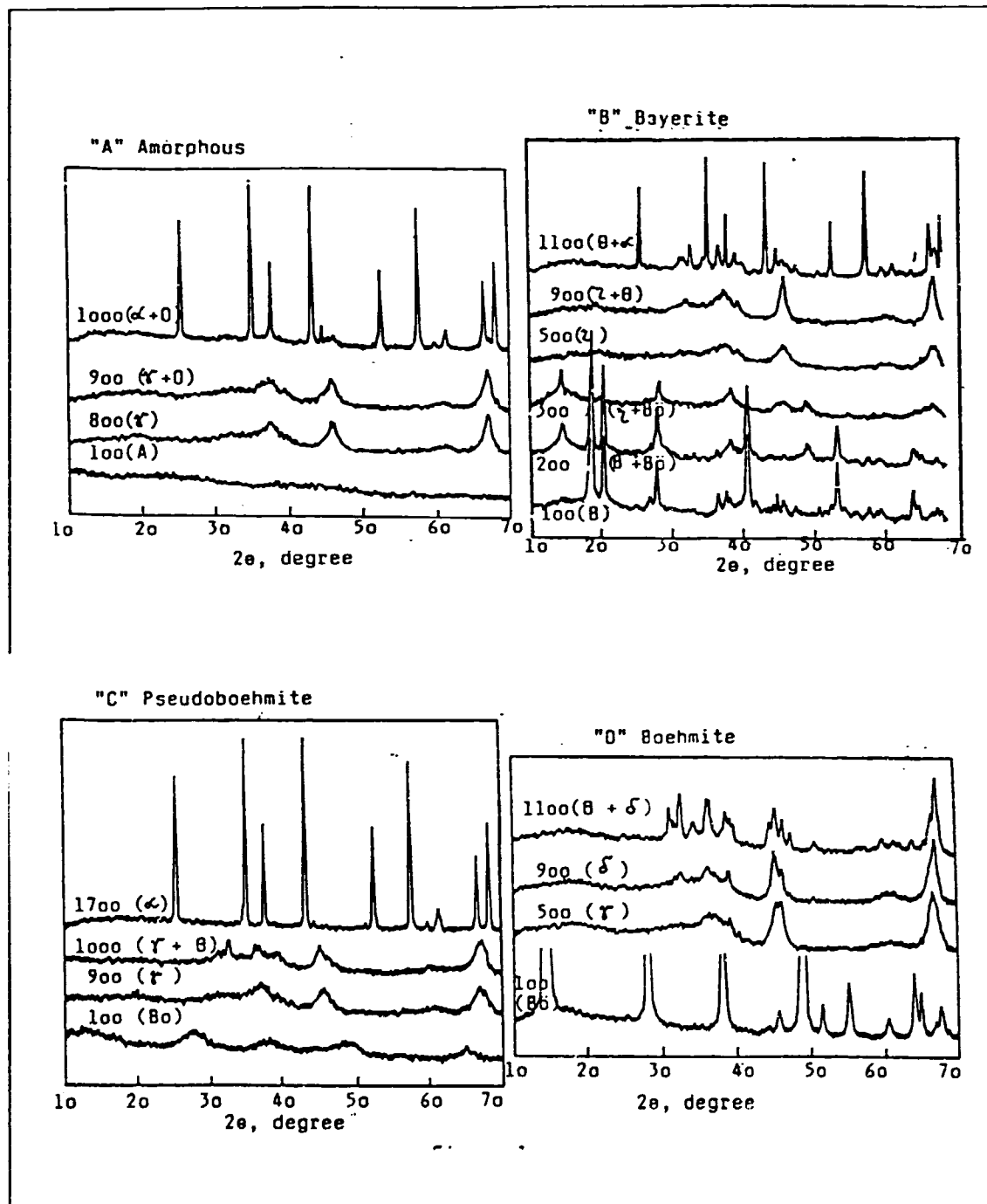
**Figure 2.2-10**
**X-ray diffractograms transitional cristalline**
**A.) amorphous, B.) Bayerite, C.) Pseudoboehmite, D.) Boehmite**

The most important properties (pore size distribution, surface area, crushing strength, abrasion resistance etc.) depend very much on the procedure of calcination.

In plant practice traditional rotary kiln can be used for mild calcination. End temperature at the mild calcination of gibbsite is usually 400-600 $^O$C. The aim of the activation isto produce highest possible specific surface area. Measuring the L.O.I. can be used for quick control of the calcination (see Figure 2.2-9).

The most up-to-date method for the activation is the so-called "flash" calcination. This method is suitable for rapid dehydration of bayerite, gibbsite, norstrandite, and boehmite. The dehydratation may be advantageously effected bya special apparatus by means of a stream of hot gases. The inlet temperature of the gases in the apparatus varies from about 400 to 1200 $^O$C, and contact time of the hydroxide with the hot gases between a fraction of second and 4-5 seconds [25].

This way, specific surface area of the activated product can be increased by 50-100 $m^2$/g comparing to that of slow calcination.

## 2.2.3.2 Decreasing of the impurities

Requirements for the purity of active aluminas are different depending on the field of application. Adsorbents used for drying air or other gases can be produced by activation (and shaping) of Bayer quality aluminium-hydroxides. Higher purity is required for activated aluminas used in the fields of chromatography, and as catalyst or catalyst supports.

### Decrease of the Na$_2$O content

Low $Na_2O$ content is required in many fields of application. According to the literature [26-28] soda may incorporate into the alumina hydrate structure in several different ways:

- in form of occluded liquor inside aggregates between individual crystals,
- on the surface in form of organic alkali salts,
- in form of $Na^+$ ions in the crystal lattice.

The alkali impurities bound on the surface of the hydrate can be decreased by intensive washing.

Low (<0.1 %) $Na_2O$ containing material can be produced by gibbsite boehmite phase transformation (mild calcination or hydro-thermal treatment) followed by washing.

$Na_2O$ content of gibbsite can be decreased down to 0.05% by special crystal growth at the precipitation.

### Decrease of the Fe$_2$O$_3$ content

Decrease of the $Fe_2O_3$ content is based on the liquor purification discussed in Chapter 2.1.

### Decreasing of the $SiO_2$ and $Fe_2O_3$ contents

SiO2 and $Fe_2O_3$ contents of the hydrates can be decreased by addition of $NH_4Cl$ or other ammonium salts at mild calcination (500-600 $^{\circ}C$).

3N purity active aluminas can be gained by washing and rapid calcination of the pseudo-boehmite.

### 2.2.3.3 Production of amorphous hydroxides

Amorphous hydroxides are used as basic materials of several special aluminas (adsorbents, activated aluminas, high purity ceramics, medicine, aluminas for chromatography etc.).

The following groups of technologies are used for production of amorphous aluminium-hydroxides:
- Acidifying cf sodium aluminate solution by different acids and salts.
- Neutralization of aqueous solution of aluminium salts (aluminium sulphate, aluminium chloride, aluminium nitrate etc.) by alkalis.
- Hydrolyses of organic - aluminium compounds.
- By reaction of amalgamated aluminium with water.

In case of production of amorphous hydroxide based on Bayer aluminate liquor the first group of the above technologies is used. Properties of the aluminium hydroxides gained by neutralization with different acids ($HNO_3$, $H_2SO_4$, HCl, week organic acids, $SO_2$, $CO_2$ etc.) are different. The best surface properties can be developed in case of amorphous hydroxides produced by special carbonization of aluminate liquor. For example a special carbonization method [29] will be discussed below. Diluted aluminate liquor ($Na_2O$ caust: $\approx 60$ gpl, $Al_2O_3$ $\approx 80$ gpl) is carbonized by $CO_2$ gas at 40 $^{\circ}C$ temperature up to reaching 9.5 pH in the solution (1st step).

The suspension of precipitated amorphous hydroxide is treated in acidic or basic solution (pH $\approx$ 11) at the temperature of 50-85 $^{\circ}C$ during 5 minutes - 5 hours. In acidic solution anion of the aluminium-hydrocarbonate will be changed, in basic solution carbonate anion will be removed from the surface of the gel. (2nd step)

The amorphous aluminium-hydroxide can be crystallized by heating the suspension up to 100-260 $^{\circ}C$. Holding time can be varied between 30 minutes and 10 hours (3rd step). Different crystalline phases (pseudo-boehmite, boehmite etc.) can be developed by variation of temperature and holding time.

Activated aluminas with high (130-360 $m^2/g$) specific surface areas can be produced by mild calcination of amorphous hydroxides gained according to above technology. The connection between parameters and product quality is summarized in Table 2.2-6.

Table 2.2-6
Conditions of treatment

| | 1st step | | | 2nd step | | 3rd step | |
|---|---|---|---|---|---|---|---|
| Treatment reagent | $Al_2O_3$ (g/l) | Ratio of reagent and $Al_2O_3$ | Resulting pH (20 $^\circ C$) | Temperature ($^\circ C$) | Time (hours) | Temperature ($^\circ C$) | Time (hours) |
| $HNO_3$ | 130 | 0.7 | 3.1 | 85 | 0.5 | 160 | 3 |
| HCl | 90 | 0.8 | 3.1 | 85 | 0.5 | 160 | 3 |
| $HNO_3$ | 130 | 0.4 | 4.6 | 70 | 2 | 160 | 3 |
| $NH_4NO_3$ | 80 | 0.2 | 6.2 | 70 | 2 | 120 | 2 |
| $NH_4OH$ | 80 | 0.6 | 10.4 | 85 | 4 | 160 | 4 |

| | Crystallization Morphology state | Dimensions in Å Width | Length | Thickness | Molar $H_2O/Al_2O_3$ | Calc. 600 $^\circ C$ ($m^2$/g) |
|---|---|---|---|---|---|---|
| HNO3 | medies | 100-150 | 1000-3000 | 30 | 1.45 | 360 |
| HCl | medies | 100-200 | 500-2000 | 30 | 1.4 | 390 |
| HNO3 | rods | 200-300 | 500-1000 | 40 | 1.3 | 250 |
| NH4NO3 | grouped lamell. | 100-150 | 150- 200 | 25 | 1.35 | 270 |
| NH4OH | distimet " | 300-700 | 300- 700 | 50 | 1.15 | 130 |

According to ALCOA carbonization process, [12] at 50-150 gpl caustic $Na_2CO_3$ concentration and 0.5-0.8 A/C ratio, pregnant liquor is carbonized in a well-stirred reactor (850 rpm) by $CO_2$ gas. Depending on the pH value after carbonization different crystalline phases can be precipitated:

pH  8.5-10.2  dawsonite
pH 10.4-10.7  amorphous  pseudo-boehmite
pH 12         gibbsite.

Temperature of the reaction has a decisive influence on properties (grain size, surface area etc.) of the product. Particle size versus temperature and holding time is plotted in Figure 2.2-11.

Basic material of very high quality active aluminas (specific surface area: 300-500 $m^2$/g, $Na_2O$ content 0.03 - 0.10 %) can be produced by the above technology. The only disadvantage of this process is the low (30-50 kg/$m^3$ $Al_2O_3$) liquor productivity.

Main advantages of the pseudo-boehmite production comparing to the other technologies are the following:

- extremely high specific surface area of the products,
- high purity of the products,
- very good handling properties of hydroxide (filterability, washability),
- high porosity of the product,

- pore size can be influenced in recrystallization phase (this is very important for catalysts and catalyst supports).
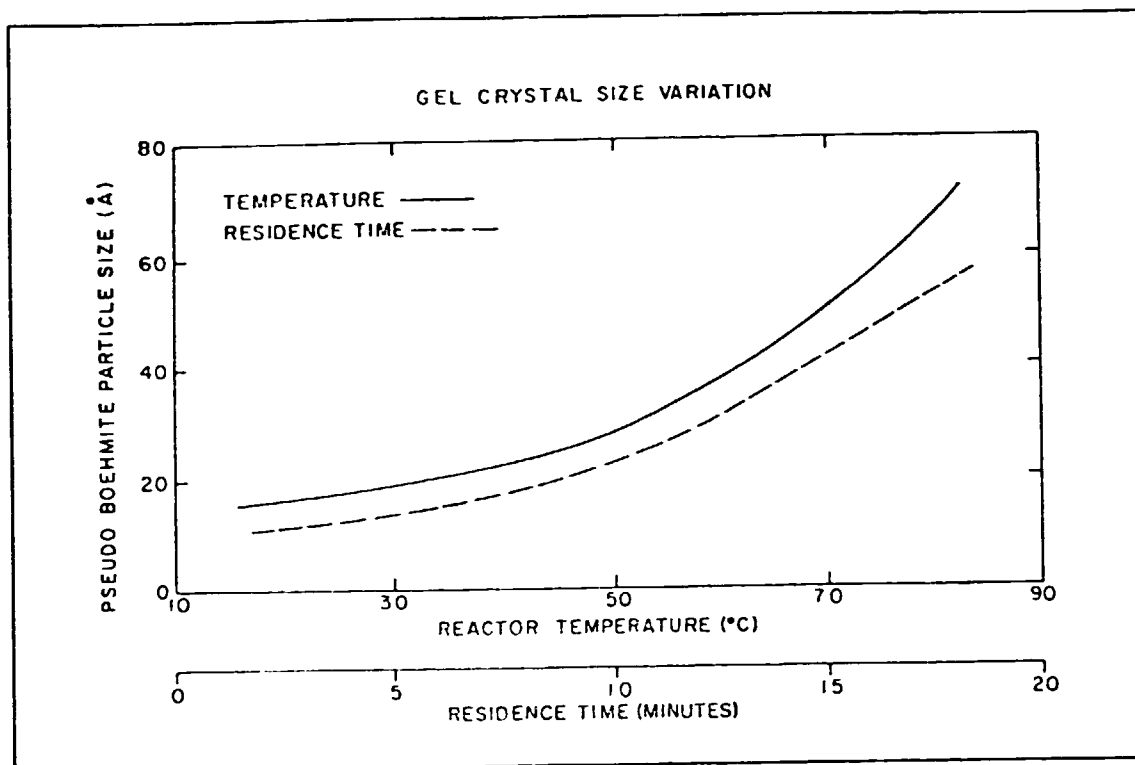


**Figure 2.2-11**
**Particle size vs. temperature and holding time at carbonization**

### 2.2.3.4 Shaping

Adsorbents are used in different form (powder, pellets, balls, tablets, shaped by extrusion press etc.).

In case of powder type adsorbents the most important properties are as follows:

- grain size distribution,
- bulk density ("loose"),
- bulk density ("tapped"),
- static adsorption capacity,
- specific surface area,

and in case of lumpy and shaped adsorbents:

- shape,
- size,
- wear resistance,
- compression strength,
- thermal stability,
- pore size, pore size distribution,

- bulk density,
- adsorption capacity
- cycle of regeneration.


**Methods used for shaping**


*Shaping by extrusion press*

Amorphous hydroxides usually are shaped by screw or piston type extrusion presses. Initial gel is handled mechanically by addition of water and any peptizator (diluted solution of oxalic acid, nitric acid, formic acid etc.), after mechanical handling it is extruded, dried and activated.


*Drop method*

The initial amorphous material is partially dissolved (in mild acidic solution) and the suspension is dropped into the so-called precipitator bath (e.g. $NH_4OH$ solution) through an oil layer used for ball formation. The small balls will be solidified in precipitator bath than washed, dried and activated.


*Forming of granulates*

This method is used first of all in case of processing gibbsite-based adsorbents (basic material: gibbsite from Bayer-cycle).

Initial material is ground before and by adding water and additives [$Mg(NO_3).6H_2O$, $Al(NO_3)_3.9H_2O$ etc.] for increasing strength it is handled in rotating plate or drum for ball formation.

## 2.2.4 Specialty calcined aluminas


Specialty calcined aluminas can be characterized by high $\alpha-Al_2O_3$ content (more than 70 %), high density and hardness, different grain size and purity (for different purposes). The main characteristic properties of this product line are summarized in Table 2.2-7.

**Table 2.2-7**
**Chemical and physical properties of specialty calcined aluminas**

| Soda content | Normal | Intermediate | Low | High purity | |
|---|---|---|---|---|---|
| Chemical composition % | | | | | |
| $Na_2O$ | 0.3-0.6 | 0.15-0.30 | <0.1 | 2 | ppm |
| $SiO_2$ | ≈ 0.04 | ≈   0.04 | ≈0.04 | 4 | ppm |
| $Fe_2O_3$ | ≈ 0.02 | ≈   0.02 | ≈0.02 | 2 | ppm |
| $Al_2O_3$ | ≈99.2 | ≈   99.5 | 99.7-99.9 | 99.99 | |
| Physical properties | | | | | |
| $\alpha\ Al_2O_3$ % | <70 | ≈   95 | 95-100 | ≈ 100 | |
| BET surface area $m^2/g$ | 0.3-5 | 0.3-5 | 0.3-5 | 5-12 | |
| Ultimate Crystal size $\mu m$ | 0.3-5 | 0.3-5 | 0.3-5 | 0.1-1 | |
| Specific Gravity | 3.9-3.95 | min 3.9 5 | 3.96-3.98 | | |
| Particle size | depends on recquirements | | | 0.3-5 $\mu m$ | |
| $d_{50}$ (Ground $Al_2O_3$) $\mu m$ | | 1-5 | 1-5 | 0.3-0.5 | |
| Pressed Bulk Density $g/cm^3$ | | 1.8-2.20 | 2.25-2.40 | 2.6-2.25 | |
| Fired Density $g/cm^3$ (1600 $^O$C/2h, 1.25% MgO+1.25SiO_2 | | ≈3.7-3.05 | ≈3.8-3.6 | >3.9 | |
| Linear Shrinkage % | | ≈24-10.5 ≈ | 20.5-14 | 14-18 | |
| Ceramic Reactivity: It depends on grindability ($d_{50}$ after grinding in the alumina) and soda content in the alumina and pressure of forming of ceramic and temperature of calcination (1500-1700 $^O$C) of ceramic. | | | | | |

Field of application is wide including glass industry, abrasives and polishing, refractories, electrical, electronic and mechanical ceramics etc. In the literature [1] products are categorized according to soda content and median crystal size. The requirements of various application fields for median grain size and $Na_2O$ content are shown in Figure 2.2-12.
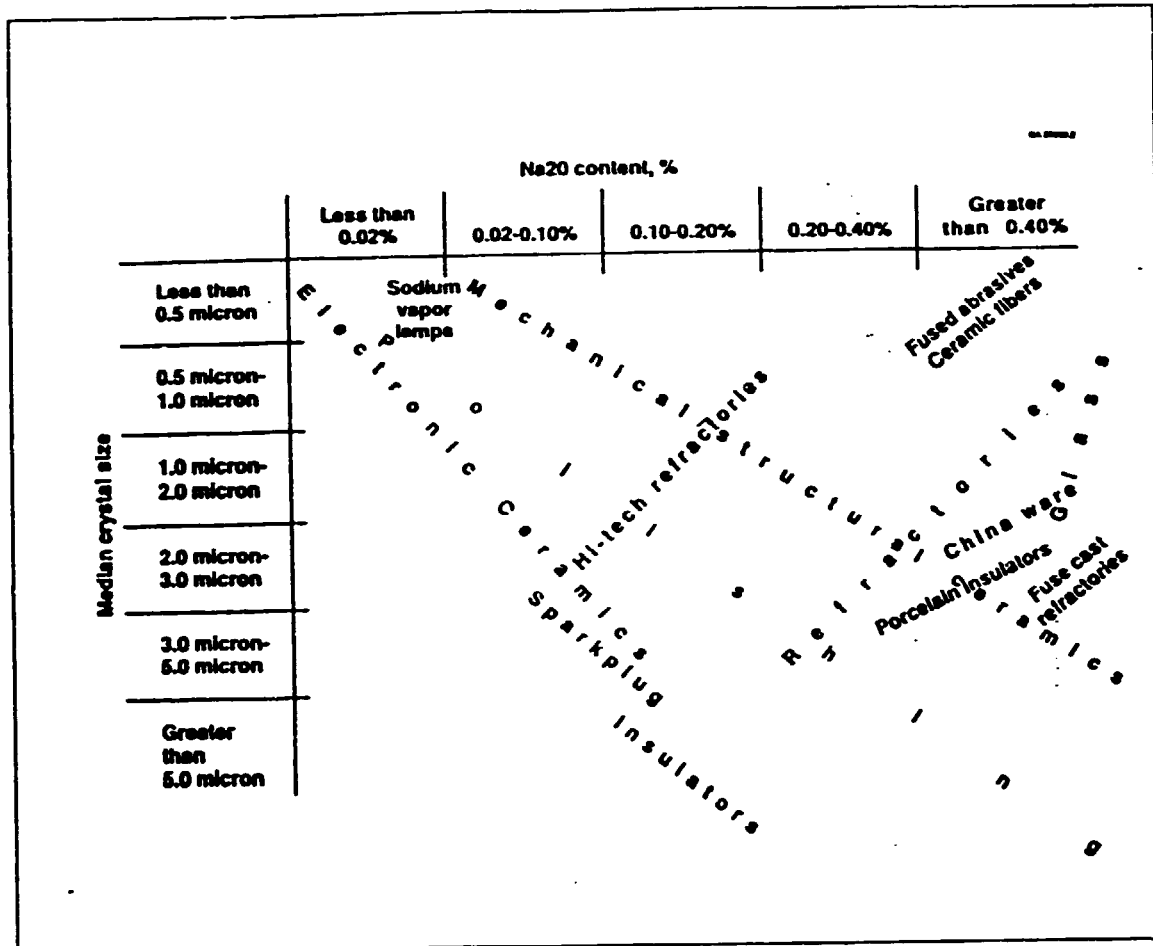
**Figure 2.2-12**
**Specialty calcined alumin. application requirements**

The largest field of application of the specialty calcined
aluminas is the ceramic industry. $Al_2O_3$ content of the so-called
$Al_2O_3$-based ceramic products is more than 80 %. As it is shown in
Figure 2.2-12 low (<0.1 %) $Na_2O$ containing basic material is
needed for production of electronic ceramics, spark-plugs,
insulators, hi-tech refractories etc.

The alkali content of the basic materials decreases specific
resistance, strength and life-time of the products.

Other important property of the aluminium oxides used in this
field is the ceramic reactivity. Ceramic reactivity can be
characterized by density and shrinkage of the test-piece sintered
under standard conditions.

Aluminas, reaching 3.8-3.95 $g/cm^3$ density, without additives, at
a sintering temperature lower than 1650 $^{\circ}C$, are nominated as
thermally reactive aluminas [30].

The most important properties required in different application fields can be developed by the following processes:

- high temperature calcination,
- calcination in presence of mineralizers,
- decrease of the impurity (mainly $Na_2O$) content,
- grinding.


## 2.2.4.1 High temperature calcination

Quality and reactivity (fired density and shrinkage) of the ceramic aluminas must be constant. Reactivity and other properties of the aluminas are highly influenced by parameters of calcination.

Higher temperature (1100-1300 $^{o}$C) is applied at the calcination of ceramic aluminas than in case of smelting grade aluminas. $\alpha$-$Al_2O_3$ content increases and specific surface area decreases by increasing calcination temperature. The crystal size of $\alpha$-$Al_2O_3$ is 1-2 $\mu$m at mild calcination and by increasing temperature of calcination it can reach 10-15 $\mu$m.

The fired density is influenced by the granulometry of $\alpha$-$Al_2O_3$ as well (in case of finer $\alpha$-$Al_2O_3$ density is higher) [31], that is why $\alpha$-$Al_2O_3$ is ground before sintering. Grinding is influenced by primary crystal size, because at the grinding, agglomerates are broken only. Practically, primary crystal size is the limit of grindability. The so-called super-fine grinding can be realized only under special conditions (special grinding method, additives, high energy consumption etc.).

Grindability of $\alpha$-aluminas used for producing of $Al_2O_3$-based ceramics should be constant (maximum fluctuation of $d_{50}$ after grinding may be ± 0.1-0.5 $\mu$m). Fluctuation in shrinkage should be less than ± 1-2%. The so-called "green density" of the ground and pressed alumina depends on the calcination temperature, it is increasing with increasing calcination temperature (at the same granulometry), that is why the shrinkage during sinter process is lower in case of higher degree of calcination. These strict requirements can be ensured only by careful, constant calcination of constant quality alumina hydrate (constant granulometry, structure, impurities etc.). Quality control system of Showa Denko K. K. is shown in Figure 2.2-13. Specialists of Showa Denko have developed a rapid measuring method for control of calcination [32]. They put 6 g ungrounded alumina into 20 mm $\phi$ mold, pressurize it at 300 kp/cm$^2$ and measure the bulk density (the unground powder pressed bulk density). They verify that there is a connection between primary grain size of $\alpha$-alumina (calcination degree) and the ungrounded powder bulk density. The relationship is shown on Figure 2.2-14.
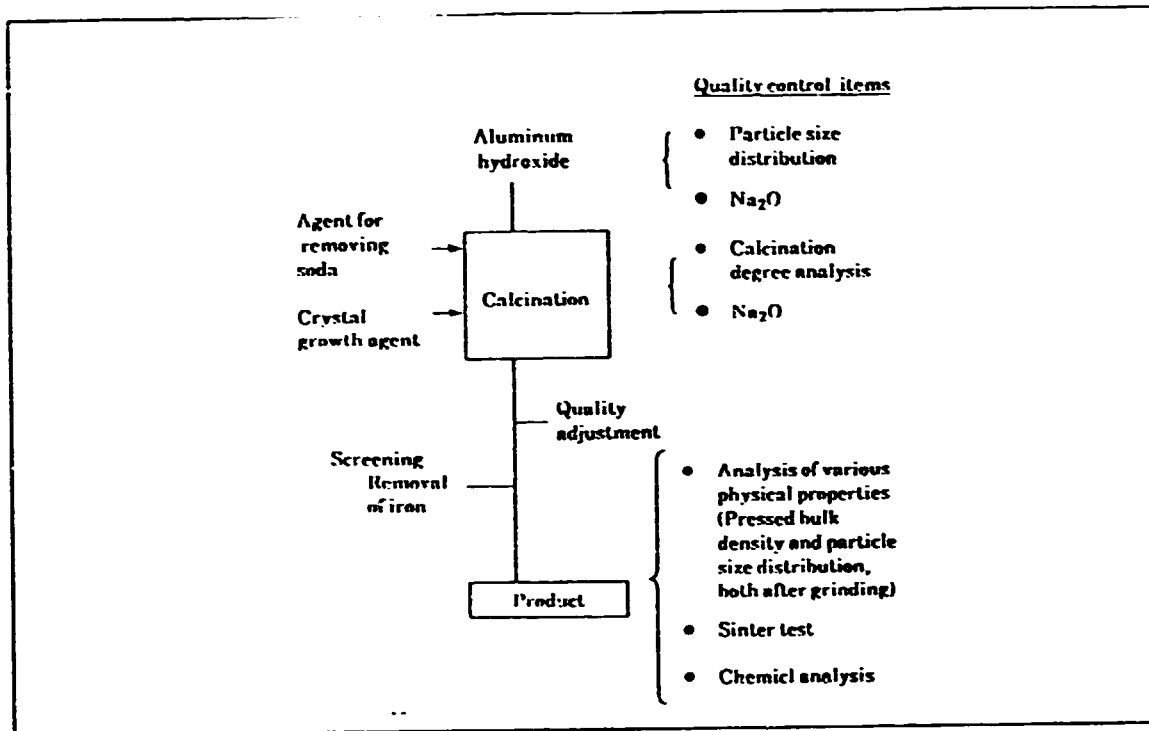
**Figure 2.2-13**
**Quality control items of alumina for ceramics**
**(see Chapter 3.1)**

**Figure 2.2-13**
**Quality control items of alumina for ceramics**
**(see Chapter 3.1)**
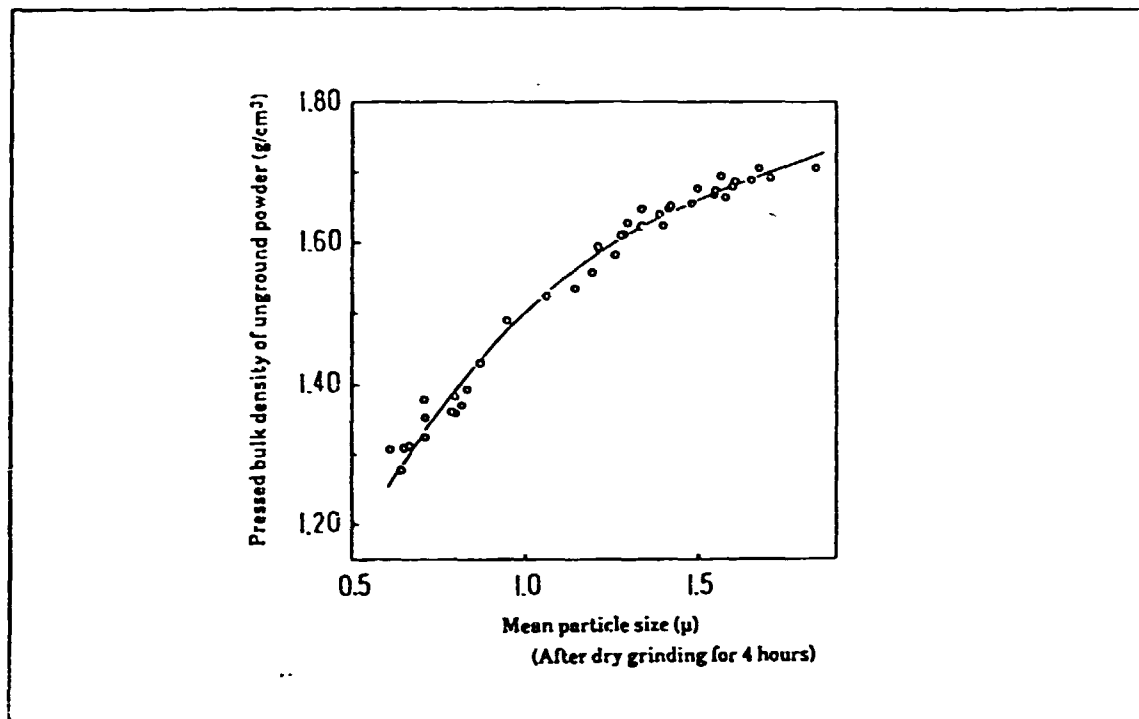
**Figure 2.2-16**
**Relationship between the size of ultimate crystals of alumina and pressed bulk
density of ungrounded powder**

## 2.2.4.2 Application of mineralizers

Transformation temperature of $\alpha$-$Al_2O_3$ can be decreased by using
mineralizers.

The most frequently used mineralizers are as follows: $AlF_3$, $NH_4F$,
$MgF_2$, $NH_4Cl$, $(NH_4)_2HPO_4$, $H_3BO_3$, $CaF_2$, $MgF_2$. Different
mineralizers are added to the alumina hydrate in a quantity of
0.2-2 %. For instance addition of 1 % $AlF_3$ decreases the $\alpha$-$Al_2O_3$
transformation temperature by 200 $^\circ$C. Mineralizers have an
influence on shape, primary crystal size and growth rate of
$\alpha$-$Al_2O_3$ crystallites. In the literature, two theories can be
found for mineralizing mechanism.

- Solid phase mechanism: $Na_2O$ in gibbsite comes out to the
  surface of alumina during calcination. This $Na_2O$ reacts with HF
  and $AlF_3$ and becomes molten salt of $AlF_3.4NaF$. $\alpha$-$Al_2O_3$ crystal
  can be grown by the dissolution of transition alumina or fine
  $\alpha$-alumina into the melt and precipitation from the melt.

- Vapour phase mechanism: thermodynamically, vapour phase AlOF is
  not stable, however, it can be an intermediate compound which
  transforms immediately to $\alpha$-$Al_2O_3$.

## 2.2.4.3 Contaminants decreasing

In case of special aluminas used as basic materials of ceramic products, $Na_2O$ is the most harmful impurity which should be decreased. The following methods are used for decreasing the $Na_2O$ content:

- Decreasing the $Na_2O$ content of the alumina hydrates (gibbsite, boehmite) before calcination according to the methods written earlier.

- ALCOA has developed a process for producing low alkali containing boehmite. Main parameters of precipitation are as follows:

  caustic $Na_2O$ conc.:                          111-123 gpl
  initial ($Na_2O/Al_2O_3$) molar ratio:   1.6-1.4
  quantity of the (boehmite) seed :      100 gpl
  temperature of crystallisation :       115-145 $^{o}C$

  According to this method fine-disperse, high purity alumina (99,9% $Al_2O_3$) can be gained after calcination [33].

- Some of the mineralizers ($H_3BO_3$, $AlF_3$ $NH_4Cl$) used at high temperature calcination help to decrease the $Na_2O$ content at temperature higher than 1100 $^{o}C$. Using these mineralizers one part of the $Na_2O$ is evaporated during calcination and the other part becomes washable. Mechanism of the above process is not cleared yet.

## 2.2.4.4 Grinding

For increasing reactivity of ceramic aluminas grinding is applied by producers or by users. Ball mills, vibrating mills and air jet mills are applied for grinding. Energy consumption of this process is quite high. Details of the grinding are not treated in this lecture.

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# 2.3 PRODUCTION OF ZEOLITE IN AJKA

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F. Valló, M. Tóth-Gyutai, I. Szabó, R. Jelinkó

## 2.3.1 Zeolites in the industry

### 2.3.1.1 General description of zeolites

Zeolites belong to the group of water-containing crystalline framework silicates.

Naturally occurring zeolites were first noted two centuries ago [1].

Natural zeolites, one of the many types of adsorbents investigated, showed the most promise. However, their scarcity and high degree of chemical and physical variability made the use of natural zeolites in commercial separation processes impractical. Recognizing both the limitations of the natural minerals and the potential of zeolite-type materials, Union Carbide set out to synthesize the pure zeolites and to develop economical methods of producing them. Since then, the continuously increasing number of industrial applications has resulted in substantially increased production capacity and the introduction of a large variety of zeolite products.

The most important industrial uses of synthetic zeolites are:

- detergent builders
- adsorbents
- catalysators.

### 2.3.1.2 Crystal structure

Zeolites have the basic formula:

$$M_{2/n}O \cdot Al_2O_3 \cdot X\ SiO_2 \cdot y\ H_2O \qquad \{1\}$$

where M is a cation of n valence.

Many zeolite species, differing in chemical composition, crystal structure and properties, are known. Among the types that have been found the most commercially useful are zeolite A and zeolite X/Y and inside of these the Type 4A and Type 13X which have the following formulas:

$$\text{Type 4A: } Na_2O \cdot Al_2O_3 \cdot 2 \ SiO_2 \cdot 4.5 \ H_2O \qquad \{2\}$$

$$\text{Type 13X: } Na_2O \cdot Al_2O_3 \cdot 2.5 \ SiO_2 \cdot 6.5 \ H_2O \qquad \{3\}$$
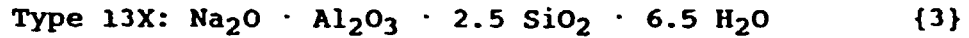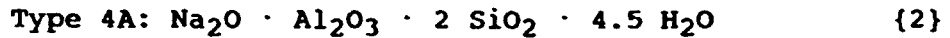
In both materials the sodium ion can be exchanged to form other useful products.

The fundamental building-block of zeolite crystal structure is a tetrahedron of four oxygen anions surrounding a smaller silicon or aluminium cation. The sodium ions or other cations serve to make up positive charge deficit in the alumina tetrahedra. Each of the four oxygen anions is shared in turn, with another silica or alumina tetrahedron. A two dimensional view of the aluminosilicate framework is shown in Figure 2.3-1.
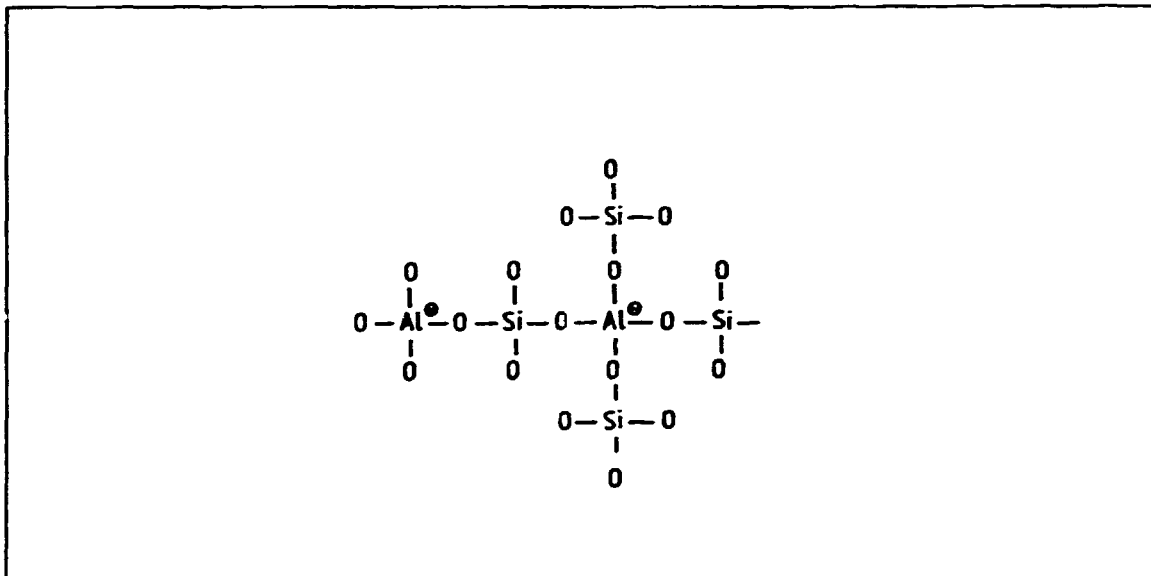


**Figure 2.3-1**
**Two dimensional aluminosilicate framework**

Zeolite A and zeolite X/Y structures consist of aluminosilicate cubo-octahedrons, which are connected to one another via oxygen bridges and form large adsorption cavites. The cavities are connected to one another by channels of exactly defined diameter, the so-colled pores. Depending on the arrangement of the cubo-octahedrons, we either get the "small-pore" zeolite A or the "wide-pore" Zeolite X/Y (Figure 2.3-2). An addition possibility of varying the pore diameter results from the fact the alkali or alkaline earth ions in the lattice are exchangeable [2].

structure of zeolite A            structure of zeolite X
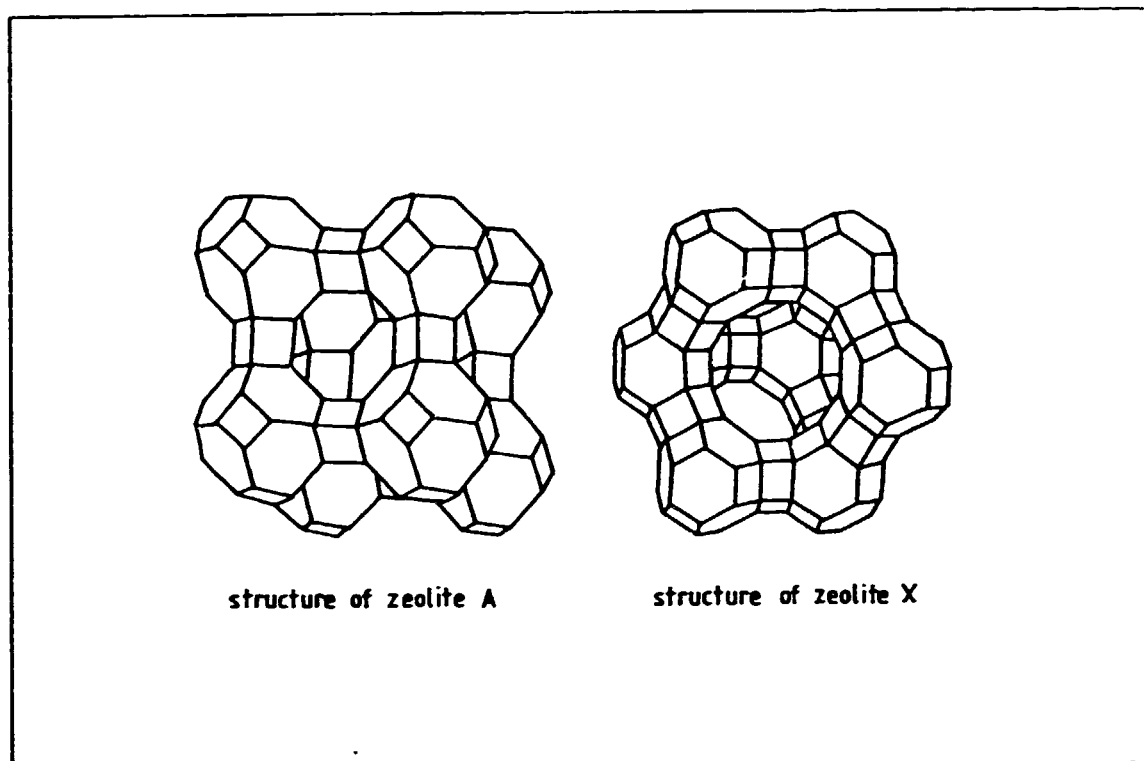
**Figure 2.3-2**
**Structure of zeolite A and X**

### 2.3.1.3 Zeolites as detergent builders

The sodium cations reside in the pore and in the central cavity of the zeolite structure and are free to be exchanged for other cations. This character gives zeolite its special properties as a detergent builder [3, 4].

The major benefit of zeolite is the high calcium exchange capacity. When a zeolite crystal is placed in water containing hardness ions, calcium diffuses into the crystal and replaces two sodium ions to maintain charge balance. Hence the water is softened and the detergent does a more effective job of washing the clothes.

Zeolite A is a free-flowing white powder. The particle size has been optimized to give the best possible zeolite performance in detergents. The mean particle size is generally 4-6 microns.

Additional important properties of zeolite are its health and safety aspects: zeolite is safe from both human and environmental standpoint.

Illustrating effectivity of zeolite in removal of hardness ions Figure 2.3-3 shows the results of an experiment. It is seen that calcium removal is much better than that of magnesium. That is why many formulations contain a co-builder with zeolite to

provide complete removal of both calcium and magnesium. This co-builder may be the conventional sodium-tripoliphosphat (STPP) or zeolite X.
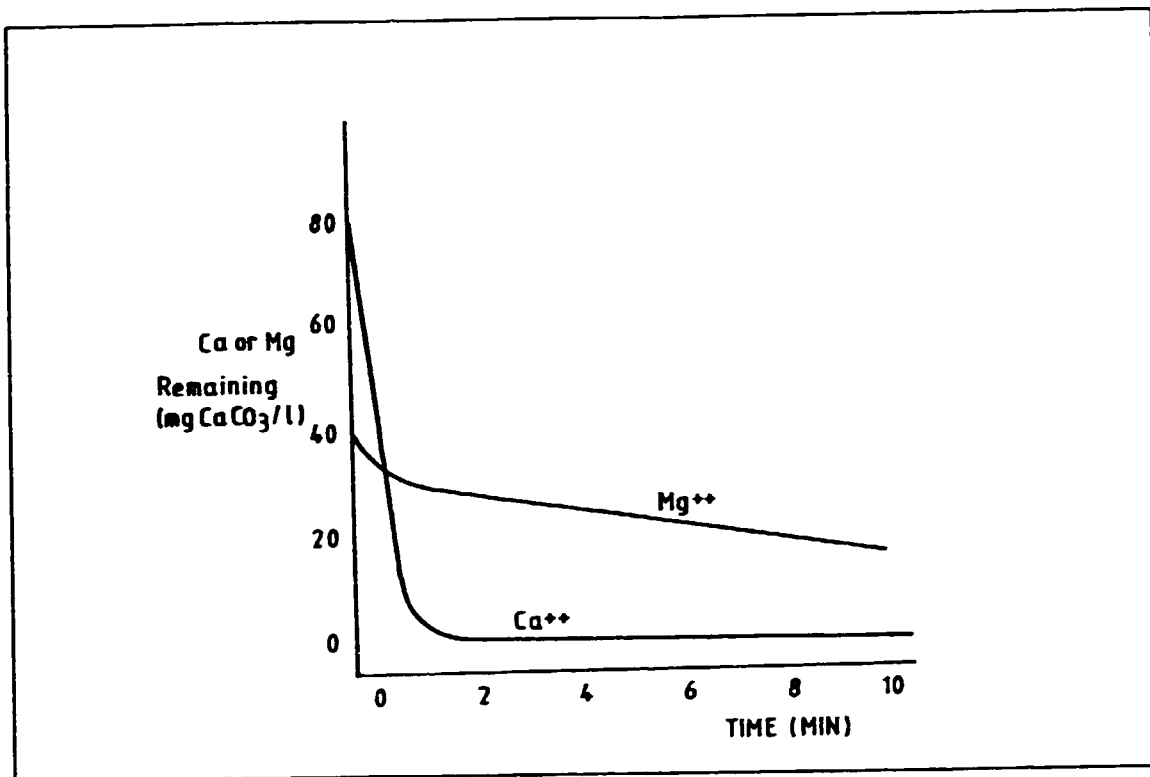


Figure 2.3-3
Hardness removal by Zeolite NaA
Initial hardness: Ca = 80 mg $CaCO_3$ /l
                  Mg = 40 mg $CaCO_3$ /l
Zeolite concentration: 0.06 %
Temperature             :    104 $^o$F (40 $^o$C)

The calcium removal performance of zeolite compared with other major builders is shown in Figure 2.3-4.
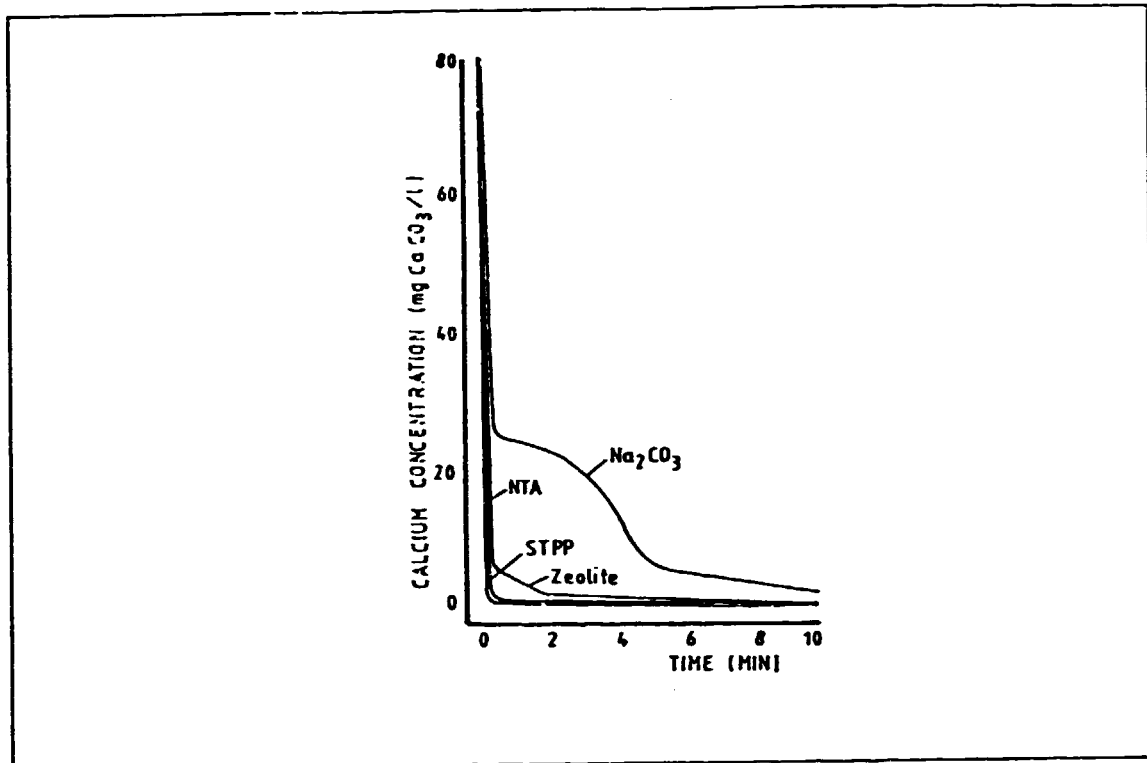
**Figure 2.3-4**
**Calcium depletion rate for major  builders**
**pH = 9.4, room temperature, 0.06 % builder**

It can be seen that the performance of NTA, STPP and zeolite are
essentially equal.


### 2.3.1.4 Zeolites and adsorbents

Synthetic zeolites are high quality adsorbents which are suitable
for a variety of applications. Their outstanding properties are
due to the characteristics of their structures [2].

Large cavity volume and  large inner surface area result in high
adsorption capacity. The fact that the pore diameters are
absolutely uniform means that it is possible to make a clear-cut
separation of different molecules on the basis of differing
molecular sizes (molecular sieve effect). The strong electrical
fields inside the cavities also make it possible to separate
mixture of adsorbed molecules due to differences in polarity or
polarizability [5].

Zeolites of type A and X can be used successfully in the
following applications:

- Drying of fluids (gases and liquids), i.e., the removal of
  water down to extremely low residual levels
- Purification of fluids, i.e. removal of other adsorbable
  impurities to extremely low residual levels

- Separation of gas mixtures, i.e., breaking them down into
  individual components, which can be obtained with a high level
  of purity.

Zeolite molecular sieves retain adsorbates by strong physical
forces rather than by chemisorption [1].

Adsorption on zeolite molecular sieves is characterized by a
Langmuir-type isotherm, where the amount of a given compound
adsorbed increases rapidly to a saturation value. An example is
shown in Figure 2.3-5. for adsorption of water vapour on zeolite
A compared with other adsorbents.
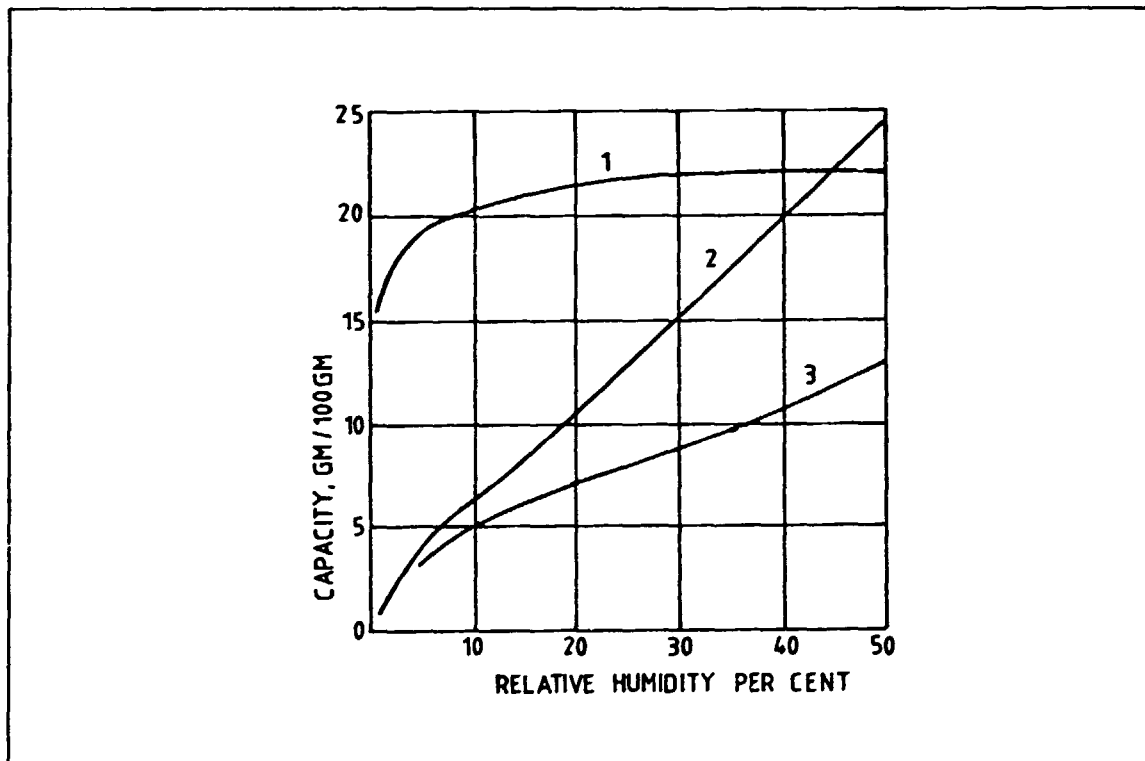


Figure 2.3-5
Water vapour adsorption at 25 °C
(Equlibrium data)
1. Molecular sieve type A
2. Silica gel
3. Activated alumina

## 2.3.2 Production of zeolite in the alumina plant

### 2.3.2.1 An individual procedure connected with the Bayer cycle

Developing work to produce synthetic zeolite started in the Ajka
Aluminium Company in 1987. Basic procedure was given by Research

Institute for Technical Chemistry of Hungarian Academy of Sciences in Veszprem.

During the laboratory tests (in bigger size) several types of materials originated from Bayer cycle of alumina plant were proved as alumina sources for zeolite synthezis. A particular kind of sodium-aluminate liquors which is a by-product of the Bayer process was found to be the best starting material of the zeolite production.

The Ajka procedure is closely connected with the alumina production line: aluminate liquor, water, steam are supplied, mother liquor and washing liquors of zeolite process are accepted by the alumina plant.

Sodium aluminate liquor for zeolite reaction is produced in the precipitation tanks of alumina plant after crystallizing of aluminium-hydroxide, therefore the capacity of the plant will not be reduced by zeolite production.

Main advantages of the zeolite producing system combinated with Bayer cycle are:

- investment costs of a zeolite plant are decreased by 10-20 %
- production cost of zeolite is reduced by 25-30 %.

## 2.3.2.2 Production of zeolite detergent

Main product of Ajka zeolite plant is detergent powder type 4A. It is produced in a gel process in which an aluminosilicate gel is first produced by reacting a mixture of sodium aluminate and sodium silicate solutions in an aqueous system. The gel is then heated to crystallize the zeolite. Careful control of reaction composition and crystallization conditions is required to minimize impurities and produce a product of the proper particle size. Following crystallization, the zeolite crystals are filtered, washed to remove excess reactants and Spray dried.

The outline drawing of zeolite detergent production is showed in Figure 2.3-6. Quality of Ajka zeolite powder is similar to some European producers' products. The most important properties of zeolite are Ca-ion exchange capacity and the particle size distribution. The usual value for the former one is 160-175 mg CaO/g zeolite, for the latter 1 $\mu$m to 10 $\mu$m. The Ajka product has got about 170 mg/g ion exchange capacity and 3-5 $\mu$m of mean crystal size. Main physical and chemical characteristics of Ajka product is shown in Table 2.3-1.
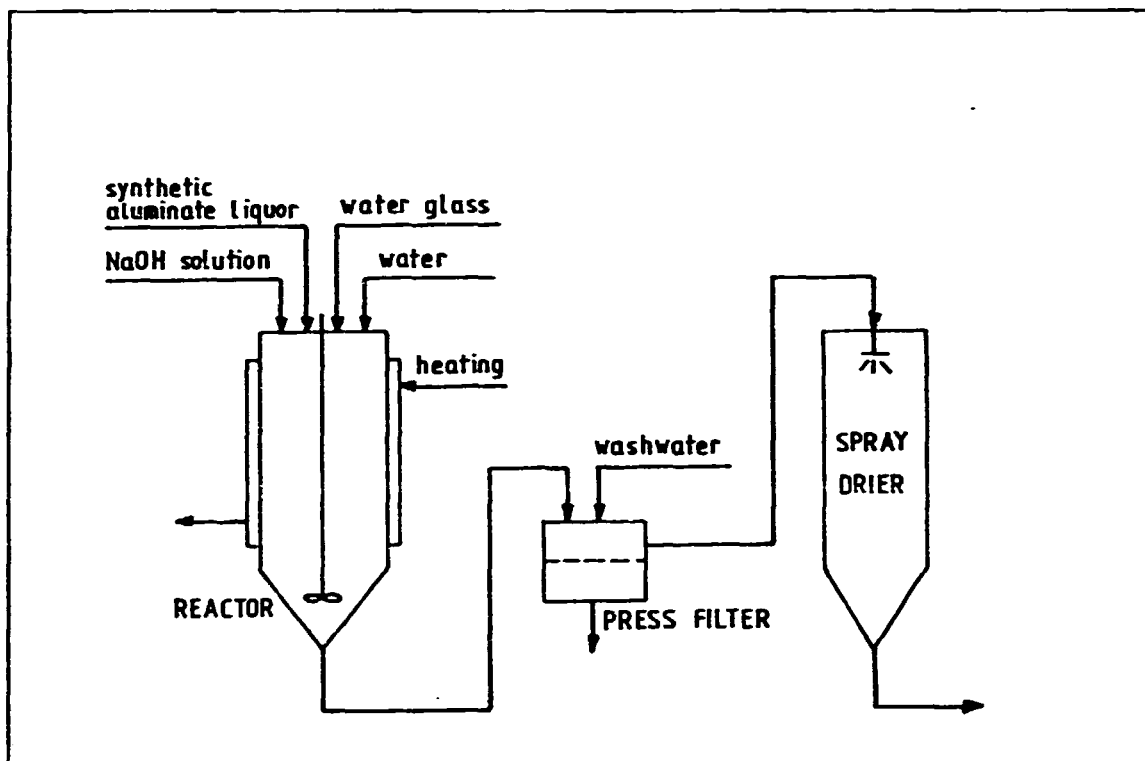
**Figure 2.3-6**
**Production of zeolite NaA powder**

**Table 2.3-1**
**Characteristics of ZEOLON-P**

| Cristallinity (%) | min. 95 |
|---|---|
| Reflactance (%) | min. 95 |
| Ca-ion exchange capacity | |
| (mg CaO/g anhidrous zeolite) | 170 |
| Chemical composition (%) | |
| $Na_2O$ | 17-19 |
| $SiO_2$ | 31-34 |
| $Al_2O_3$ | 28-30 |
| L.O.I. (1 h at 800 °C) (%) | 20 |
| Impurities (ppm) | |
| Fe (total) | max. 250 |
| Pb | max. 3 |
| As | max. 1 |
| pH-value (in suspension of 10 %) | 11.5 |
| Medium crystal size ($d_{50}$) ($\mu$m) | |
| Residue on sieve 45 $\mu$m (%) | max. 0.4 |
| Bulk density (kg/m$^3$) | 350-450 |

The 4A zeolite powder produced in Ajka is used by laundry detergent producers in Austria, Germany and Switzerland. The product stored after drying in silo is filled into bags and silo camion or tank car and delivered on road or by rail.

## 2.3.2.3 Development of zeolite adsorbents

A kind of zeolite adsorbents has been developed on 4A zeolite powder. It is processed in rotary granulating drums, mixing the zeolite powder with binder material and water. Wet granulates are dried and then activated in a shaftkiln. The warm product is packaged hermetic in polyethylene bags. Outline of the process is shown in Figure 2.3-7.
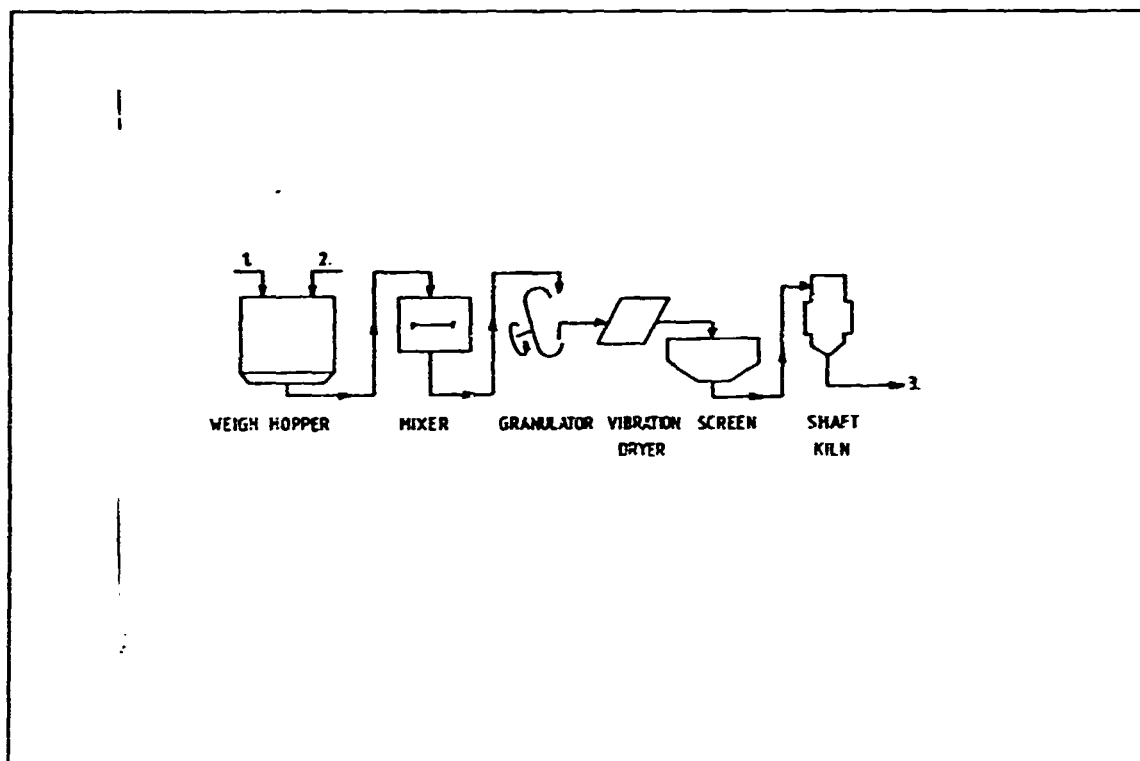


**Figure 2.3-7**
**Outline of zeolite producing process**

The product consist of spherical beads or balls with diameter of 2-3 mm.

In order to 4A pore size of zeolite NaA it is extremely suitable to adsorbeate water molecules. Ajka hygroscopic zeolite adsorbent has a large water adsorption capacity. Properties of zeolite granulates can be seen in Table 2.3-2.

Product of the Ajka pilot plant is used for drying air in insulating glasses and during protection of equipments. Adsorbed water molecules are desorbed by heating and they leave zeolite crystals in the same chemical state as before adsorption, that is zeolite adsorbent can completely be regenerated.

Zeolite granulates have also been used for drying organic liquid and as filler material in fire proof doors.

Table 2.3-2
Characteristics of ZEOLON-G

| | |
|---|---|
| Shape: | spherical grain |
| Particle size: | 1.0 - 2.5 mm |
| | 2.5 - 3.5 mm |
| Bulk density: | 0.6 - 0.7 kg/dm$^3$ |
| Density: | 1.5 - 1.6 kg/dm$^3$ |
| Zeolite content: | 70 - 80 % |
| Binder content: | 20 % max. |
| Moisture content: | 1 % max. |
| Colour: | slightly pink |
| Temperature of regeneration: | 400 - 500 °C |
| | |
| Adsorption capacity for water vapour: | |
| In case of vapour saturated air: | 23 - 28 % |
| In case of 55 % vapour-content: | 13 - 17 % |

## 2.3.2.4 Other developments of $SiO_2$ based materials

Connecting with renewing of products of alumina plant, several kinds of silica based materials have been developed in Ajka. Dissolving of solid sodium silicate will be realized. Recently, bought water glass solution has been used for production of zeolite and silica based materials.

A new procedure to produce X/Y zeolites in agitated tank has been developed in laboratory. Some types of zeolite A have been made by ion exchange in pilot size.

Silica filler material for rubber and plastic industry is being processed in pilot size to produce samples for users' trials.

Forming methods are developed and proved to make products for different purposes from zeolite and silica. Products may be granulates, extrudates, pastes or shaped bodies with or without binder.

Direction of development of silica based materials is illustrated in Figure 2.3-8.
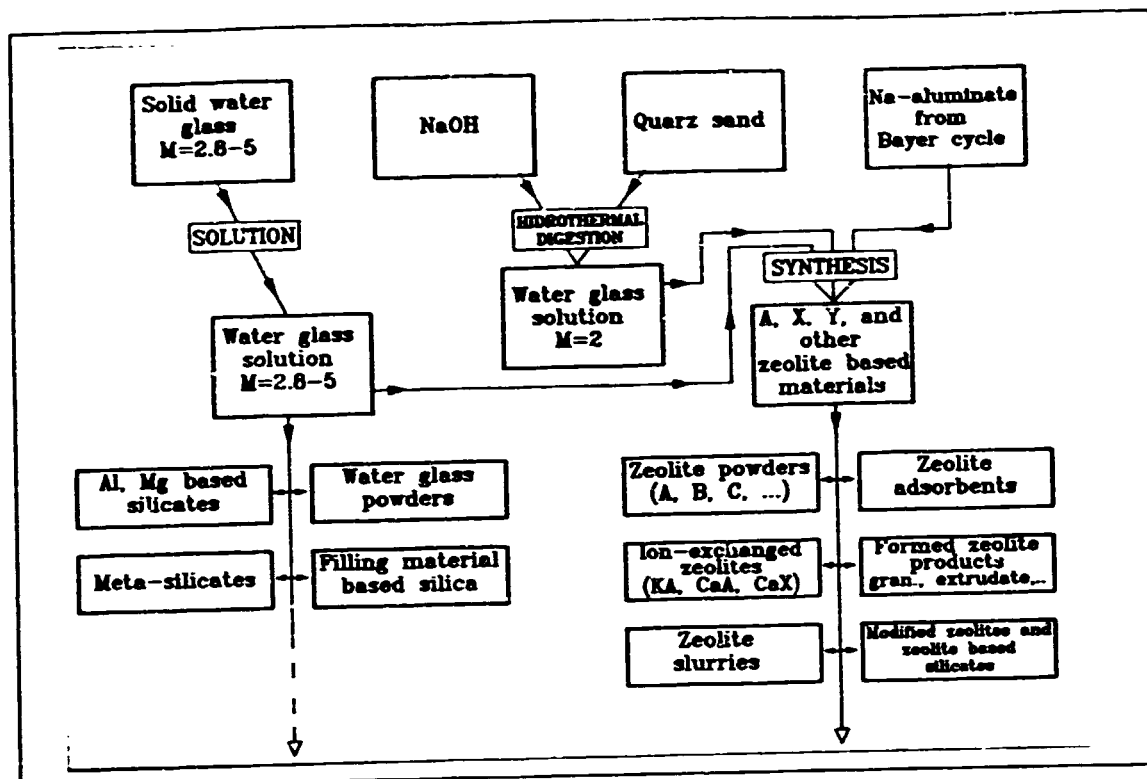
Figure 2.3-8
Direction of development silica based materials

# Reference

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## 2.4 PRODUCTION OF ALUMINIUM SULPHATE

T. Szalai

Aluminium sulphate is a compound of white colour with a slight yellowish or greyish tint at most, it comprises crystal water and is fairly water-soluble.

Composition of the technical crystalline aluminium sulphate corresponds to the formula below:

$$Al_2(SO_4)_3 \cdot 13.5 - 14.5\ H_2O \qquad \qquad \{1\}$$

Aluminium sulphate was shown at World's Fair in Paris in 1844 and was recommended to substitute for common alum i.e. potassium aluminium sulphate. Thus aluminium sulphate industry has been developed by the end of the last century. The first notable productive capacities have been established around 1900.

### 2.4.1 Areas of utilization

Main application area of crystalline aluminium sulphate is the paper industry. It represents an important auxiliary material for the paper production, i.e. it facilitates the agglutination of cellulose fibres when gluing paper.

The other major area of its application is water purification wherein aluminium sulphate is used as flocculent.

In addition, aluminium sulphate is used in producing printer's ink, in tanning leather, furthermore as mordant with dyeries and for stripping and deodorizing with the petroleum refining. It may also be considered as a basic material for the production of other aluminium compounds (e.g. aluminium, fused alumina, aluminium stearate, etc.). It is also used for preserving wood and adhesives (Table 2.4-1).

**Table 2.4-1**
**Consumption of indigenous aluminium sulphate by industry branches**
**1990**

| Industry branch | Consumption (t) | Distribution (%) |
|-----------------|-----------------|------------------|
| Paper industry  | 9.182           | 42.98            |
| Water treatment | 7.316           | 34.25            |
| Others          | 4.862           | 22.77            |
| Total:          | 21.360          | 100.00           |

On grading aluminium sulphate the $Al_2O_3$-content, free acid and iron content is specified in general.

For the case of pretentious consumption, e.g. in water purification the freedom from arsenic is further required. There are three kinds of aluminium sulphates generally in trade:

- commercial iron-free aluminium sulphate. (Min. 17 % of $Al_2O_3$-, max. 0.005 % Fe-content. This product can be manufactured by starting out from alumina hydrate; its main application areais the paper industry.)

- commercial crystalline aluminium sulphate. (Mn. 17 % of $Al_2O_3$-, max. 0.5 % of Fe-content. It can be manufactured by starting out from low-iron aluminium oxide minerals; its main application areais the water purification.)

- the mixture of aluminium sulphate and iron sulphate. (Products obtained industrially by treating bauxite with sulphuric acid; its main application areais the sewage purification.)

Indigenous stipulations for the quality of aluminium sulphate are laid down in two standard specifications.

Quality stipulations for the aluminium sulphate of industrial use are given in (Hungarian) standard specifications MSz 1013-78. The characteristics of Hungarian products aresummarized in Table 2.4-2.

**Table 2.4-2**
**Quality stipulations for aluminium sulphate of industrial use**

| Composition figures (%) | Grade I. (%) | Grade II. (%) | Characteristic of MOTIM product |
|---|---|---|---|
| Aluminiumoxide ($Al_2O_3$) content | 17.0 | 15.8 | 17.0 – 17.5 |
| Free acid ($H_2SO_4$) content | 0.01 | 0.01 | 0.00 |
| Alkalinity (referred to $Al_2O_3$) | 0.5 | 0.5 | 0.2 – 0.4 |
| Iron (Fe-content) | 0.035 | 0.035 | 0.004– 0.006 |
| Water insoluble part | 0.3 | 0.3 | 0.08 – 0.120 |

Quality stipulations for aluminium sulphate for the use of water purification are given in the standard specification MSz 16975-83 as it is shown in the Table 2.4-3.

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### Table 2.4-3
### Quality stipulations for aluminium sulphate for the use of water purification

| Composition (ppm) | Standard stipulations (%) | Characteristic figures of MOTIM product |
|---|---|---|
| Arsenic content | max. 0.001 | max. 3 - 5 |
| Cyanide content | max. 0.001 | max. 0.01 |
| Mercury content | max. 0.0001 | max. 0.01 |
| Cadmium content | max. 0.0005 | max. 0.2 |

## 2.4.2 Short review of aluminium sulphate manufacturing process

Aluminium sulphate may be produced by starting out from two kinds of basic materials:

- from aluminium oxide bearing ores, as well as aluminium silicate easy to disclose
- from alumina hydrate.

Aluminium sulphate manufacturing processes include two main stages:

a./ production of aluminium sulphate solution
b./ production of crystalline aluminium sulphate from the solution.

In addition to the two main manufacturing stages, occasionally deironing of the solution, crushing and classification of the solution, crushing and classification of the final crystalline product is also performed.

### 2.4.2.1 Production of aluminium sulphate from aluminium ores

As a raw material, primarily bauxite of low iron oxide content, clay or china clay can be taken into consideration. Prior to the digestion with sulphuric acid raw materials are usually heat-treated.(1) In the course of heat-treatment dewatering and rearrangement of aluminium silicates at different rate depending on the parameters of heat-treatment takes also place and as a result, hardly digestible aluminium silicates convert into silicon dioxide of little acid solubility and into more or less acid-soluble aluminium oxide. It can be stated, in general, that the heat-treatment within the range of 500-900 $^\circ$C improves digestibility. Heat-treatment takes place in the presence of additives (e.g. $Na_2CO_3$, NaOH) to form sodium silicates.

Heat-treated raw material is treated with sulphuric acid of various concentration depending on various quality stipulations

imposed on the aluminium sulphate product [2, 3]. The so-called raw sulphate is obtained by treating with concentrated sulphuric acid. Though this material comprises all the impurities of the starting material, still it can be used for water purification purposes.

In case of more pretentious applications digestion is carried out with medium-concentrated 40-60 % sulphuric acid and the unextracted residue is removed from the aluminium sulphate solution by settling or filtration.

In more up-to-date plants digestion is performed continuously in series-connected reactors, dissolving vats. The separation of aluminium sulphate solution from unextracted residue is performed in series-coupled settlers and counter-current washing is adopted. Digestion efficiency can be increased by the addition of hydrogen fluoride or hydrogen silicofluoride [4].

If a product of higher purity is requested deironing is performed prior to evaporating the solution. Ondeironing is performed. In case of digesting with particularly dilute sulphuric acid the aluminium sulphate solution may namely comprise considerable portion of the iron content of basic material i.e. of bauxite.

Several processes have been elaborated for the removal of iron content:

Some more familiar methods are as follows:

- iron precipitation with cyanides
- separation of iron (III) sulphate by hydrolysis
- crystallizing aluminium sulphate from the iron bearing solution (indirect method)

The process also nowadays most commonly used for deironing is performed by means of cyanides. Here iron content of the aluminium sulphate is either oxidized to the III-valency state then potassium ferrocyanide is added to precipitate Berlin blue, or it is reduced to the II-valency state and by adding potassium ferricyanide the resulting Turnbull blue precipitate is obtained. Solids are removed from the deironed solution by filtration. Conditions of precipitation are of high importance to the filterability.

Crystallization or rather solidification of the hot, concentrated aluminium sulphate solution is carried out even to-day on 4-8 ton capacity trays fitted mostly with an acid-proof lining (measonry or aluminium sheets). Aluminium sulphate is poured onto the trays to form a 100-200 mm layer. Here on cooling the entire melt solidifies.

Formerly solid aluminium sulphate from the trays has been removed manually, however, nowadays this procedure is more and more mechanized. Final product is traded in tabular form or is classified after crushing depending on further utilization.

## 2.4.2.2 Production of aluminium sulphate from alumina hydrate

This method is considerably more simple and unpretentious as to the equipment than the technologies elaborated for aluminium ores because the procedure for filtering insoluble impurities and that of deironing is omitted. For aluminium sulphate production from alumina hydrate several processes have been similarly elaborated. With the recognized procedure, alumina hydrate is repulped with water then fed to a digester with a lead or acid-proof enameled lining. Here concentrated sulphuric acid is added and the slurry is allowed to boil by the use of direct or indirect steam. Resulting aluminium sulphate solution is then evaporated to obtain 17-18 % of aluminium content. Concentrated solution is allowed to crystallize in the tray solidifiers mentioned above and is further processed [5].

## 2.4.2.3 Technology of the aluminium sulphate plant unit of MOTIM

The aluminium sulphate plant unit of MOTIM also adopts essentially the recognized batch process outlined above.

Aluminium sulphate is manufactured in reactors provided with acid-proof lining by suitable admeasurement of basic materials (alumina hydrate, sulphuric acid). Reaction heat generated during the dissolution of alumina hydrate in sulphuric acid is sufficient for the evaporation of aluminium sulphate solution to the required concentration. Thus, by optimum dewatering, after the accomplishment of dissolution reaction of alumina hydrate a product of required composition, i.e. aluminium oxide content can be achieved. After an adequate holding time the resulting aluminium sulphate solution is allowed to pour through the conical bottom of the reactor into the cooling trays for solidification. Solidified aluminium sulphate is picked up by shovel pick-up trolley trucks and crushed in hammer mills.

Ground product is fed to the classifying sieve to produce three kinds of grain fractions.

## 2.4.3 Basic materials used

## 2.4.3.1 Technical grade sulphuric acid

Quality stipulations for the technical grade sulphuric acid are comprised in the standard specification MSz. 902-71.

The composition of sulphuric acid used in the aluminium sulphate plant unit of MOTIM, according to the contract for supply made with "Tiszamenti Vegyimüvek" reads as follows:

sulphuric acid content:      93.5 - 95.0 %
iron content:                max: 0.005 %

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As-content:                      max: 0.001 %

## 2.4.3.2 Aluminium trihydroxide

Quality stipulations for alumina hydrate in the manufacturing
technology read as follows:

Adhesive moisture:               11.0-12.0 %
$Al_2O_3$ content:               57.5-58.5 %
iron content:                    0.013-0.015 %

## 2.4.4 Review of technologies for manufacturing aluminium sulphate

Besides the recognized technologies for manufacturing aluminium
sulphate several other technologies have also been elaborated.
According to one of Montecatini's methods alumina hydrate is
treated in a revolving cylindric reactor at temperatures of 145-
160 °C with sulphuric acid of adequate concentration to obtain a
product of required aluminium oxide and water content after the
accomplishment of dissolution reaction.

By the high-productivity process of Giulini there is a
possibility to obtain a product with $Al_2O_3$ content of as high as
20 %. Alumina hydrate is repulped with water then fed to a
pressure-tight reactor provided with an agitator. Here sulphuric
acid of calculated amount and concentration heated up to 40-50 °C
is quickly added to the slurry to get it dissolved. Dissolution
reaction takes place at temperatures of 170-180 °C within 10-12
minutes.

In the case of tray solidification characteristic of the
recognized processes, processing of product i.e. discharging of
tray is a labour-intensive operation. Therefore, in majority of
aluminium sulphate producing plants the stepwise production of
aluminium sulphate and the subsequent continuous crystallization
i.e. solidification is the characteristic feature of operation.

To make solidification procedure continuous there are solutions
herein aluminium sulphate is sprayed into a revolving drum thus
obtaining granular final product (Boliden process).

Nowadays the most up-to-date operation for a continuous
solidification is the adoption of the Sandvik-type cooling band.
The endless conveyor belt made up of steel or rubber travels over
a cooling vat consisting of open compartments. Bottom side of the
belt facing the vat is in constant contact with cooling water
circulating in the vat, thus good heat transfer can be achieved.
An about 8-12 mm thick layer of aluminium sulphate solution is
made on the top side of the belt where it gets solidified.

Continuous solidification can similarly be achieved by atomizing
crystallizing process. According to this process hot aluminium
sulphate solution is atomized into a 10-15 m high crystallizing

tower. Falling material solidifies and gets onto a water-cooled metal band at the bottom of the tower. Post-cooling of aluminium sulphate takes place on the metal band.

Summarizing the manufacturing technologies start out from aluminium ores and alumina hydrate, respectively, as the basic materials, have been detailed formerly.

## References

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[2] Römpp: Chemie Lexikon Vol. 1. 1966.

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# 2.5 DEVELOPMENT AND PRODUCTION OF NON-METALLURGICAL GRADE ALUMINAS IN HUNGARY

M. Tóth, J. Zábráczki

## 2.5.1 The largest special alumina producer in Central-Eastern Europe - the ALOXID Ltd.

In Central-Eastern Europe these are the affiliates of HUNGALU Group dealing with the manufacturing of special aluminas:

- HUNGALU MOTIM Ltd. has been producing different products for refractory industry since many years
- HUNGALU Ajka Aluminium Ltd. deals with grinding of hydrates, precipitation of special hydrates and production of zeolites
- HUNGALU ALOXID Ltd. produces activated aluminas and special calcined aluminas.

In a narrow sense idea of special aluminas (non-metallurgical grade aluminas) generally means the specially calcined oxides. These kinds of products are manufactured in Hungary or in Central-Eastern Europe at Almásfüzítô Alumina Ltd. (ALOXID Ltd.), that's why we can claim Almásfüzítô to be the base of the special alumina production of this field.

The aim of this lecture is to overview the production of activated and special calcined aluminas through the activity of HUNGALU ALOXID.

Almásfüzítô Alumina Ltd. (abbreviated as ALOXID Ltd.) is an affiliated company of HUNGALU and successor of the Almásfüzítô Alumina Plant belonging to the former Hungarian Aluminium Company.

The plant is located at the bank of Danube at about 80 kms from Budapest. It processes Hungarian bauxite with Bayer technology. Its capacity is about 300.000 tons/year. Recently the metallurgical grade alumina production has been decreased and our capacity converted for producing non-metallurgical grade special aluminas. The reality of this kind of activity is confirmed by the fact, that the research and development of different varieties of special aluminas have already been made for several decades, and a lot of patents and know-hows of the subject have been presented, a lot of types of trade marked products in large scale quantity have been put into circulation on the Western-European markets as well.

At ALOXID Ltd. both the production and the development activity is concentrated on two fields, namely:

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- calcined   special   aluminas   and   their   further   processed
      varieties

    = ceramic aluminas - press powders - grinding balls
    = abrasive and polishing aluminas, pastes and waxes
    = high value refractory materials

- tabular alumina
- calcium aluminate cement
- activated aluminas

    = activated   aluminas   **from   Bayer-hydrate**   and   formed
      (granulated) adsorbents and catalyst carriers made   of
      these   aluminas
    = alumina-hydroxides   -   **not   directly   from   Bayer-process**
      (pseudoboehmite).

Amongst the listed activities of ours we are the strongest on the
field of ceramic aluminas. In the 80-s our production capacity of
this has been growing to some ten thousand tons/year. In other
fields  research  and  development  works,  introduction  of  new
products onto the market are continuously going on.

We  do  not  begin  the  presentation  of  our  activity  with  our
strongest side, but start out of the hydrate, corresponding to the
system of special aluminas (Figure 2.5-1) applied all over the
world.
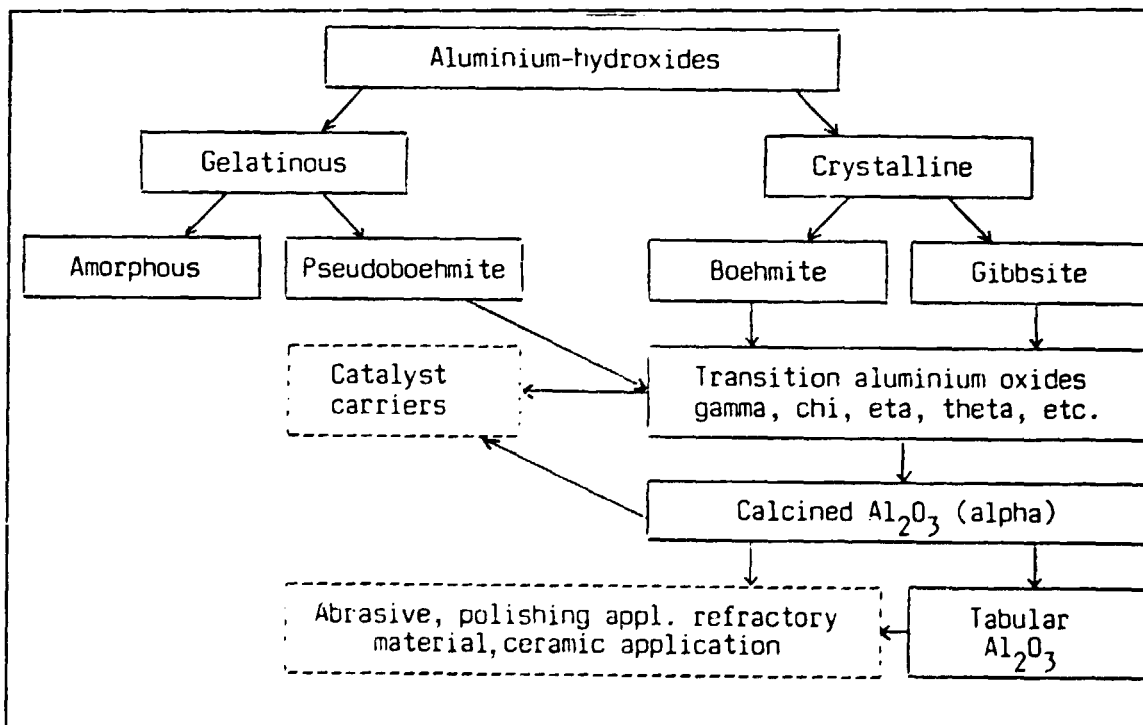


Figure 2.5-1
**Activated and calcined special aluminas**

## 2.5.2 The production and development activity of ALOXID Ltd.

### 2.5.2.1 Activated aluminas (adsorbents, catalyst carriers)

In the field of catalyst carriers our activity, which at present consists mainly of development and introduction of products to market and in less measure of production, has two separate lines, namely (Figure 2.5-2):

- connected with Bayer technology (Bayer-hydrate line)
- alumina-gel line.
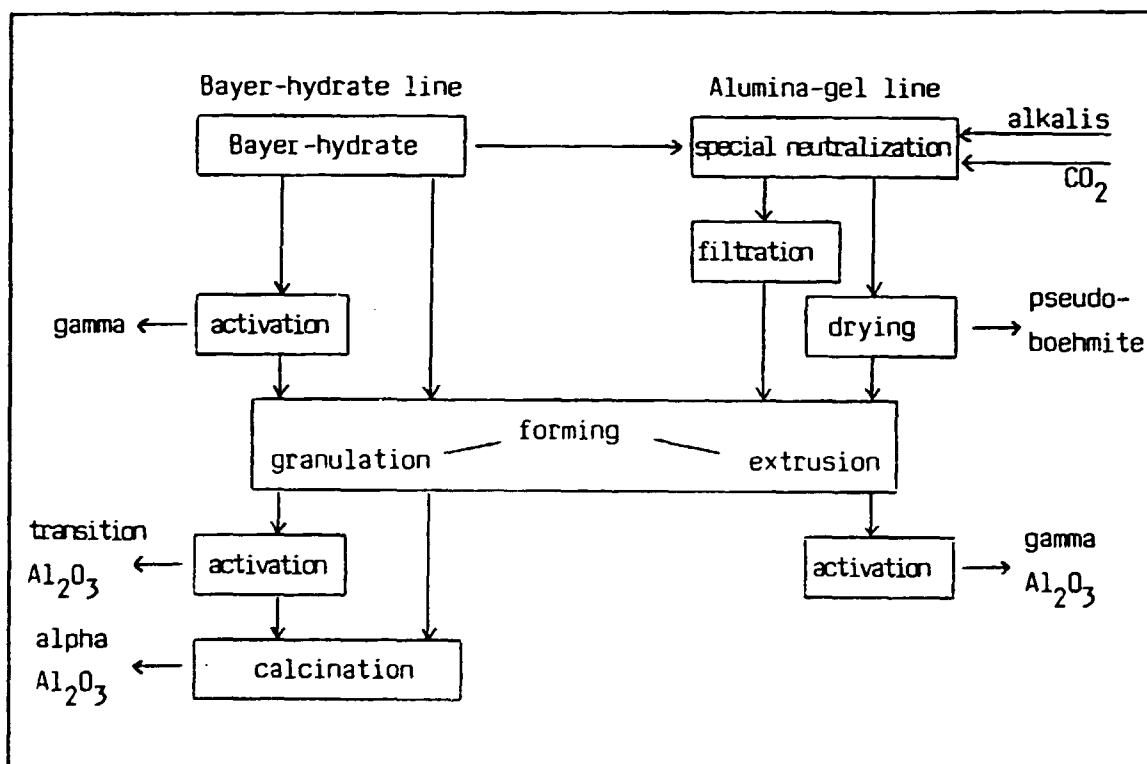


**Figure 2.5-2**
**Catalyst carrier process flow diagram**

### The Bayer-hydrate line

By Bayer-hydrate line we mean the production of catalyst carriers, whose raw material is the aluminium hydroxide arising from Bayer process. As it is known, a lot of adsorbents, catalysts and catalyst carriers belong to this group, but here we would like to mention only three of them (see Table 2.5-1: K-10, AG, $\alpha$-$Al_2O_3$ ball) which are in the centre of our interest at the moment from the point of view of the production or the development.

Table 2.5-1
Activated aluminas under production and development

| Product Trade Mark | | Under Production K-10 | AG | Under Development Experimental Product $\alpha$-Al$_2$O$_3$ | Pseudo- |
|---|---|---|---|---|---|
| Catalyst | | | | ball | boehmite |
| support | | | | | |
| Appearance extrudate[****] | | powder | ball $\phi$ 3-6[*] mm | ball $\phi$ 3-6[*] mm | fine white powder |
| Chemical Analysis | | | | | |
| Na$_2$O | % | 0.3[**] | 0.4-0.6[*] | 0.02-0.2 | 0.02 |
| 0.03 | | | | | |
| Fe$_2$O$_3$ | % | 0.03 | 0.05-0.06 | | 0.02 |
| 0.02 | | | | | |
| SiO$_2$ | % | 0.03 | 0.03-0.04 | | 0.02 |
| L.O.I. | % | 9 | 3-6 | | 27 |
| XRD Analysis $\Gamma$-Al$_2$O$_3$ | | $\Gamma$-Al$_2$O$_3$ | $\Gamma$-Al$_2$O$_3$ | $\alpha$-Al$_2$O$_3$ | Pseudo- |
| | | boehmite | | | boehmite |
| Specific 250 Surface (B.E.T.)[***] | m$^2$/g | 230 | 200 | 1-5 | 350-390 |
| Volume of 0.5-0.7 Pores[***] | cm$^3$/g | 0.3 | 0.2-0.3 | 0.1 | 0.8-1.2 |
| P$_{50}$ 80-90 | Å | 40-60 | 30-50 | 300 | 100-160 |

[*]    other sizes available
[**]   soda content may be reduced
[***]  Micromeritics Accu Sorb
[****] produced not at ALOXID, only the raw material originates from here


*K-10*

At present the so called "commercial activated alumina", the K-10
(Table 2.5-1) is produced in industrial-scale on Bayer-hydrate
base. Besides the main components, namely the gamma- and chi-
aluminas this alumina contains large quantity of boehmite as
well. It is manufactured in rotary kiln, that means a slow
dehydration, so the achievable specific surface has an upper
limit ($\approx$260 m$^2$/g). It is very well usable for a lot of different
applications, and can be produced economically with relatively
low prime cost. However there are fields of application, where

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much bigger specific surfaces and porosity larger than 0.3-0.4 $cm^3$/g are required. In this case we have two possible directions:

- Starting out of Bayer hydrate to change the conditions        of dehydration, that is:

        = the manner, time and speed of heat transfer
        = the pressure and relative humidity of atmosphere
        = the grain size of starting material

- Producing aluminium hydroxide-gels.

We have a lot of pilot-plant scale experimental results for the first direction, so we succeeded in achieving a specific surface as high as 340 $m^2$/g, and a total porosity of 0.6 $cm^3$/g, however we have stopped the apparative development. At the same time we make an intensive development concerning aluminium hydroxide-gel.

## Alumina used in the alkylation technologies

The enlarging and new establishing of alkylation plants have come to the front nowadays by the environmental protection efforts and the utilization of lead free petrol. In the alkylation by HF the treatment of product is made by alumina. Here the alumina doesn't work as adsorbent, but it concerns a chemical reaction.

The alkyl-fluorides are decomposed to olefines by aluminas, where in addition aluminium-fluoride and water arise.

Such an alkylation plant was built not long ago in Hungary as well [1]. This plant has been applying AG trade marked balls (Table 2.5-2) with good efficiency for many years.

Table 2.5-2
Characteristics of the AG adsorbent used in alkylation technologies

| Chemical properties | | |
|---|---|---|
| $Al_2O_3$ | %: | 93-96 |
| $Na_2O$ | %: | 0.4-0.6 |
| $Fe_2O_3$ | %: | 0.05-0.08 |
| $SiO_2$ | %: | 0.03-0.04 |
| L.O.I. (1100 °C) | %: | 3-6 |
| **Physical properties** | | |
| shape | | balis $\phi$=3-5 mm |
| specific surface | $m^2$/g: | 160-240 |
| bulkdensity | g/$dm^3$: | 900-1100 |
| dynamic sorption | %: | 22-30 |
| volume of pores | $cm^3$/g: | 0.3 |
| $P_{50}$ | Å: | 50-70 |
| static adsorption: E 01 | %: | 2.5-3 |
| E 06 | %: | 8-10 |
| E 09 | %: | 21-25 |
| abrasion resistance | %: | 100 |
| | | |
| **$AlF_3$ adsorption** | | |
| $AlF_3$ content at input | %: | 63 |
| $AlF_3$ content at output | %: | 1.5 |

## Alpha-$Al_2O_3$ ball

The alpha-alumina catalyst carrier ball is a high strength porous ball-shaped catalyst carrier, ignited (sintered) at high temperatures, which can be applied in processes where:

- due to the fluid bed technology the carrier must be mechanically strong
- on the high surface gamma-$Al_2O_3$, just due to its high surface the residence time is probably longer, so the selectivity is worse
- at using other types of catalysts the water causes their decay or/and sintering.

This is for example at:

- oxidative dehydrogenation of toluol
- dehydrogenation of alcohols
- hydrogenation of acetylene
- oxychlorination of methane.

## Alumina-gel line

In certain petrochemical reaction, mainly in the hydro-treating area (hydrocarbon converting processes) such as catalytic cracking, hydro-cracking, hydro-treating, reforming, isomerization, hydrogenation, dehydrogenation, oligomerization,

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alkylation, dealkylation, demetallization, etc. the most widespread catalyst carrier is the alumina, showing the next characteristics:

- large specific surface
- wide pores
- high cumulative pore volume
- well defined pore distribution.

These features are present together mainly in the gamma and aluminas, made by activation of pseudoboehmite and bayerite.

The alumina-hydroxide gel and the pseudoboehmite are not unknown ideas amongst chemists. The alumina gel became well known by its medical applications, while the pseudoboehmite - which directed the attention of scientists to its uncertain structure, too - by catalyst base material utilization. The latter is the raw material of wide pore catalyst carriers utilized mainly in the petro-chemical industry, and combined with zeolites is the base of fluid crack catalysts as well.

The name "pseudoboehmite" was given by Calvet and others. After them its structure was investigated by numerous scientists, and it was many times prepared. On the basis of their works the pseudoboehmite can be defined as an intermediate stage in the ageing of gel, containing very small particles in it, to cause X-ray line broadening [2].

There is a lot of patents for its production. One group of them is the neutralization of sodium aluminate liquor by $CO_2$ gas.

As to its principle it is not a new process. The novelty is in its realization and in special purpose modification of its characteristics. At ALOXID Ltd. the carbonization of aluminate liquor has already been made within the large scale production of pharmaceutical gels, now by the modification of the process we are ready to produce catalyst carriers as well.

For t          For this very reason a large laboratory scale pilot line has been established in order to examine the effects of technological parameters on the product features.

In order to obtain a material having well defined pore size distribution and specific surface it is very important to keep the following experimental parameters constant:

- the caustic-soda concentration
- the temperature
- the time of neutralization
- the pH change versus the time.

Properties of the pseudoboehmite produced in pilot plant and the one produced in large scale production line are very close to each other, however we are yet working on the perfection of the latter. Phase composition of the material consists of pure pseudoboehmite, there are no even traces of bayerite or gibbsite

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(Figure 2.5-3), its grain size is not characteristic, because it depends on the circumstances of spray-drying, but as shown on the SEM (scanning electron microscope) photos of Figure 2.5-4 the size of single crystals is about some tenths of micrometers. The mean pore diameter $p_{50}$ = 150 Å (Table 2.5-3).

The pseudoboehmite is only a raw material of catalysts. For its utilization as catalyst carrier or catalyst it must be formed (extruded, pelletized or granulated), activated, and simultaneously or after these impregnated with metals. So far we have not furnished yet for forming but had our experimental product tested by two famous catalyst producers. Both producers could make a catalyst satisfying the international requirements of this material which qualifies favourably both the raw material and the forming technology (Table 2.5-4).
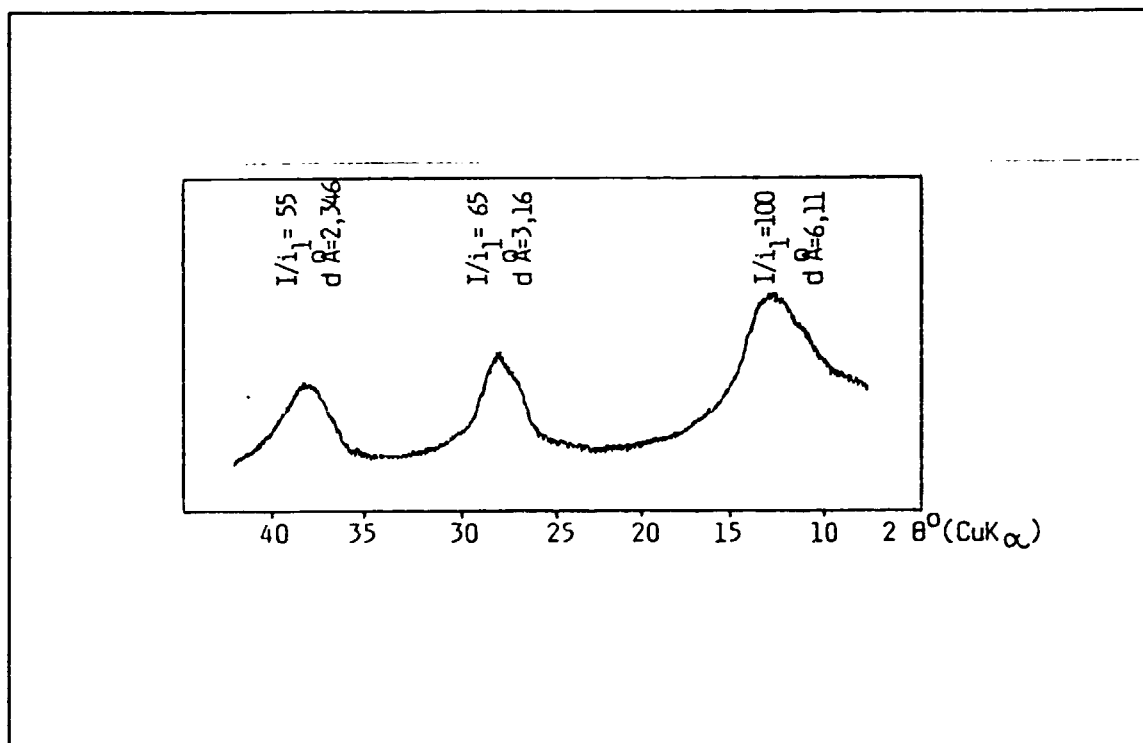


**Figure 2.5-3**
**X-ray powder fiffraction pattern of pseudoboehmite**
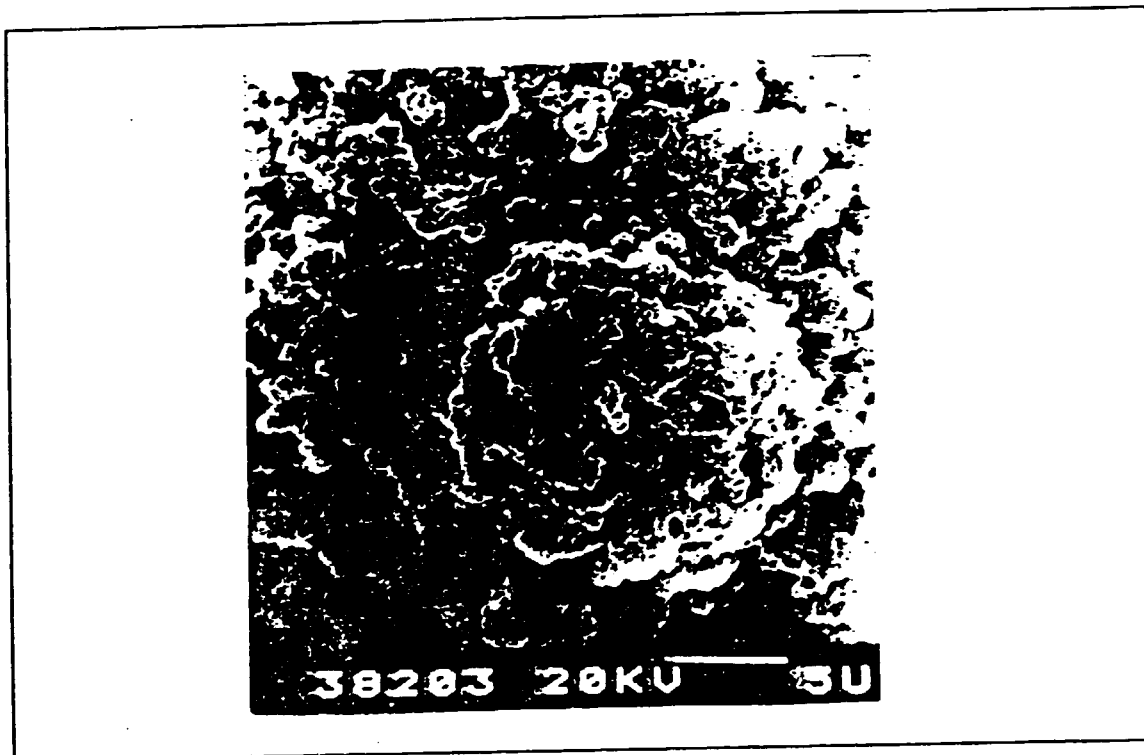
**Figure 2.5-4**
**Morfology pseudoboehmite testeb SEM**

**Table 2.5-3**
**Specific properties of pseudoboehmite**

| Chemical analysis: | | |
|---|---|---|
| $Na_2O$ | %: | 0.02-0.07 |
| $Fe_2O_3$ | %: | 0.02-0.04 |
| $SiO_2$ | %: | 0.02-0.04 |
| L.O.I. | %: | 27 |
| XRD analysis: | | pseudoboehmite (see Figure 2.5-3) |
| Specific surface (B.E.T.) | m²/g: | 300-380 |
| Volume of pores | g/cm³: | 0.7-1.5 |
| $P_{50}$ | Å: | 150-170 |

**Table 2.5-4**
**Properties of catalyst carriers from Almásfüzítö pseudoboehmite**

| Shape | | extrudates | extrudates | extrudates | extrudates |
|---|---|---|---|---|---|
| Size diameter | mm | 1.7 | 2.4 | 1.4 | 1.4 |
| | | | | | |
| Chemical analysis | | | | | |
| $Na_2O$ | % | 0.04 | | | |
| $SiO_2$ | % | 0.03 | | | |
| $Fe_2O_3$ | % | 0.02 | | | |
| | | | | | |
| XRD analysis | | $\Gamma$-$Al_2O_3$ | $\Gamma$-$Al_2O_3$ | $\Gamma$-$Al_2O_3$ | $\Gamma$-$Al_2O_3$ |
| Physical properties | | | | | |
| pore volume | ml/g | 0.60 | 0.57 | 0.66 | 0.83 |
| P50 | Å | 82 | 123 | 82.0 | 160.0 |
| Pavarage | Å | 84.5 | 119 | 80.5 | 154.9 |
| specific surface | m²/g | 248 | 170 | 226 | 211 |
| side crushing strength N/cm² | | - | - | 200 | 228 |
| abrasion | % | 0 | 0.9 | - | - |

## 2.5.2.2 Calcined special aluminas and their further processed varieties

As mentioned earlier, this activity of ALOXID Ltd. concerning
non-metallurgical grade aluminas is its strongest side both from
development and production point of view. Almost every kind of
calcined special aluminas of almost every application fields are
delt with, and an efficient development activity in order to
produce not only raw materials, but highly processed
sophisticated products, too is deployed.

Calcined special aluminas are mainly applied in the following
fields:

- ceramic and refractory industry
- abrasive and polishing material industry.

### Ceramic and refractory aluminas and their further processed varieties

Categorisation, special features, and comparison of trade marked
types of products of ALOXID Ltd. to other products being present
on the market of this group of aluminas are delt with in details
here, however we have a lot of publications on the subject as
well [3-8]. The characteristics of the three basic types are
shown in Table 2.5-5.

Our G type, low soda-content alumina which was developed in the
80-s is used exclusively for spark plug production by three
European factories.

## Table 2.5-5
### Special calcined alumina produced by Almásfüzítő

| Soda content | | Basic types Normal Inter- Low mediate | | |
|---|---|---|---|---|
| Trade mark | | T-1-Á-R[*] | T-1-Á-S[*] | G[*] |
| **Chemical analysis** | | | | |
| $Na_2O$ | %: | 0.30 | 0.15 | 0.05 |
| (max): | | 0.45 | 0.30 | 0.10 |
| $Fe_2O_3$ | %: | 0.035 | 0.025 | 0.025 |
| (max): | | 0.045 | 0.035 | 0.035 |
| $SiO_2$ | %: | 0.025 | 0.025 | 0.025 |
| (max): | | 0.035 | 0.035 | 0.035 |
| $Al_2O_3$ | %: | 99.2 | 99.5 | 99.7 |
| L.O.I. | %: | 0.1-0.2 | 0.1-0.2 | 0.05-0.15 |
| **XRD analysis** | | | | |
| $\alpha-Al_2O_3$ | %: | >90 | >95 | >95 |
| $\beta-Al_2O_3$ | %: | well detec- table | detec- table | – |
| Ultimate crystal size $\mu m$ | | $\approx 1$ | 3-4 | 2-3 |
| Specific gravity $g/cm^3$ | | 3.7 | 3.8 | 3.9 |
| Average particle size $\mu m$[**] | | 30-45 | 30-45 | 30-60 |
| Specific surface (B.E.T.) $m^2/g$ | | 4-7 | <1 | <1 |
| **Ceramic Reactivity[***]** | | | | |
| Fired density (1550 °C) $g/cm^3$ | | | 3.6 | 3.7 |

[*] available in ground form as well
[**] determined by laser diffraction p.s. analyser Malvern    Master Sizer
[***] after milling with additives, 10 g/20 mm $\phi$, pressed at 300

### Ground aluminas

On the field of ceramic and refractory production the first step
is generally grinding which requires a lot of energy and time.
That's why these manufacturers - in order to decrease their first
costs and modernize their technology - prefer buying of ground
aluminas. In order to satisfy this requirement - and due to the
fact, that grinding is cheaper in larger quantity and made with
modern technology and that the quality is better controllable -
producers of special aluminas are generally prepared for the
necessary grinding of their products as well. There are some
different methods of grinding. ALOXID Ltd. is furnished with air
jet mills and ball-mills for grinding [6, 7]. All the aluminas
shown in Table 2.5-5. are achievable in ground form as well,
milled in Alpine 530 AF air jet mill. The characteristic features
of the basic types depending on the grinding fineness are
presented in Figure 2.5-5. In addition to these basic types, a

lot of other ones can be manufactured, too, according to the consumers' requirements, combining the caharacteristics of original aluminas and grinding parameters.
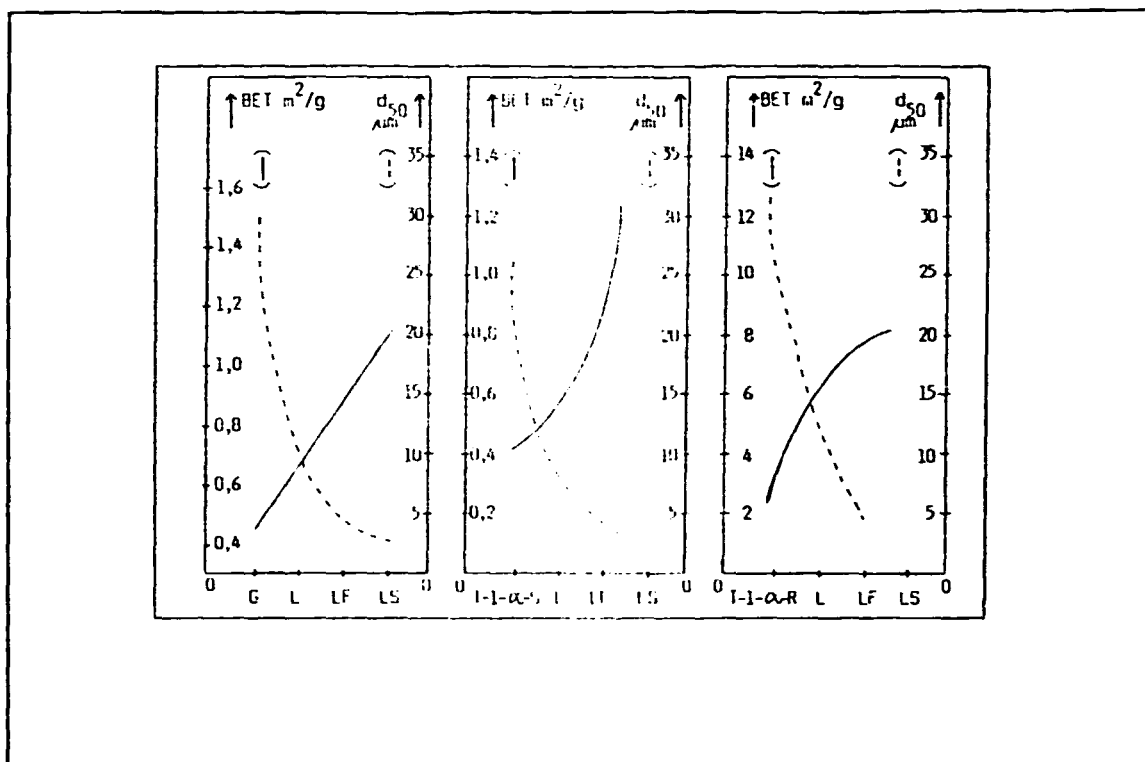


**Figure 2.5-5**
**Granulometric properties of the ground alumina**

## Press powder and grinding ball production

The consecutive steps of ceramic technology shown in Figure 2.5-6 are well known. From this technological procedure more and more steps are adopted by alumina plants. One of the processes including all the steps of a ceramics manufacturing production is the manufacturing of the high alumina concentration grinding ball. This kind of manufacturing process has been started at ALOXID Ltd. The characteristics of high $Al_2O_3$ content grinding ball produced here are shown in Table 2.5-6.
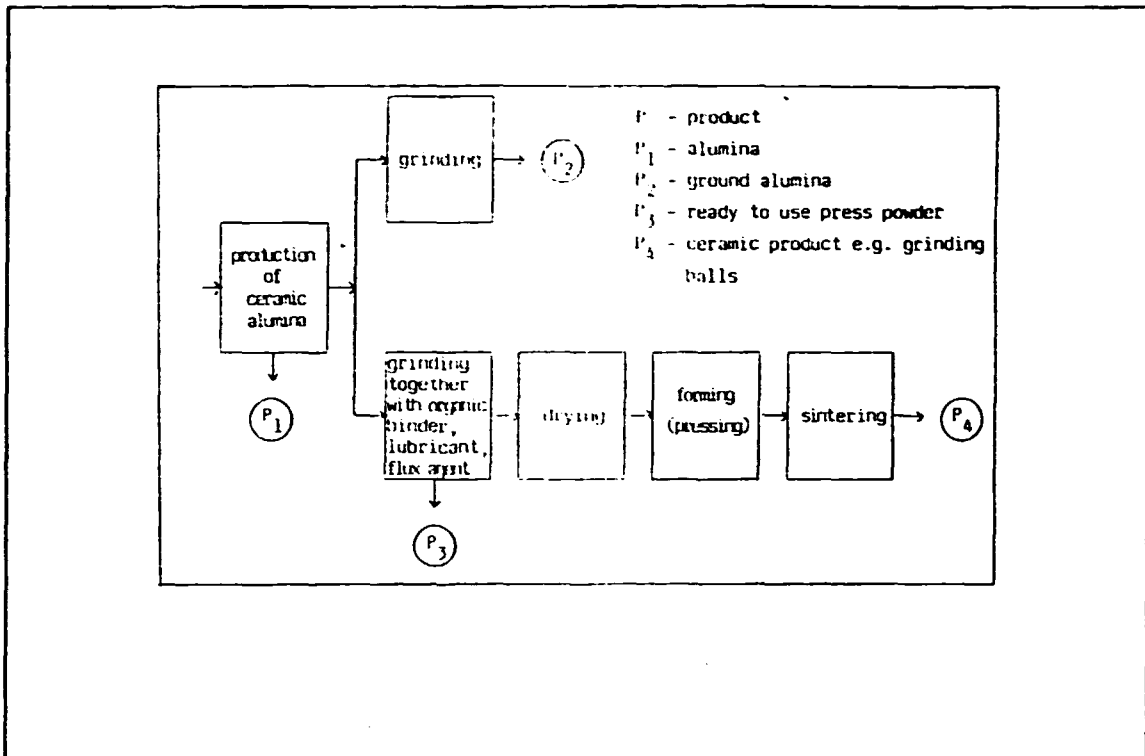
Figure 2.5-6
The steps of ceramic technology

Table 2.5-6
Characteristics of the high alumina grinding ball

| Composition: $Al_2O_3$ | % | 94 - 96 |
|---|---|---|
| Density | $g/cm^3$ | 3.6 |
| Hardness (Mohs' scale): | | 9 |
| Open porosity | $cm^3/g$ | 0 |
| Water absorption | % | 0 |
| Available size mm: | | 25, 50, 70 |
| Crushing strength | $MN/m^2$ | 2000 |

## Polishing aluminas and waxes

The legal predecessor of ALOXID Ltd., namely the Almásfüzítő
Alumina Plant had already produced abrasive and polishing
aluminas, but the production and development of these products
has stagnated for some years. At present some new experimental
products have been put on the market (Table 2.5-7) having
narrower grain size intervals than the earlier ones
(monodisperse) and more varieties in superficial features.

Table 2.5-7
Abrasive and polishing aluminas of ALOXID Ltd.

| | | TP-100 | TP-112 | TP-113 | TP-114 | TP-430 | TP-445 | TP-448 | TP-511 |
|---|---|---|---|---|---|---|---|---|---|
| Chemical analysis | | | | | | | | | |
| $Al_2O_3$ | % | min.99 | min.99 | min.99 | min.99 | min.99.4 | min.99.4 | min.99.4 | min.99.5 |
| $Na_2O$ | % | 0.25-0.4 | 0.25-0.4 | 0.25-0.4 | 0.25-0.4 | 0.08-0.2 | 0.08-0.2 | 0.08-0.2 | 0.03-0.1 |
| $Fe_2O_3$ | % | 0.035-0.045 | 0.035-0.045 | 0.035-0.045 | 0.035-0.045 | 0.035-0.045 | 0.035-0.045 | 0.035-0.045 | 0.035-0.045 |
| Physical properties | | | | | | | | | |
| Particle Size Distr. | | | | | | | | | |
| + 63 μm % | 20-40 | | | | 5-20 | 20-50 | max.20 | min.80 | |
| + 45 μm % | 30-60 | | | 0-1 | 15-40 | | | | |
| + 20 μm % | | | 1-5 | 8-20 | | | | | 0-1 | |
| Oil absorption | % | 38-48 | 24-32 | 28-36 | 32-42 | 25-30 | 18-25 | ≈30 | 13-18 |
| Primary crystal size | μm | ≈ 1 | ≈ 1 | ≈ 1 | ≈ 1 | 5-10 | 5-10 | 5-10 | 3-4 |
| Bulk density | g/l | 900-1100 | 400-500 | 450-600 | 750-900 | min.1300 | min.1100 | min.1300 | 500-650 |
| Degree of calcination | | high | high | high | high | high | high | high | high |
| Cut effect | | 2-3 | 2 | 2 | 3 | 7-10 | 4-5 | 9-10 | 3 |
| Polishing effect | 7 | 9-10 | 9 | 7-8 | 2-3 | 6-7 | 2 | 7 | |
| pH (10 % suspension) | | 8-9 | 8-9 | 8-9 | 8-9 | 7.5-8.5 | 7.5-8.5 | 7.5-8.5 | 7-8 |

## Tabular aluminas

This is a popular group of high-tech refractory materials. Its production needs a high level skill. The technology is generally strictly confidential. Cooperating with foreign firms the ALOXID has already produced some items of marketing quantity, which were tested and found to be satisfactory by its potential consumers.

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## 2.6 CERAMIC ALUMINAS AND THEIR CHARACTERISTICS

M. Tóth, J. Zábráczki

### 2.6.1 Definition of ceramic aluminas, and their classification

A considerable part of non-smelter grade special calcined aluminas is used by the refractory and ceramic industry. Its quantity - depending upon the source of statistic data and the principle of classification - is about 1.5 million tons/year. The data's diversity in most cases is due to the fact that it's impossible to draw a line of demarcation between the refractory and the ceramic industrial products. In this field there are more than a hundred products of trade mark released by a good many manufacturers circulating on the market. The principle of their classification is similar to that of other special aluminas, namely:

- field of application
- typical properties
- production processes

### 2.6.2 Field of application

In accordance with destination and utilization purposes those lines of industry or product groups are specified, where the given aluminas are the sole raw materials or are used as more or less a substantial proportion of the raw material. The field of application is naturally in close correlation with the essential features of the aluminas, but the suitability - due to the differences in technology - cannot be generalized. The most important refractory and ceramic applications are listed in Table 2.6-1.

Table 2.6-1
Fields of application of calcined (ceramic) aluminas

| Quality grade | Field of application |
|---|---|
| **Normal $Na_2O$ content alumina ($Na_2O$ %: 0.25-0.5)** | Refractory industry: bricks, ceramic fibres, mortars cements, spirels, refractory oxide-ceramics, mullites, firing auxiliary materials, coatings, glazes, filling materials, ceramic filters, sanitary and table porcelain wares, building ceramics, linings, grinding bodies |
| **Intermediate $Na_2O$ content alumina ($Na_2O$ %: 0.1-0.25)** | Refractory industry (see above), manufacturing of electro-porcelains: insulators, high voltage supporting insulators, spark plugs, oxide ceramics |
| Corundum purpose alumina ($Na_2O$ %: ≈0.2) (other impurities are also important $Fe_2O_3$, $SO_3$) | |
| **Low $Na_2O$ content alumina ($Na_2O$ %: ≤0.1)** | Oxide ceramics, spark plugs, refractory mortars, cements, binding materials, electric insulators, high wear parts, grinding balls mill linings, technical ceramics, catalyst carriers |
| Reactive aluminas | as above, and cutting tools, mainly technical ceramics (engine components), subtrates of micro electronics, bioceramics |
| High purity aluminas ($Al_2O_3$ % ≥ 99.9 - 99.99) | Bio-ceramics, translucent ceramics, telecommunication ceramics |

## 2.6.3 Typical properties

Amongst the chemical impurities of the ceramic aluminas the $Na_2O$ content is so important, that the classification of the alumina is made according to it. So there are:

- normal
- intermediate and
- low

soda aluminas (Table 2.6-2)

## Table 2.6-2
### Typical properties of ceramic aluminas

|  | Normal Na2O content * | ** | Intermediate Na2O content * | ** | * | Low Na2O content *** |
|---|---|---|---|---|---|---|
| **Chemical composition (%)** | | | | | | |
| Al2O3 | 99.0 -99.7 | 99.2 | 99.2 - 99.7 | 99.5 | 99.3 - 99.8 | 99.7 |
| Na2O | 0.25 - 0.55 | 0.3 | 0.1 -0.25 | 0.15 - 0.25 | ≤ 0.1 | 0.05 - 0.1 |
| SiO2 | 0.01 - 0.03 | 0.025 | 0.01 -0.03 | 0.25 | 0.02 - 0.05 | 0.025 |
| Fe2O3 | 0.01 - 0.04 | 0.35 | 0.01 -0.03 | 0.35 | 0.01 - 0.04 | 0.035 |
| L.O.I. | 0.1 - 0.9 | >90 | 0.1 -0.2 | 0.1 - 0.2 | 0.07 - 0.15 | |
| **Phase composition (%)** | | | | | | |
| α-Al2O3 | 65 -90 | >90 | | >95 | >95 | >95  >95 |
| β-Al2O3 | | detectable | | detectable | - | - |
| **Single crystal** | | | | | | |
| size (μm) | 0.3 -6 | ≈1 | 3 - | 6 (10) | 4 - 5  2 -10 | 2 - 4 |
| **Specific surface m²/g** | 6 - 15 | 4 - 7 | <1 | <1 | <1(0.15) | <1 |
| **Average grain size μm** | + | 30 - 45 | + | 30 - 45 | + | + |
| **Sinterization properties** | | | | | | |
| Fired density g/cm³ | | | | >3.6 | 3.2 - 3.7 | ≥ 3.7 |
| Firing temperature °C | + | + | >1600 | | >1600 | |

```
+     = not characterisitc
*     = trade marked products of different manufacturers
**    = HUNGALU-ALOXID T-1-α-S
***   = HUNGALU-ALOXID G
```

As shown in Figures 2.6-1 - 2 the total sodium-oxide content has a close connection with the beta-$Al_2O_3$ content of the alumina, while the soluble sodium-oxide correlates well with the conductivity of the alumina suspension (Figure 2.6-3). The different types of ceramic aluminas are macroscopically very similar, but the photos made by SEM (scanning electron microscope) show the different morphologies of these aluminas (Figures 2.6-4 - 6). On the SEM photos the well discernible shape and size of the single crystals are besides the sodium oxide content the second very important peculiarities of these aluminas. These and the degree of calcination (characterised by the alpha-$Al_2O_3$ content and specific surface) influence the grindability and sinter-activity of alumina which are its very important applicability features from the oxide-ceramic point of view. By grindability we usually mean the grinding time-dependence of one of the granulometric features (specific surface, $d_{50}$) (Figure 2.6-7). As it is shown in Figure 2.6-8, in addition to the character of material in this question the grinding conditions play an important role, too.
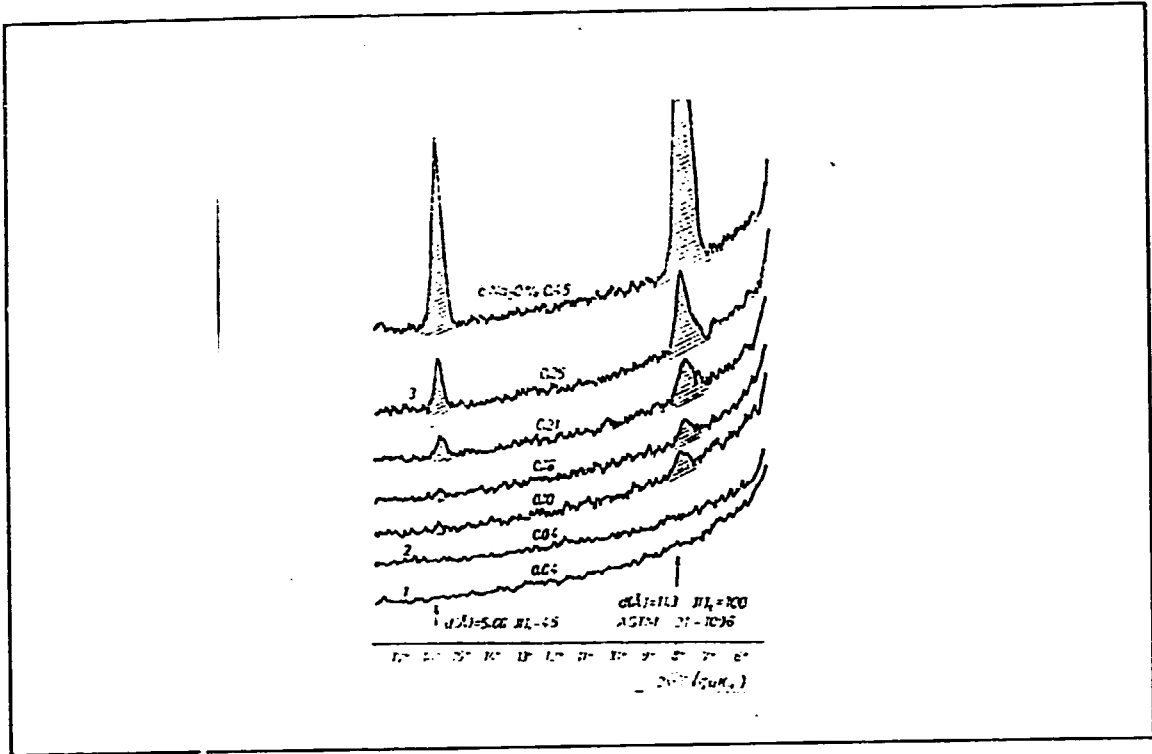
Figure 2.6-1
$\beta$-$Al_2O_3$ phase in ceramic aluminas
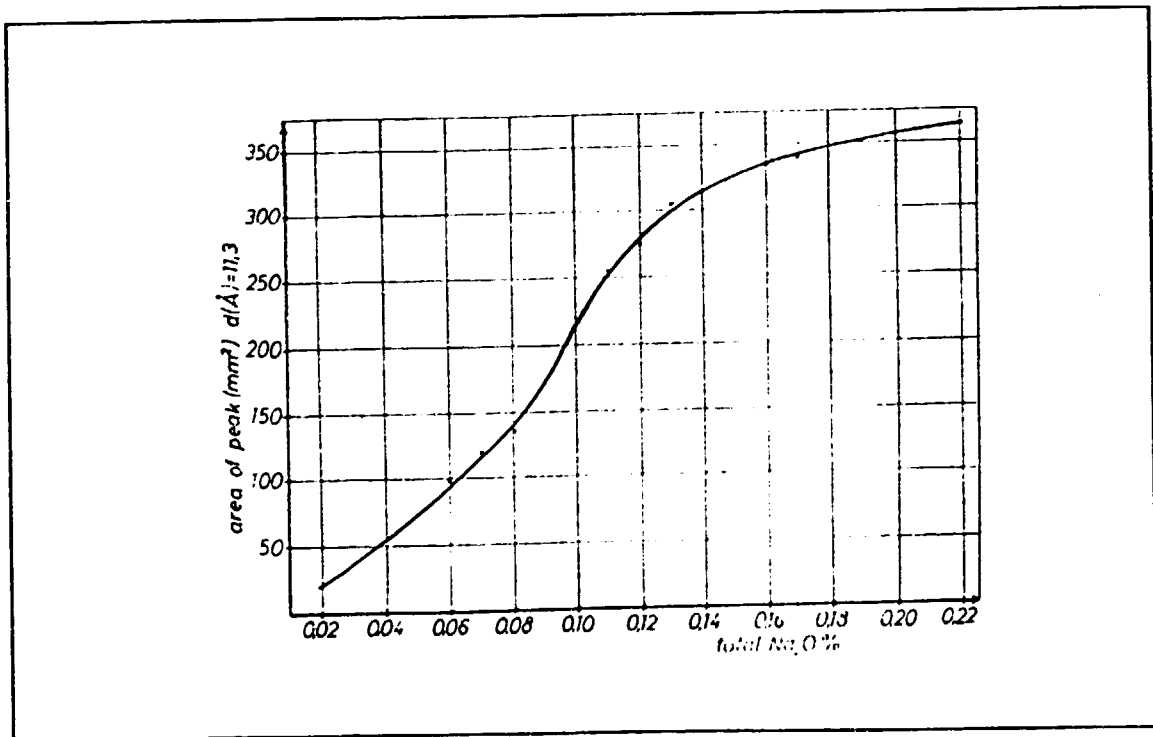


Figure 2.6-2
Intensity of $\beta$-$Al_2O_3$ versus total $Na_2O$
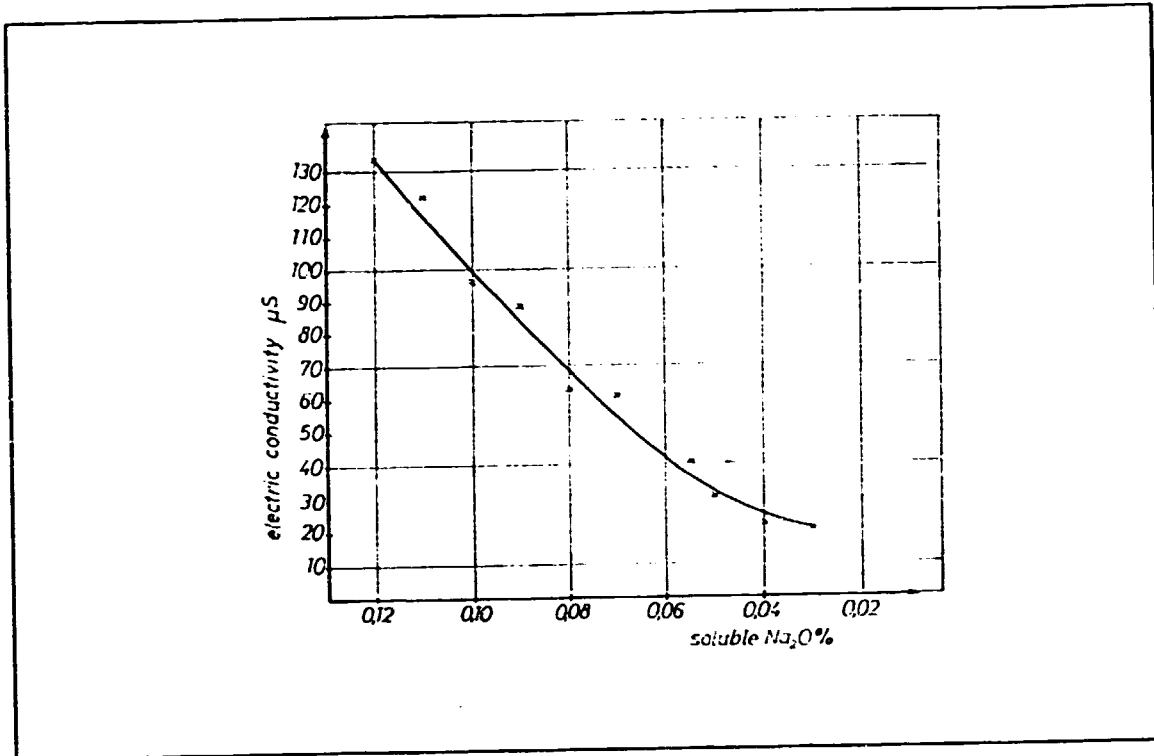
Figure 2.6-3
Electric conductivity versus Na$_2$O

Figure 2.6-4
Morphology of the ceramic alumina tested by SEM



Figure 2.6-5
Morphology of the ceramic alumina tested by SEM

Figure 2.6-6
Morphology of the ceramic alumina tested by SEM
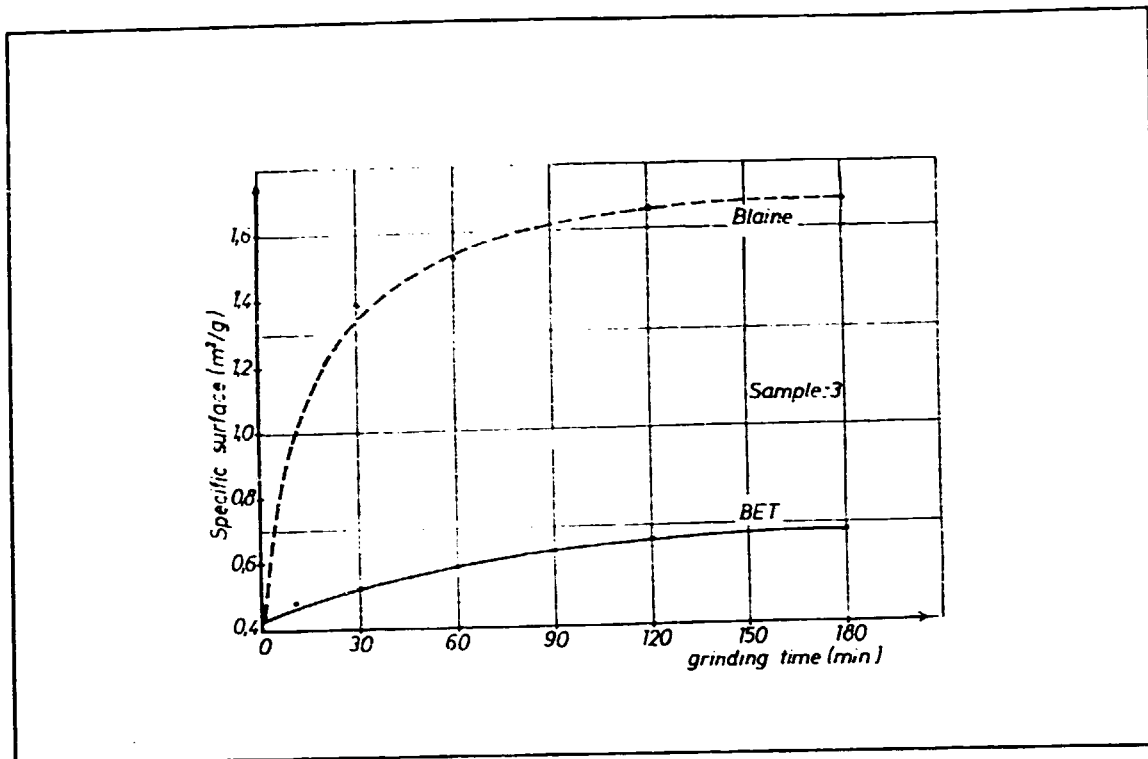
**Figure 2.6-7**
**Specific surface versus grinding time**
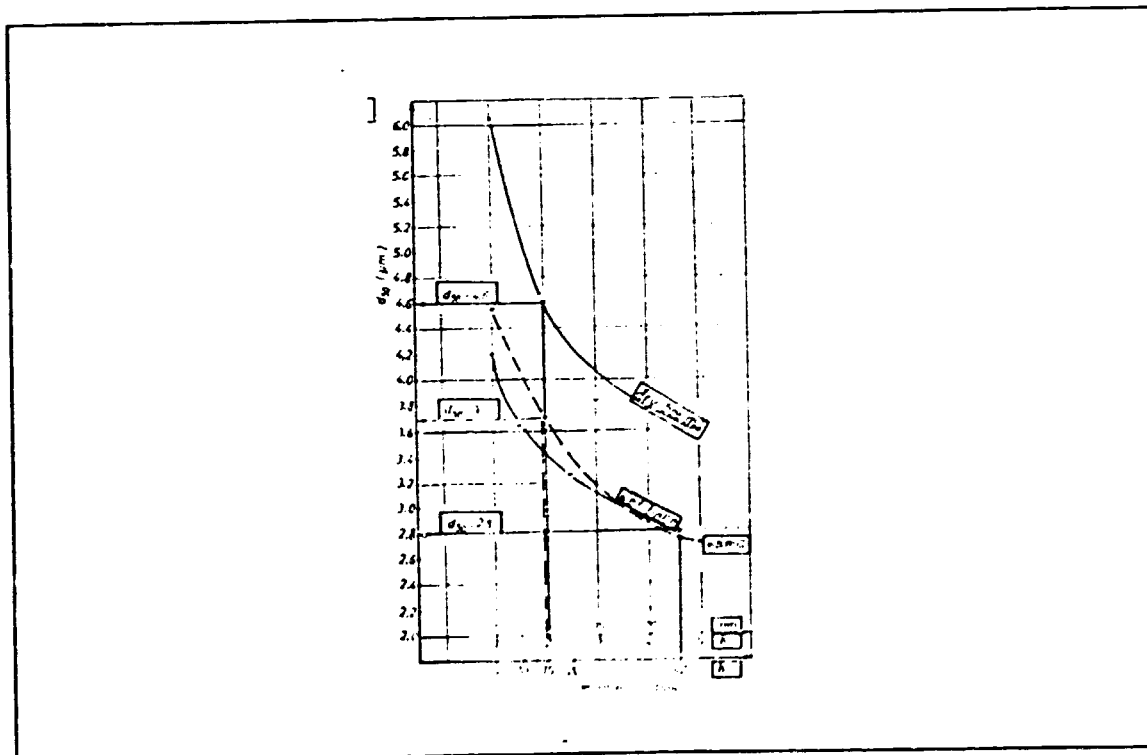


**Figure 2.6-8**
**The d$_{50}$ value versus grinding method**
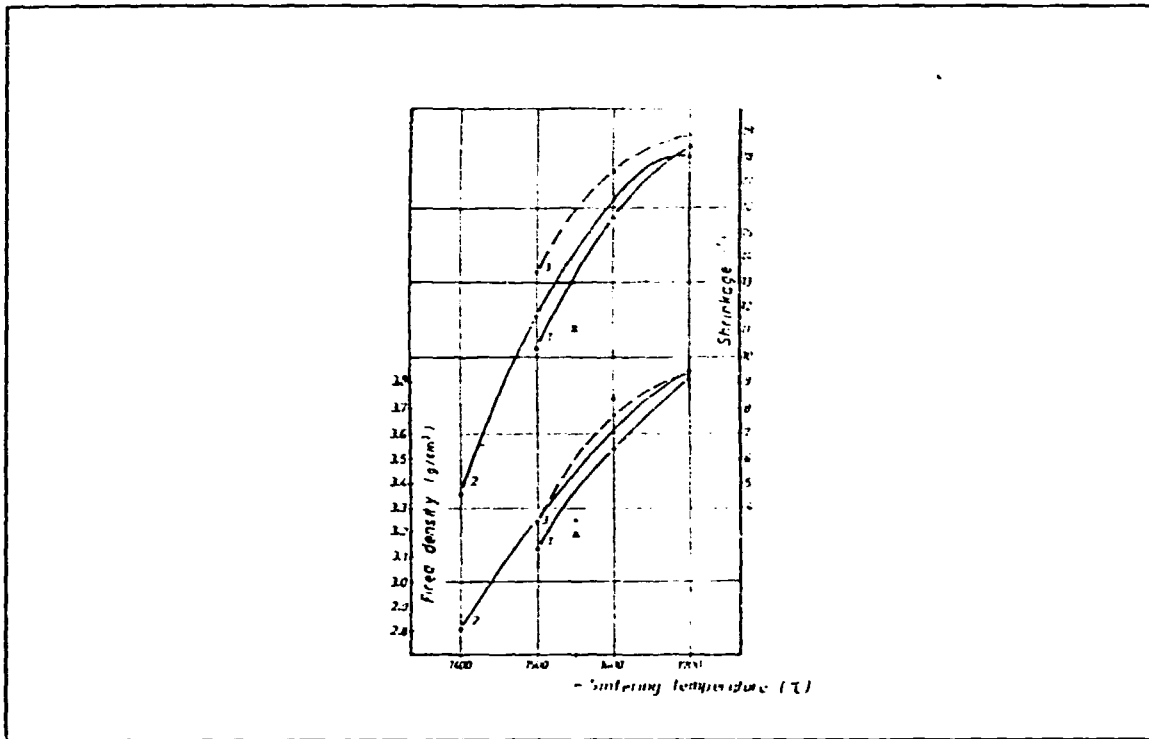
**Figure 2.6-9**
**Ceramic properties vs sintering temperature**
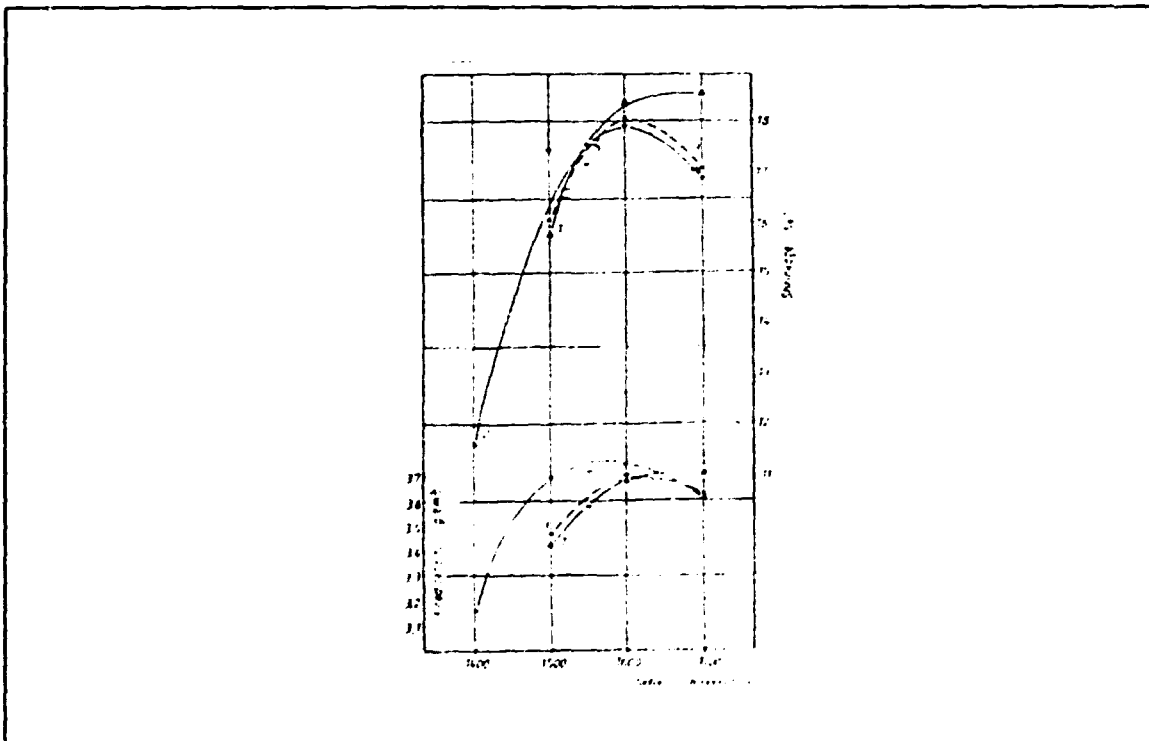


**Figure 2.6-10**
**Ceramic properties vs sintering temperature**

---------------------------------------------------------------------

The theoretical questions of sinter-activity are very complex.
Special research groups, institutes deal with the solid state
reactions of sinterization. In practice these parameters are
determined in a manner, where the alumina powder is pressed into
a steel form of a given size, the pressed density is measured
(green density, compressed density) then the pressed body is
fired ($\geq$1500-1800 $^{O}$C) and the change in size due to the firing
(shrinkage), together with the density (fired density) and water
adsorption are determined (Figures 2.6-9 - 10). As it can be seen
from the Table 2.6-2 the specific surface of the aluminas
belonging to the above mentioned three categories (well calcined
types with $\geq$95 % of alpha-$Al_2O_3$ content) is generally 0.1-5 $m^2$/g,
and the diameter of single crystals is 2-10 $\mu$m. With these
parameters it is impossible to achieve higher fired density than
that of 3.7-3.75 g/$cm^3$. However the low soda aluminas have a
special subgroup - required by the high-tech manufacturing of
technical ceramics - namely the so called sinter-active or
thermally activated aluminas. During the above sintering process
these aluminas almost achieve the theoretical density of alumina
(around 3.9 g/$cm^3$) without any glass forming additive, and even
at a 100-200 C lower temperature of , than usual. This special
feature of theirs is due to their extra small crystal size ($d_{50}$ <
1 $\mu$m, generally 0.5 $\mu$m) and as a consequence that of their
relatively high specific surface (5-15 $m^2$/g) in relation to the
calcination, enhancing the proceeding of the solid state
reaction.

The high purity aluminas have to be mentioned as well. Generally
the 99.9 and 99.99 % purity aluminas belong to this group. All of
them possess not only high purity, but special fineness (fine
disperse systems) and high activity. Owing to the submicron sizes
we got over the colloid-chemical features.

## 2.6.4 Production processes

The decisive part of ceramic aluminas is manufactured by the
calcination of normal or specially precipitated hydrates of Bayer
technology. In the precipitation of specials by parameters
different from the smelter grade precipitation we mean:

- lower aluminate liquor saturation (other concentration, caustic
  ratio, temperature, seeding rate)
- other precipitation time and
- more intensive washing,

by the condition of calcining of specials we mean

- higher temperature of calcination
- addition of mineralizers
- several steps of calcination.

  The calcination can be made in

- conventional rotary kiln

- fluid bed kiln.

A big part of ceramic aluminas gets onto the market after grinding only . The grinding technologies are:

- air jet milling (there is no contamination by the balls)
- ball milling (super grinding)
- vibro milling

Amongst the high purity aluminas the 99.9 % purity can be produced on Bayer-hydrate base, but the 99.99 purity needs a different method, which can be done:

- by solution of aluminium metal in acids, caustics or waterless organic liquids (alkoxid)
- through aluminium salt (chloride, nitride, sulphate)
- with other methods (for example with anodic oxidation of aluminium or plasma technology)

Dealing with the future trends of ceramic technologies as far as manufacturing is concerned we have to mention two things:

- the alumina manufacturers are getting more and more close to the technologies of ceramics so they produce complete press powders mixed with the necessary chemical binding materials, and ready for forming or for other utilization
- the so called sol-gel technologies - as basic technologies of ceramic composite materials - are very promising.

# 2.7 PRODUCTION OF SPECIAL OXIDE CERAMICS

J.György, M. Dimitrova-Lukács

## 2.7.1 Special ceramics

Recent progress in the field of ceramics science and technology (discovery of sialons [1] and transformation toughening in $ZrO_2$-based ceramics [2] in the middle 70's, development of efficient chemistry approaches for production of pure and fine powders, tremendous improvements of shaping and sintering technics) has resulted in developing a new generation ceramics - special ceramics (referred to as advanced, high technology, high performance, fine, engineering, technical ceramics as well).

**Special ceramics are inorganic non-metallic materials:**

- **produced by means of high technologies** under well defined and strictly controlled conditions from very pure and fine powders of specified composition and shape;

- **with carefully tailored microstructure and excellent** mechanical, thermal, chemical **or special** electrical, magnetical, optical **properties** ("high performance ceramics": for example zirconia toughened ceramics exhibit extremely high toughness, strength, hardness, wear and corrosion resistance; in case of sialons their high strength, hardness and wear resistance is combined with high thermal stability, oxidation and thermal-shock resistance);

- **with a wide range of special applications:** artificial bones, cutting tools, parts of ceramic engines, turbine blades, structural parts in devices for emerging technologies etc.;

- very **often operated under severe conditions** of wear, corrosion, or/and high temperature or/and mechanical stress.

**Special ceramics** are usually made of common, readily available raw materials using less energy intensive but high knowledge intensive technology processing, so they **are high value-added products**, therefore very attractive from the economical point of view as well.

Because of their superior properties and growing potential for profitable wide scale-application advanced ceramics have been exciting extremely high interest ("ceramic fever" in Japan) both in scientific and commercial circles, being referred to as

"materials of the future".

With reference to the main chemical component they contain special ceramics can be divided into two main groups:

- **oxide ceramics**, based on oxides such as $Al_2O_3$, $ZrO_2$, MgO, $TiO_2$. Representative examples are different grades of alumina ceramics, different types of zirconia ceramics. This group includes as well oxide composites as zirconia toughened alumina (ZTA) and chemical compounds between oxides (spinals, granats, titanates, mullite etc).

- **Non-oxide ceramics** based on non-oxides such as $Si_3N_4$, SiC, AlN, BN, TiN and including carbonitrides ($Si_3N_4$-SiC), oxynitrides such as AlON ($Al_2O_3$-AlN) and different types of SiAlON-s, oxycarbides, oxycarbonitrides and $Si_3N_4$-$ZrO_2$ and SiC-$ZrO_2$ composites, too.

The following topics are dealt with in the present paper:

1 The main results of 20-year-activity of the Special Ceramics (SC) Department in the field of research, development and production of high quality alumina powders and ceramics for different applications.

2 Characteristics of zirconia toughened alumina (ZTA) and some zirconia-based ceramics all developed in the SC Department as research products.


## 2.7.2 Alumina ceramics

Alumina ceramics are the oldest, best known and widely used technical ceramics. According to their different application fields several grades of alumina ceramics are available. The properties of some of them (our data) are given in Table 2.7-1. The data of the above Table suggests that the properties of alumina ceramics are explicitly determined by $Al_2O_3$ content and the grain size of the microstructure. This confirms the well known fact that the quality of the starting powder is of great importance in tailoring the requested microstructure and properties of special ceramics. Particular care should therefore be taken in selecting the starting alumina powders.

Table 2.7-2
Chemical and mechanic properties of high-purity alumina ceramics

| Properties | Units | ASTM 603-78 | DIAKOR$^R$ |
|---|---|---|---|
| $Al_2O_3$          Content | % | 99.5 | 99.97 |
| $SiO_2$ + $Na_2O$ + $K_2O$ |  | 0.1 | 0.01 |
| Density | $g/cm^3$ | 3.90 | 3.96 |
| Average grain size | $\mu m$ | 7 | 5 |
| Microhardness | HV | 2300 | 2200 |
| Bending strength | MPa | 400 | 420 |
| Young's modulus | GPa | 380 | 380 |
| Corrosion resistance |  |  |  |
| in Ringer-Solution | $mg/m^2/day$ | max. 0.1 | 0.075 |
| Wear resistance | $mm^3/h$ | max. 0.01 | 0.01 |
| Diameter tolerance | $\mu m$ | - | ± 5 |
| Spherity tolerance | $\mu m$ | - | 0.1 |

## 2.7.2.3 Alumina bioceramics

Biomaterials are structural materials which substitute for some
parts of the human body temporarily or finally. There is a
steadily growing market of around 15 % a year [3] for hip, knee,
ankle, shoulder, elbow, wrist and finger replacement joints, a
market which by 1996 is estimated to demand 2 000 000
reconstructive implants [3]. Stainless steel, other metals and
their alloys and dense polymers are the materials still commonly
used at present but they have two major disadvantages - they wear
out and they are only b_otolerant but not bioinert (a fibrous
capsule around the implant is formed) - which lead to
deterioration of their mechanical properties and finally to
failure. The solution of both problems has been found in
**bioceramics** - a distinguish group of advanced ceramics with
tremendously increased lifetime as implants and hence with
growing significance.

In respect to their behaviour in the living organism the
bioceramics can be divided into two main types: **bioinert-** and
**bioactive ceramics.**

**Bioinert ceramics** are high-purity and high-strength oxide
ceramics of which medical grade alumina ceramics play an
important role at present. Different types of zirconia-based
ceramics and $Al_2O_3$-$ZrO_2$ composites represent the next generation
bioinert ceramics. All bioinert ceramics are capable of getting
included in the bony tissue without any need of conjunctive
tissue. Thus the bony tissue forming in the course of healing
entirely encloses the ceramic implant providing a strong
mechanical link and long lifetime of the implant.

- Bioactive ceramics are compact or porous - usually $Ca_3(PO_4)_2$
  based - structural materials conforming in composition with the
  mineral composition of the bones and entering into organic
  bonding with the living bony tissue.

Chemical, microbiological and toxicological investigations have demonstrated that **DIAKOR** alumina ceramics meet in every respect the requirements specified in the standard ASTM 603-78 (Table 2.7-2). On the basis of the positive results of **DIAKOR** bioceramics investigation carried out by the authorities the development of implant and prosthesis constructions suitable for clinical testing and use has been started in the SC Department in co-operation with several groups of physicians. Since 1987 the SC Department has been continuously producing a wide range of bioceramic implants and prosthesis such as: various ceramic roots for teeth implants and jawbone elements for use in dental surgery; auditory and larynx elements, hip-joint balls (Figure 2.7-4). In the course of the 7 years of clinical application of the **DIAKOR** bioceramics perfect biocompatibility of the material has been proved.
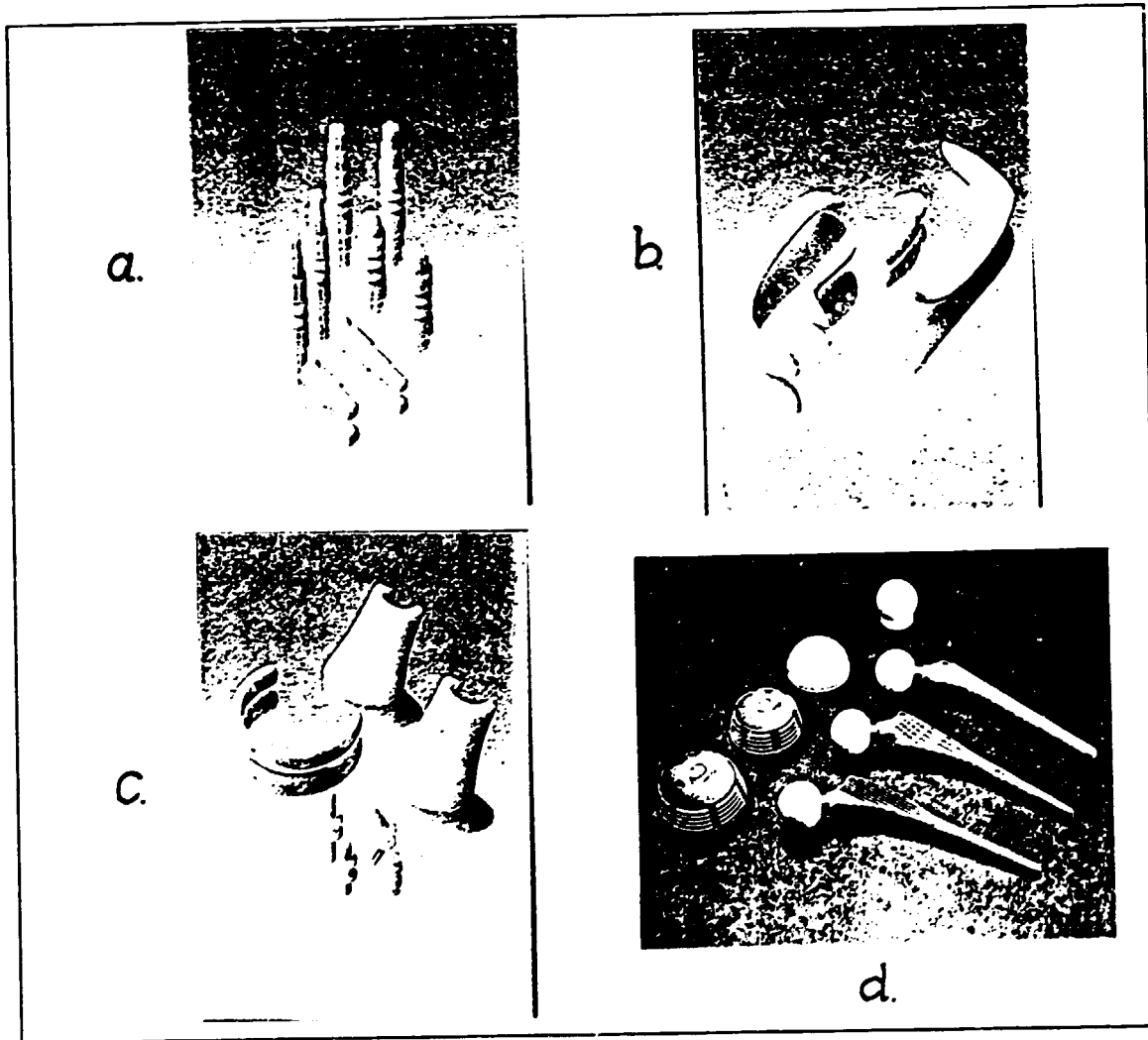


Figure 2.7-4
DIAKOR bioceramics
a.) teeth roots, b.) jaw-bones, c.) auditory and larynx elements, d.) hip-joint balls

### 2.7.3 Outlook for development of alumina ceramics

Griffits equation:

$$S = YK_{Ic}/\sqrt{a} \tag{4}$$

(where Y is a geometrical factor) suggests that there are two fundamentally different approaches to increase the strength S and hence the reliability of given material [4, 5]:

- accepting brittleness, strict microstructural **flow size (a) control** through better preparation first of all using high purity, monodisperse powders, colloidal processing, clean room fabrication, high tech. shaping and sintering technics
- **toughening** - reducing the brittleness resp. increasing the toughness of the material characterized by its critical stress intensity factor $K_{Ic}$.

In our department activity for development of alumina ceramics is in progress in both mentioned directions:
- on the one hand, for producing new aluminium oxide powders finer than any available so far by means of special sol-gel and plasma-technologies resulting in ceramics of fine grained crystalline structure with uniform grain size distribution which accounts for their enhanced mechanical properties
- on the other hand, for developing toughened $Al_2O_3$-based composites.

### 2.7.4 Zirconia toughened alumina ceramics (ZTA)

Different toughening mechanisms have been reported [4] for toughened $Al_2O_3$ based composites: **whiskers, fibres or platelets reinforcement** in the case of $Al_2O_3$-SiC system, **ductile reinforcement** (metal particles' dispersion) in the case of $Al_2O_3$-Al and $Al_2O_3$-Ni systems and **transformation toughening** in the case of $Al_2O_3$-$ZrO_2$ composites - the system being one of the subjects of our latest R and D activity.

#### 2.7.4.1 Transformation toughening mechanisms

Due to the tetragonal to monoclinic (t --> m) transformation of metastable tetragonal $ZrO_2$ particles (t-$ZrO_2$) zirconia alloying is very efficient tool for increasing both the strength and the toughness of many ceramics ($Al_2O_3$, $Si_3N_4$, SiC [5, 6] via two different mechanisms:

- Stress induced transformation toughening: under operating conditions applied stresses generated around the crack cause the metastable t - $ZrO_2$ particles of sufficient size to undergo t --> m transformation resulting in absorbtion of the crack energy which accounts for the increase in material's resistance to the crack propagation and resp. results in toughening.

- Microcracking: - taking place in a ceramic matrix which incorporates monoclinic $ZrO_2$ particles (m - $ZrO_2$) of sufficient size and caused by the volume expansion (3 - 5 %) of the $ZrO_2$ particles occurring during their t --> m transformation upon cooling from sintering temperature. Microcracks absorb or dissipate the energy of the crack thereby increasing the toughness of the ceramics.

## 2.7.4.2 Properties of our ZTA ceramics

In the case of ZTA ceramics microcracking is considered governing their toughness. Some literature data [7] and our own experience however suggest that for achieving maximum toughness and strength in ZTA ceramics both toughening mechanisms should be put in operation. From a technological point of view this means that the initial composition and all the stages of the processing should be properly selected and strictly controlled to assure the presence of both m - $ZrO_2$ and t - $ZrO_2$ particles of sufficient size and quality in the $Al_2O_3$ matrix. This way efficient technology has been developed in the SC Department for pilot scale production of high quality ZTA ceramicsot the following main properties:

- bulk density                  4.9      $g/cm^3$
- average grain size:           1 - 1.5 $\mu m$
- bending strength:             600 - 800 MPa
- fracture toughness:           8.5      $MPam^{1/2}$

These ceramics exhibit two-fold increase of fracture toughness and strength with reference to alumina ceramics. Our results are consistent even with those reported for HIP-ed ZTA ceramics [7, 8, 9].

## 2.7.5 Transformation toughened zirconia ceramics

Extensive research exploring the concept of stress induced transformation toughening in zirconia has resulted in developing a new class $ZrO_2$-based ceramics with superior mechanical properties, namely:

- partially stabilized zirconias (PSZ: Mg-PSZ, Y-PSZ, Ca-PSZ) in which fine t - $ZrO_2$ particles are precipitated in the cubic $ZrO_2$ matrix and

- tetragonal zirconia polycrystals (TZP: Y-TZP, Ce-TZP) consisting of nearly 100 % fine grained tetragonal phase.

According to a vast number of publications the stress induced transformation toughening is considered to be the dominating toughening mechanism in both PSZ and TZP ceramics.

time with high strength (Table 2.7-3). So they can compete with
3Y20A-TZP sintered ceramics (TOSOH powder source), with the
commercial Ce-TZP ceramics and even with some HIP-ed and much
more expensive Y-TZP ceramics. In addition Ce-TZP do not show
degradation of their mechanical properties at low (200 - 300 °C)
temperatures well documented for many Y-TZP ceramics. Sintered
Ce-TZP and Ce-TZP-Al$_2$O$_3$ ceramics parts of different shape and
size produced by means of cold isostatic pressing and injection
moulding technics are shown in Figure 2.7-7. Ceramics of this
quality can be successfully used as reconstructive implants,
blades for knifes and scissors bearing parts, grinding media,
golf club faces etc.

### Table 2.7-3
#### Main properties of our sintered TZP ceramics

| Type of ceramics (Powder source producer) | Bulk density g·cm$^{-3}$ | Average grain size $\mu$m | Bending strength MPa | Fracture toughness MPa·m$^{\frac{1}{2}}$ |
|---|---|---|---|---|
| Ce-TZP | 6.1-6.2 | 0.5-1.5 | 500-1000 | 12-17 |
| Ce-TZP (TOSOH production) | 6.2 | - | 500 | 20 |
| 3Y20A-TZP (TOSOH powder) | 5.5 | 0.3-0.5 | 1000-1150 | 9-10 |
| Ce-TZP-Al$_2$O$_3$ (composites) | 6.0 | 0.3-0.5 | 600-800 | 8-13 |

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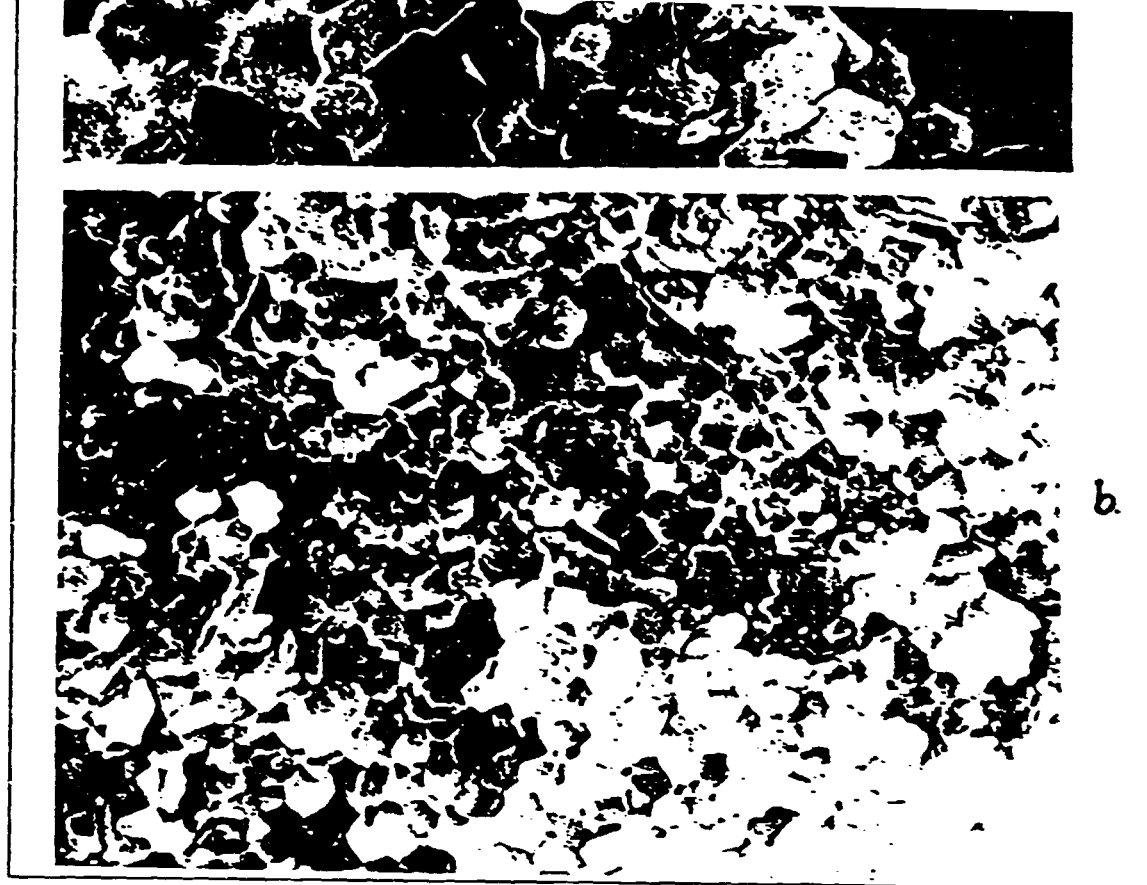
Figure 2.7-5
Microstructure (SEM images) of
a.) 12Ce-TZP and b.) 12Ce-TZP + 5 % $Al_2O_3$ ceramics sintered at 1450 $^{\circ}$C

# 2.9 VANADIUM PENTOXIDE PRODUCTION

T. Szalai

The production technologies for vanadium pentoxide particularly concerning the possibilities of recovery of vanadium from bauxite, is the most important indigenous source of vanadium. Vanadium does not occur in elementary state in nature. However, it represents one of the most current elements. Vanadium constitutes 0.015-0.016 % of the earth's crust indicating that it exceeds the amount of e.g. copper, nickel, zinc, lead or tin.

Despite its wide-spread occurrence, few areas comprise real vanadium ores only. Characteristically vanadium ore deposits are not widely scattered, however, they can be found in great quantities in some places. Apart from vanadium ores, the metal occurs also in other ores e.g. iron ores, uranium ore, chromium ore, lead ore and it can be recovered as by-product when processing it. The bulk of world vanadium production is linked up with the production of uranium and iron. In the United States of America vanadium figures as the by-product of the uranium industry. In the Soviet Union an iron ore comprising 0.1 % of vanadium represents the source of vanadium production enabling the formation of slag with 10 - 12 % of $V_2O_5$. In addition to the foregoing vanadium may also be found in certain sorts of carbon and crude oil. Their combustion residues may thus represent a potential source of vanadium. Though bauxite possesses less importance as a source of vanadium, however, it represents the sole notable vanadium carrier in Hungary.

## 2.9.1 Bauxite as the source of vanadium

Figure 2.7-6
X-ray diffraction patterns of
a.) 12Ce-TZP and b.) 12Ce-TZP + 10 % Al₂O₃ ceramics
(reference line: baddeleyte)

Figure 2.7-6
X-ray diffraction patterns of
a.) 12Ce-TZP and b.) 12Ce-TZP + 10 % $Al_2O_3$ ceramics
(reference line: baddeleyte)
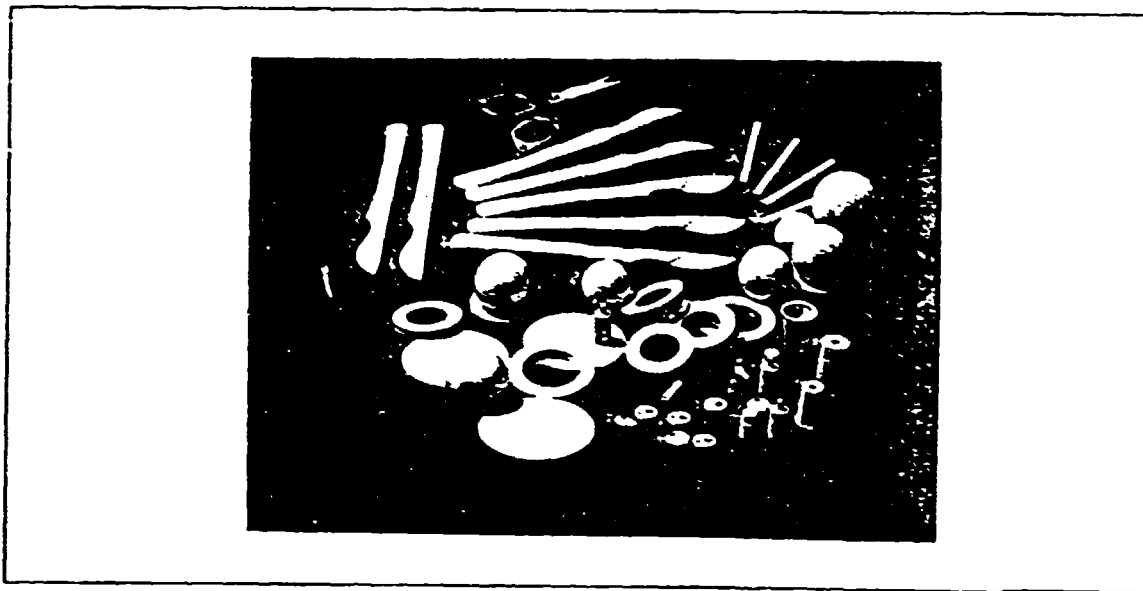


Figure 2.7-7
CID-ed sintered or injection molded-sintered Ce-TZP-$Al_2O_3$ ceramics (pilot
scale production)

quality, by the temperature and pressure of digestion, the
concentration and impurity of digestion liquor, the charging of
various additives during digestion and the treatment of bauxite
prior to digestion, too. Publications dealing with the solubility
of vanadium content of bauxites in caustic liquors  agree all,
that only a part -  about 30 - 40 %  - of the vanadium content of
bauxites dissolves in the digestion liquor [1].

In the course of digestion of bauxite vanadium gets dissolved and
is present in the digestion liquor in the form of sodium
orthovanadate ($Na_3VO_4$) and gets enriched corresponding to its
equilibrium solubility [2, 3].

Further 60 - 70 % of $V_2O_5$-content of bauxites is disposed off
along with red mud to the red mud storage area. Owing to lack of
economic recovery method this amount of vanadium content cannot
be made use of.

Caustic soluble accompanying elements e.g. phosphorus, fluorine,
arsenic also dissolve during digestion and get enriched in the
process liquor circuit.

## 2.9.2 Recovery of vanadium from bauxites

Using Bayer-type alumina process technology about 60 - 70 % of
vanadium content dissolved from bauxite can be recovered in the
form of vanadium crystals or vanadium salt.

Necessity of vanadium separation is motivated partly by the
demand for the recovery of a vanadium bearing basic material,
partly by the condition that vanadium and the above impurities
get enriched in alumina causing deterioration of quality.
Moreover, their spontaneous precipitation from the process liquor
circuit could result in operating troubles.

There are various methods for the recovery of vanadium crystals

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# 2.8 PLASMA MATERIALS FOR CERAMICS

P. Lukács, E. Juhász

## 2.8.1 Plasma state and types of plasmas

The investigation of plasma state has continued to attract the interest of ever increasing numbers of scientists and technologists and solid evidence of commercial application for chemical and metallurgical processes is now available. Interest in plasma technologies has grown immensely during the last two decades. This is mainly due to their wide application in the production of ultrafine high hardness and high-melting temperature carbide, nitride and oxide powders that are synthesized in thermal plasma reactions.

Plasma processing makes use of the plasma state, which is frequently referred to as fourth material state , because more than 99% of the universe inside of human conception is in the plasma state.

### 2.8.1.1 Some behaviours of the plasma state

Plasma can be characterized like a diamagnetic material. The most important behaviour of the plasma, making the big difference to the usual gas state, is the influence of the outside electric and magnetic fields on the elastic plasma medium.

From the point of view magnetical hydrodynamics plasma is a compact medium, in which there is a possibility for formation of current flow. The interaction of these current and the magnetic field give that electrodynamic power, which equibalance the gas dynamics pressure.

Figure 2.8-1 shows the influence of an outside magnetic field on the plasma torch.

The plasma shows a quasi-neutrality outside, whenever there are free electric charges in the plasma: negative and positive charges compensate each other.

In case of a dense medium it is very important that the linear size of field should be much bigger, than the Debye radius of the screening (see Figure 2.8-2.)
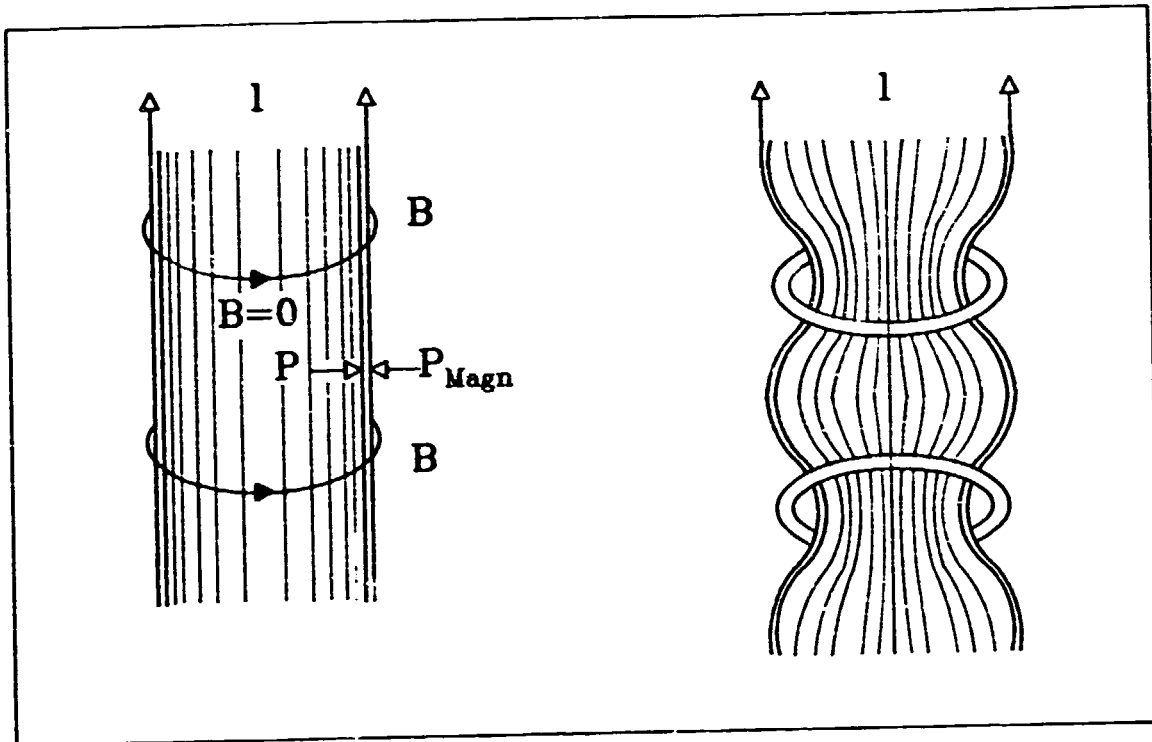
Figure 2.8-1
The behaviour of the plasma torch
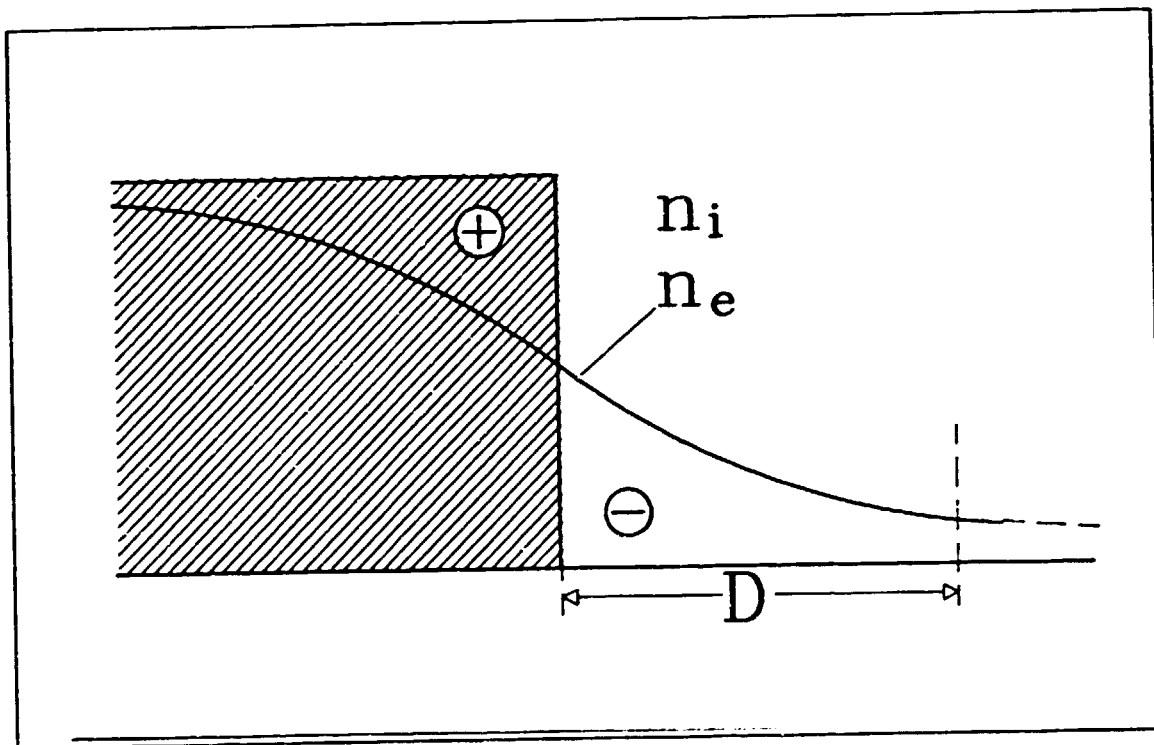


Figure 2.8-2
Debye radius of screening

--------------------------------------------------------------------------

The above characteristics of a plasma could be used successfully for technological cases.

To generate a plasma state one can use the thermal heating. No solids or liquids exist above 5000°K (at 1 atm pressure) and above 10000°K no molecules and very few atoms exist, since they become ionized at these temperatures. (Figure 2.8-3).
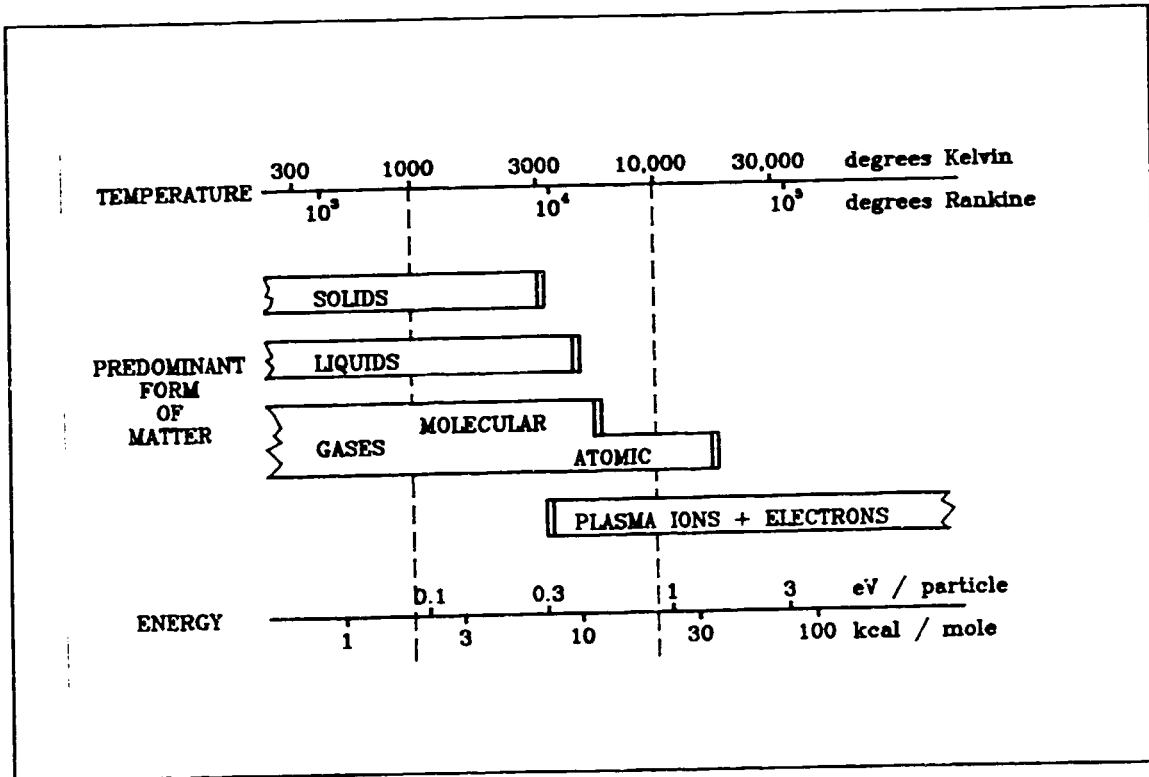


**Figure 2.8-3**
**View of the behaviour of ions of matter at high temperatures [1]**

In general, a plasma consists of a mixture of electrons, ions and neutral species.

Plasma chemistry utilizes the high temperature and high energies produced in plasmas. The heat content of monoatomic and diatomic gases as a function of temperature at 1 atm can be seen Figure 2.8-4 [1].

Although there are free electric charges in a plasma, negative and positive charges compensate each other, i.e. the overall a plasma is electrically neutral.

Plasmas may be generated by passing an electric current through a gas. The passage of an electrical current through the electrode gap leads to an array of phenomena known as gaseous discharges. Such gaseous discharges are the most common, but not the only means for producing plasmas. For certain applications plasmas are produced by electrodless high frequency or capacity discharges. Finally, plasmas may also be produced by heating gases (vapours)

in a high temperature furnace.
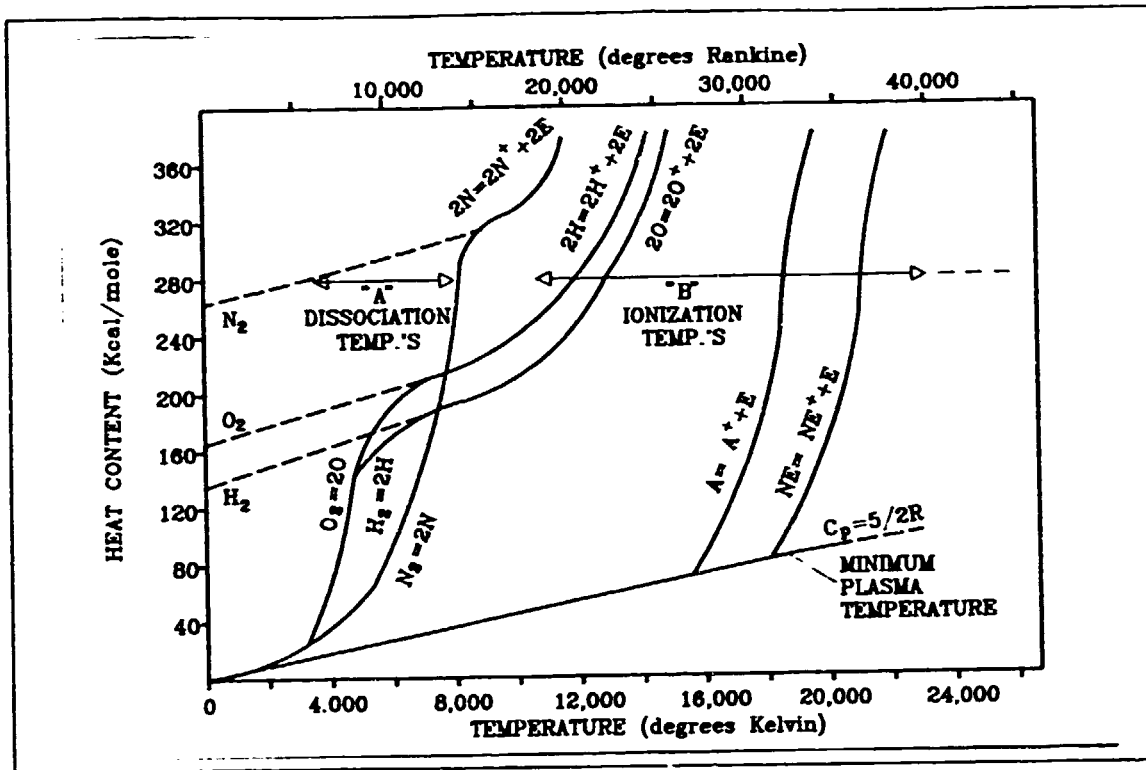


**Figure 2.8-4**
**Heat content of monoatomic and diatomic gases**

## 2.8.1.2 Types of plasmas produced by electrical discharges

Plasmas produced by electrical discharges could be divided into
two types:

- "Hot equilibrium thermal plasmas", which are characterized by
  an approximate equality between heavy particle and electron
  temperature. The thermodynamic state of the plasmas approaches
  equilibrium or, more precisely, local thermodynamic equilibrium
  (LTE). LTE comprises not only kinetic equilibrium ($T_e = T_h$;
  $T_e$ = electron, $T_h$ = heavy particle temperature) but also
  chemical equilibrium, i.e, particle concentrations in a LTE
  plasma are only a function of the temperature.
  Typical examples of thermal plasmas are those produced in high
  intensity arc and plasma torches.

- "Non - equilibrium cold plasmas". In contrast to the thermal
  plasmas coldness are characterized by high discharge
  temperatures and rather low temperature of the heavy particles.
  ($T_e \gg T_h$). Plasmas, produced in various types of glow
  discharges and in corona discharges are typical examples of
  such non-equilibrium plasmas.

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Thermal as well as non-equilibrium plasmas cover a wide range of temperatures and electron densities.

For practical uses there are two other important features of plasmas.

- thermodynamically

$$\triangle G = \triangle H - T*\triangle S = - RT \ln(K_p) \text{ and } \ln(K_p) = f(1/T) \tag{1}$$

In this case $\triangle H = f(T)$ and $\triangle S = f(T)$.

All these mean that at high temperatures and p=constant pressures the dissociation and decomposition predetermine the chemical reactions.

- kinetically the reaction velocity constant

$$K_j = K_o \exp (-E/kT) \tag{2}$$

because of the fact $E_{act} << kT$ can be expressed for a gas phase reaction

$$A_i + B_j ---> C_K + D_l \tag{3}$$

like

$$K_j = \int_{\vec{v_A}} \int_{\vec{v_B}} \sigma(ij, v_{AB})*(v_{AB})*f_{Ai}(v_{Ai})*f_{Bj}(v_{Bj})*dv_{Ai}*dv_{Bj} \tag{4}$$

where $f(ij, v_{AB})$ = the efficient reaction cross section
$v$ = velocity of the reactive particles
$f(v)$ = particle distribution as a function of velocity

Finally

$$K <> f(T) \tag{5}$$

All these mean, that we can use the high temperature rate of the plasma as well, as the efficiency of the plasma state separately the temperature.

## 2.8.2 Apparatus

ALUTERV-FKI Ltd. has got a laboratory for complex plasma technologies, in which there are DC, RF, microwave, capacity plasma equipments.

Both direct current (DC) and radio frequency (RF) plasmas are commonly used for material synthesis.

Although the DC torch has been used successfully for many

applications in plasma synthesis, the problem of material
contamination by the electrodes has limited the use of such
systems for synthesis of ultrapure materials. The conversion
efficiency is low as a consequence of high velocities and short
residence times characteristic of the DC plasma.

These problems have led to the development of the inductively
coupled RF plasma. Radio-frequency plasmas have a number of
important applications including deposition of ceramics,
synthesis of high purity and fine ceramic powders.

Capacity plasma has the same advantages, as non-equilibrium
plasma.

## 2.8.3 Non metallurgical, special aluminas

According to the forecast the consumption of the special aluminas
is expected to increase during the next years. Market trends for
non - metallurgical aluminas in the period 1988-2000 show, that
ceramic materials ranked fifth place. It means, that advanced
ceramics are already a major market for the high-purity, fine
grade alumina.

World market price of special aluminas exceeds that of
metallurgical alumina, in some cases it is two times higher.

### 2.8.3.1 Production of non-metallurgical alumina

Various processes have been proposed for the production of high
purity alumina. A lot of them manufactures aluminas by the after
treatment of raw materials produced by the Bayer process.
Aluminas prepared by the Bayer-process all contain alkali ions,
which can not easily be removed to concentration, which would not
affect the quality of sintered alumina products.

For the production of good quality ceramics high purity,
ultrafine, granulated, α-alumina is needed with determined grain
size.

Since traditional manufacturing processes can hardly keep pace
with the rapidly increasing qualitative requirements, an
intensive research and development work is in progress to satisfy
them.

### 2.8.3.2 Production of non-metallurgical alumina by plasma technique.

For the preparation of ceramic materials such as alumina, plasma
technique represents a very important field. Alumina based
ceramic powders have already been successfully synthesized in
thermal plasma reactors.

Different types of plasma equipment were developed and technologies for the production of alumina were evaluated in the Plasma Laboratory of ALUTERV-FKI Ltd. as well.

One of the new methods could be the production of special alumina by thermal oxidation of anhydrous aluminium chloride in plasma.

The basic reaction of the process is:

$$2AlCl_3 + 1.5\ O_2 = Al_2O_3 + 3Cl_2 \qquad \{6\}$$
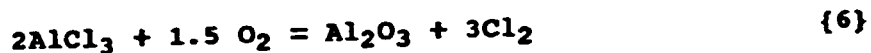
The main process steps of the thermal oxidation in plasma equipment are:

1. Continuous feeding of aluminium chloride
2. Oxidising decomposition of the aluminium chloride
3. Cooling of the alumina containing gas and separation of the product from the exhaust gas.

Tests were carried out in a DC plasma and in a RF plasma equipment as well.

1. Sketch drawing of the DC plasma equipment and the attached reactor is given in Figure 2.8-5. In this case aluminium chloride were introduced in vapour state at 350 °C into the reactor. Direct current plasma was generated in the presence of tungsten cathode and copper anode. The plasma forming gas was the air.
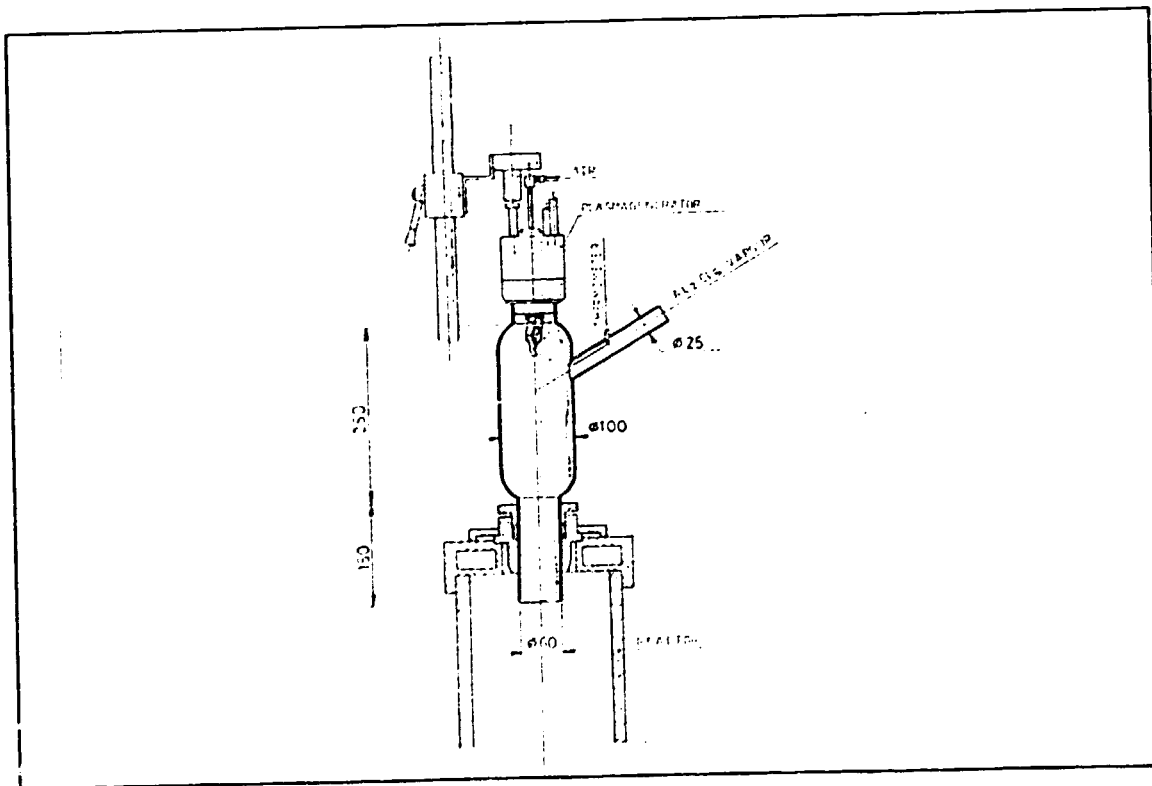


Figure 2.8-5
Sketch drawing of the DC plasma equipment and the attached reactor

The operational parameters and the feature of alumina synthesized
in DC plasma are given in Table 2.8-1.

Table 2.8-1

**The operational parameters and the feature of alumina synthesized in DC plasma**

| | | |
|---|---|---|
| Nominal power | 20 | kW |
| Arc current | 100 | A |
| Arc voltage | 135 | V |
| Plasma power | 13.5 | kW |
| Plasma forming gas | 5.5 | $Nm^3$/h air |
| Specific surface area | 10.9 | $m^2$/g |
| Phase analysis | | |
| teta- $Al_2O_3$ | 90 | % |
| $\alpha$- $Al_2O_3$ | 10 | % |

Tests were carried out in RF-plasma equipment as well. The
flowsheet of this process is given in Figure 2.8-6. A quartz tube
of 100 mm inner diameter was used as reaction chamber. The
reaction zone was developed by the use of RF induction plasma
(Figure 2.8-7). Aluminium chloride of homogenous, narrow grain
size distribution was introduced in solid state with air stream
into the reaction area. The place of material feeding, the amount
of plasma forming gas and the plasma power were changed during
the process.
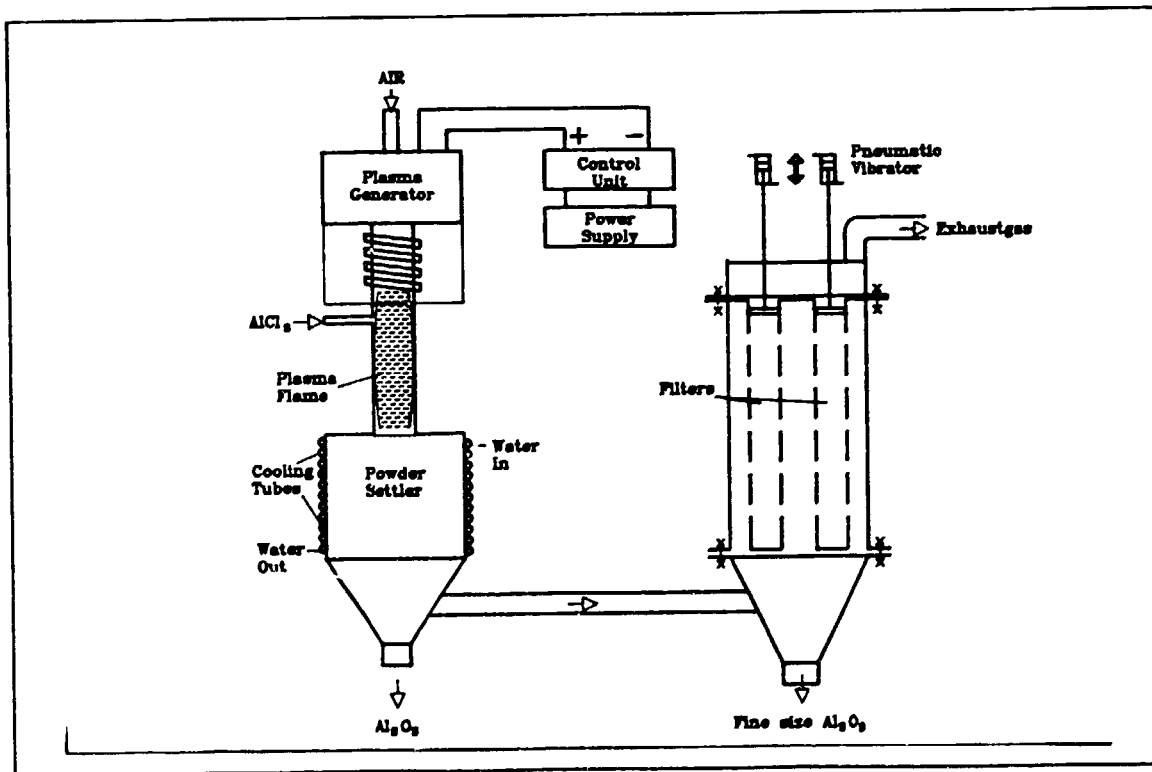


Figure 2.8-6
Flowsheet of RF-plasma equipment

Exhaust gas mixture comprising the fine product was conducted through a cooling/quenching unit to a bag filter.



**Figure 2.8-7**
**The reaction zone of RF induction plasma**

Operational parameters of the technology and the features of alumina products are given in Table 2.8-2.

**Table 2.8-2**
**Operational parameters and the feature of the alumina produced in RF plasma**

| | | |
|---|---|---|
| Nominal power | 65 | kW |
| Plasma power | 38.2 | kW |
| Plasma forming gas | 16.0 | $Nm^3$/h air |
| Carrier gas | 1.5 | $Nm^3$/h $O_2$ |
| Carrier gas | 1.5 | $Nm^3$/h air |
| Specific surface area | 30 | $m^2$/g |
| Phase analysis | | |
| delta+teta - $Al_2O_3$ | 30 | % |
| $\alpha$- $Al_2O_3$ | 70 | % |

SEM images of $Al_2O_3$ powder are given in Figures 2.8-8 and 2.8-9.
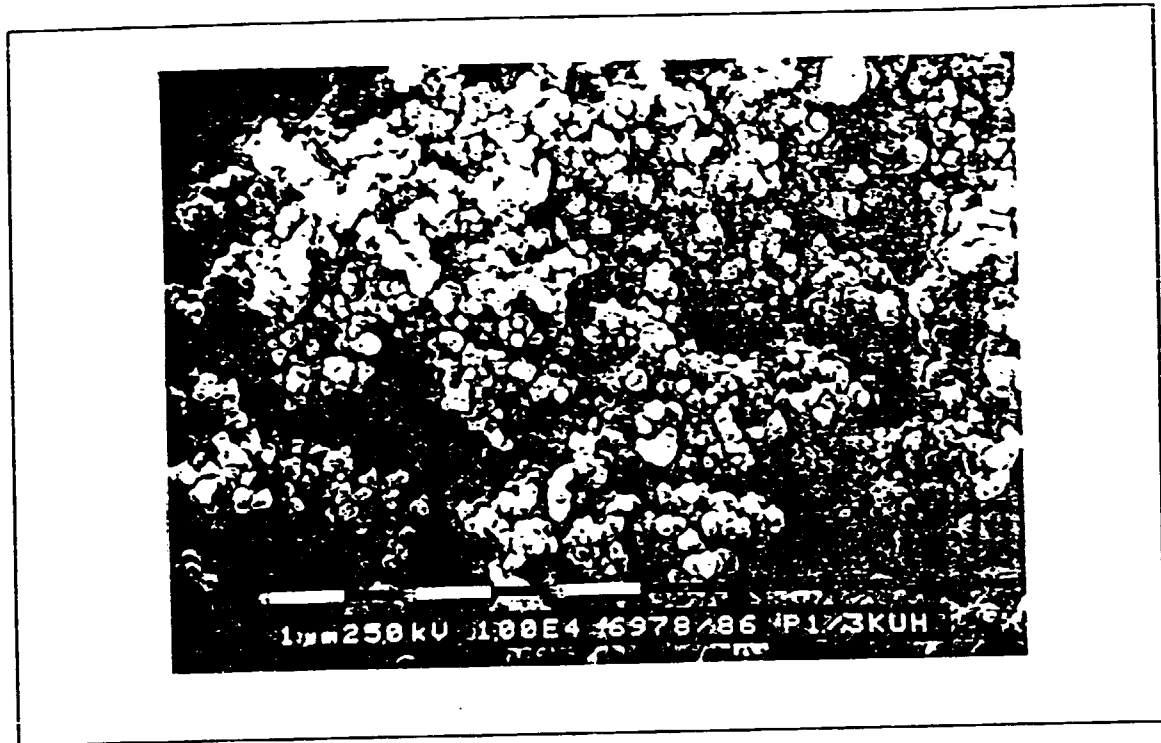
Figure 2.8-8
SEM images of $Al_2O_3$ powder
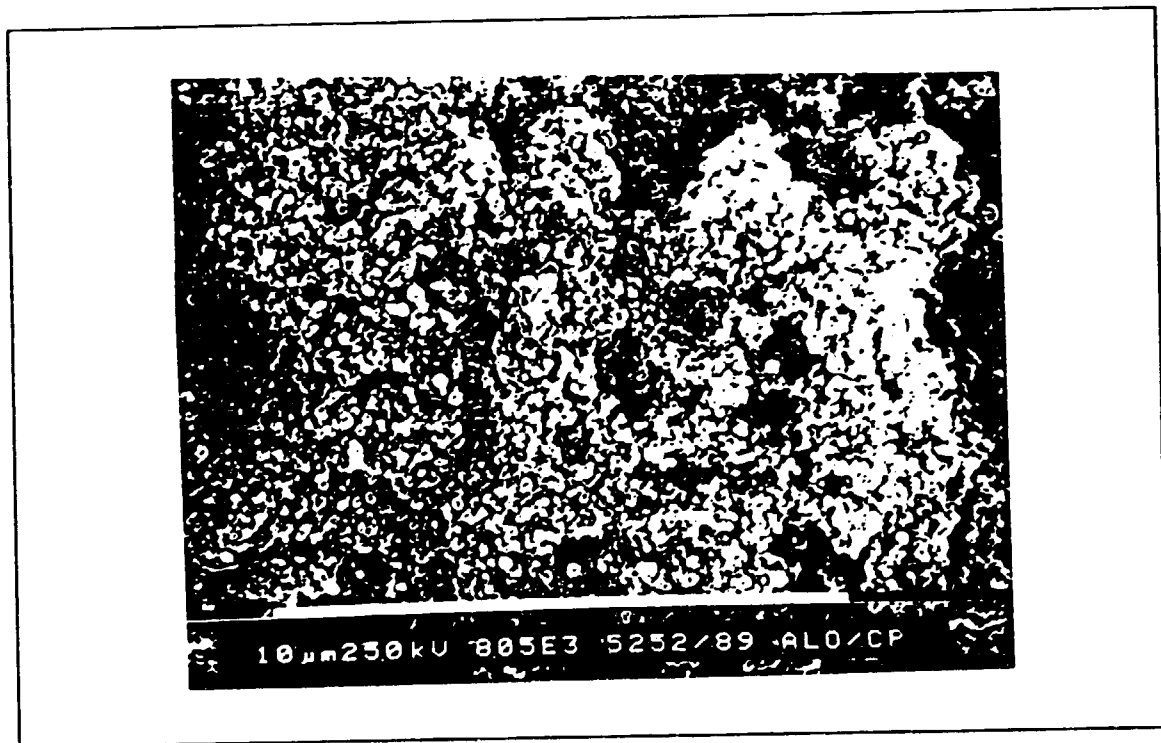


Figure 2.8-9
SEM images of $Al_2O_3$ powder

recovered thereof. Alumina hydrate wash waters enriched to the
extent of 1-2 gpl of $V_2O_5$ are used to wash the evaporators.
During washing procedure the solution concentrates for caustic
soda, moreover sodium fluoride deposits from the last stages of
the evaporator bodies get also dissolved. The latter highly
reduces the solubility of vanadium. On cooling wash water to 40
°C crystals comprising more than 10 % of vanadium content
precipitate and can be separated by means of a filter or a
centrifuge [6].

Technologies in practice in indigenous alumina plants for the
separation of vanadium salt set out from spent liquor or strong
liquor. Common basic principle lies in cooling liquors and
separating crystals after adequate retention time. The difference
may be particular plant conditions, cooling methods determined by
the equipment available and the use of separating machines [7].

## 2.9.3 Processing of vanadium salt

From among vanadium raw materials Hungary possesses the vanadium
salt raw material separated from the aluminate liquor of the
alumina production only. Processes treating vanadium sludges and
salts from an alumina plant may be fairly diverse depending on
the composition of starting raw material, the purification
procedures of the vanadate solutions and the quality stipulations
imposed upon the final product.

Generally, the majority of processes producing vanadium pentoxide
is characterised by the following particular operational stages:

- beneficiation
- dissolution of crystals
- purification of vanadate solution
- separation of vanadium
- producing vanadium final product.

## 2.9.4 Beneficiation

Beneficiation is required when vanadium pentoxide content of
vanadium salt separated from aluminate liquor of the alumina
production is as low as 1 - 5 %. In this case the sludge is
treated with sufficient amount of hot water to dissolve its
vanadium content. Insoluble fraction is removed by filtration.
Alkaline filtrate is cooled allowing crystallization of a
vanadium salt more riche in vanadium. Vanadium content of salt
compounds obtained by the methods adopted for the separation of
vanadium salt in our alumina plants comes to 8 - 18 % thus no
particular beneficiation is required.

## 2.9.5 Dissolution of crystals

All the constituents comprised in vanadium salt are present in the form of sodium salt. On dissolving with water the solution exhibits strong alkaline reaction.

Beside sodium vanadate ($Na_2VO_4$) as main component,

- sodium phosphate ($Na_3PO_4$),
- sodium arsenate ($Na_3AsO_4$),
- sodium fluoride (NaF),
- sodium carbonate ($Na_2CO_3$),
- and sodium aluminate ($NaAlO_2$)

may be found in the aqueous solution of the vanadium salt. Beside monomeric molecules there are also polymeric molecules as a function of the pH-value in the aqueous solution of vanadates.

## 2.9.6 Purification of vanadate solutions

From the point of view of quality of vanadium compounds produced as final product the degree of purity of sodium vanadate solutions is of decisive importance. Removal of impurities (phosphorus, arsenic, fluorine, aluminium) present in vanadium salt represents the most important phase of production. Several processes have been developed and patent specifications elaborated for the production of vanadium compounds from vanadium salt which mainly differed from each other by the method of achieving proper quality of the final product only. Consequently, the vanadium producing processes and technologies proceeding from vanadium salt as the basic material can be grouped as follows:

### 2.9.6.1 Processes based on the removal of impurities

Further possible subdivision is:

> Technologies adopting crystallization
> Methods based on fixing impurities

### Removal of impurities by crystallization

According to the patent specification of E. Bogárdi et al. [8], after the dissolution of vanadium salt with hot water the phenolphtalein alkalinity of solution is reduced by 10-40 % (pH value reduces by a few decimals only), then the solution is cooled to 20 °C to precipitate large amounts of crystals. The mass virtually lacks of sodium fluorovanadate. Resulting crystals represent a mixture of sodium fluorophosphate and sodium fluoroarsenate. In this way one can get rid of the bulk of phosphorus, fluorine and arsenic content of the sodium vanadate solution. About 80-85 % of phosphorus content and about

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90-95 % of arsenic content of liquor can be crystallized by this
method.

According to a patent specification of Montecatini [9], partial
removal of impurities from sodium vanadate solution can be
achieved when the alkaline solution obtained by dissolving
vanadium salt with hot water is treated with sulphuric acid to
set the pH-value to a slightly alkaline range. On cooling this
slightly alkaline solution considerable portion of the phosphorus
content separates in the form of sodium hydrogen phosphate, large
part of the arsenic content in the form of sodium hydrogen
arsenate and the fluorine content in the form of cryolite having
been combined with aluminium present in the liquor. From vanadate
solution partially purified vanadium may be obtained either in
the form of ammonium metavanadate or get precipitated in the form
of vanadic acid by further acidifying the solution with sulphuric
acid .

## Methods based on fixing impurities

These methods are characteristic of the condition that the
impurities present in sodium vanadate solution are generally
removed as calcium salts in the form of their insoluble
compounds. According to an Italian process, aqueous solution of
vanadium salt is treated with lime milk. Essence of the process
lies in the condition that one part of vanadium salt is dissolved
in two and a half part of water and 3.5 moles of calcium
hydroxide is added for every mole of $P_2O_5$-content in excess of
the amount of lime milk necessary for the causticization of
sodium carbonate content of the vanadium crystals. The lime milk
suspension is heated up and gets filtered. The precipitate
comprises the impurities while the filtrate is cooled causing
sodium orthovanadate to crystallize.  In the course of further
processing vanadium pentoxid is formed. The advantage of the
process is, that after crystallization the final liquor can be
returned to the process liquor circuit of the alumina production
owing to its purity and comparatively high caustic soda
concentration while the lime precipitate comprising mainly
dicalcium phosphate may be utilized as fertilizer component.
However, there is a disadvantage, too since beside calcium
phosphate hard to dissolve calcium vanadate also forms causing
certain losses as to the efficiency of vanadium recovery. In a
process vanadium losses can be reduced by acidifying the highly
alkaline solution obtained by dissolving vanadium salt with
water. Then the solution is treated with calcium oxide at room
temperature in order to prevent the formation of calcium
vanadate.

There is a process according to which the precipitation of
phosphorus with calcium hydroxide takes place under pressure in
the digester. In this procedure the formation of calcium
phosphate increases upon the increase of pressure while the
formation of calcium vanadate decreases. Apart from lime milk and
burnt lime, calcium sulphate represents one of the best known and

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current auxiliary material adopted for fixing impurities of the sodium vanadate solution [10].

In order to purify sodium vanadate solution e.g. fine-grained compact alabaster gypsum is added. On heating up the solution phosphorus precipitates in the form of calcium phosphate and can easily be filtered. The ground compact alabaster gypsum has been later on substituted by the precipitated gypsum obtained as by-product of tri-sodium phosphate production, however, other sorts of waste gypsum may also be used for dephosphorization.

## 2.9.6.2 Processes based on fixing vanadium

Within the framework of processes based upon fixing vanadium, two groups can be distinguished:

- calciferous processes
- processes adopting ammonium salts

## Calciferous processes

To the alkaline solution obtained after the dissolution of vanadium salt with hot water burnt lime or lime milk is added fairly in excess. Lime precipitate obtained comprises insoluble calcium salts of impurities and vanadium in the form of calcium vanadate. The filtrate can be returned to the process liquor circuit of the alumina production due to its $Na_2O$-content. The calciferous or calcium vanadate bearing precipitate is decomposed by sulphuric acid in the course of which major part of vanadium dissolves, together with a part of the impurities, too . It is a disadvantage of the process that the final product is contaminated and the value of percentual recovery for $V_2O_5$ is low.

## Processes adopting ammonium salts

Root of these processes is that in the sodium vanadate solutions obtained by leaching the vanadium salt, exhibiting a $V_2O_5$ to $P_2O_5$ ratio or roughly 1 : 1, vanadium is fixed with ammonium salt /mostly $NH_4Cl$, $(NH_4)_2SO_4$, $NH_4NO_3$/, namely by the use of multiple quantity of that of the stoichiometric required to bind vanadium. In this way ammonium metavanadate is produced  and after its calcination high purity $V_2O_5$ is obtained [11].

## 2.9.6.3 Processes adopting ion exchange

Recovery of vanadium content of the vanadium salt by ion exchange can be performed by two methods:

- by means of liquid ion exchange media in so-                    calle
  d extraction processes
- by means of ion exchange synthetic resins.

**Processes adopting liquid ion exchangers**

The extracting agents of both liquid anion exchange and liquid cation exchange are adopted by the processes performed by the help of the liquid-liquid extraction. The liquid cation exchanges are alkyl-phosphoric acid derivatives (e.g. diethyl-hexyl-phosphoric acid), however, the anion exchanges are various primary, secondary and tertiary amines. Recovery of vanadium by extraction can take place as follows: according to the following. the amine present in an inert organic solvent (petrol, Diesel fuel, kerosene) is mixed up with the vanadium bearing aqueous solution. Vanadium passes into the organic phase which is then separated from the aqueous part. After the reextraction with ammonium and ammonium salt, respectively, of the organic phase ammonium metavanadate is produced [12, 13].

**Processes adopting ion exchange synthetic resins**

Owing to various kinds of vanadium compounds present in the aqueous solution, similarly with extraction, both anion and cation exchanges can be used for the process of vanadium separation adopting ion exchange synthetic resins. Owing to special operating conditions and the use of expensive reagent plant-scale, processing of vanadium crystals could not be realised [14].

### 2.9.6.4 Electrochemical processes for the recovery of $V_2O_5$

Recovery of vanadium by electrolytic way means that the aqueous solution of the vanadium salt is electrolysed by the use of movable mercury cathode and caustic insoluble anode (e.g. iron, carbon, nickel). The terminal voltage comes to 6-8 V, current density of the anode 4-5 $A/dm^2$ and temperature of the electrolyte 70-80 °C.

In the course of electrolysis, 5-valent vanadium present in the alkaline vanadate solution reduces to 4-valent tetravanadate and precipitates as an alkaline electrolyte insoluble compound due to the impact of reducing hydrogen depositing with high overvoltage on the mercury cathode reducing hydrogen depositing with high overvoltage on the mercury cathode, .

## 2.9.7 Short review of the technology for $V_2O_5$-production in Magyaróvár (MOTIM)

From the primary vanadium carriers Hungary possesses only bauxite ore which can be regarded as a raw material suitable for plant-scale production of vanadium salt.

In the course of digestion with caustic soda under pressure according to the Bayer-type alumina production technology, apart

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from alumina representing the bulk of bauxite, trace elements
(vanadium, phosphorus, fluorine, arsenic, etc) also dissolve to
form vanadium compounds.

Methods for processing vanadium salt have been outlined with
special regard to the technology established in Mosonmagyaróvár
in 1951 for the production of laminar vanadium pentoxide and
which has been operating ever since.

For the production of vanadium pentoxide vanadium salt is
received from the alumina plants (Ajka and Mosonmagyaróvár).
Average composition of vanadium salt separated in indigenous
alumina plants operating according to the Bayer-technology is
given in Table 2.9-1.

Table 2.9-1.
Composition of vanadium salt

| | |
|---|---|
| Adhesive moisture | 30 - 50 % |
| $V_2O_5$ | 5 - 22 % |
| $P_2O_5$ | 3 - 15 % |
| As | 1 - 5 % |
| F | 5 - 15 % |
| $Al_2O_3$ total | 5 - 20 % |
| $Na_2O$ caust | 1 - 15 % |
| $Na_2O$ total | 40 - 55 % |

Vanadium salt which is fairly water soluble is dissolved in a
vanadium bearing solution obtained in the course of
recrystallization of phosphorus-fluorine-arsenic compound
crystals. Alkalinity of the solution is slightly weakened by the
use of concentrated sulphuric acid. The solution treated with
sulphuric acid is cooled in order to remove P-, F- and As-
content. The crystalline mass separating on cooling comprises
about 90-95 % of P- and As-content of the original solution and
about 55-65 % of the fluorine content in the form of sodium
fluoroarsenate and sodium- fluoro-phosphate. In addition to the
impurities, the PFAs-crystal comprises also 1.5 - 3.5 % of $V_2O_5$.

For the separation of salt and vanadate solution an uniplanar
vibration sieve is used. Prior to the separation of vanadium the
prepurified vanadate solution should entirely be purified from
the impurities. The P- and F-content of sodium vanadate solution
is precipitated by adding further amounts of sulphuric acid and
calcium salt. Separation of precipitated impurities and the
liquid phase is done by means of frame filter presses.

Sulphuric acid and ammonium salt is added to the pure sodium
vanadate solution. As a result polyvanadate of the formula of
$/R_{1,2,3}/_6$ $V_6O_{18}$ precipitates wherein R cation may be sodium,
hydrogen or ammonium. Dewatering and transferring into laminated
structure, of polyvanadate precipitated from the sodium vanadate
solution takes place in oil-fired furnaces at temperatures of
600-700 °C. The chemical characteristics of the product are
summarized in the Table 2.9-2.

Table 2.9-2
Trade quality of the laminar vanadium pentoxide

|  |  | First | Content in %<br>Second<br>quality | Third |
|---|---|---|---|---|
| $V_2O_5$ | min. | 98.0 | 95.0 | 92.0 |
| $SiO_2$ | max. | 0.30 | 0.40 | 0.40 |
| $SO_3$ | max. | 0.05 | 0.10 | 0.10 |
| $P_2O_5$ | max. | 0.03 | 0.10 | 0.10 |
| $Fe_2O_3$ | max. | 0.30 | 0.30 | 1.00 |
| As | max. | 0.02 | 0.05 | 0.08 |
| $Na_2O$ | max. | 2.00 | 4.00 | 7.50 |
| Adh.moist. | max. | 0.50 | 0.50 | 0.50 |

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# 2.10 GALLIUM RECOVERY FROM BAYER CYCLE

I. Somogyi, K. Fodor, M. Földvári, I. Somosi, J. Vitéz

## 2.10.1 General review of gallium

Gallium as the heavier atom weight homologous of aluminium was predicted by the Russian chemist Mendeleev on the bases of his periodic system in 1895. It was named eca-aluminium.

This homologous of aluminium, gallium was discovered by Lecoq de Boisbaudran in 1875 and he produced it shortly and named it gallium after the ancient Latin name of France (Gallia).

Gallium can be found in the third group of Mendeleev periodic system between aluminium and indium. Gallium is a silver-white metal, its melting point is 29.78 $^{O}$C and boiling point is 2403 $^{O}$C. The melted gallium density is 6.095 (at 29.8 $^{O}$C), the solid gallium density is 5.904 g/cm (at 29.6 $^{O}$C), so its volume increases during freezing. It has a rhombohedral crystal form. The chemical properties of gallium are similar to aluminium, nevertheless the two metals show some substantial differences. One of the best solvent of gallium is the aqua regia. In solutions of alkalis the gallium dissolves with the evolution of hydrogen forming alkali-gallates. The reaction rate of gallium with acids and alkalis decreases considerably if the purity of the metal exceeds 99.999 %.

In nature no individual mineral with gallium as a major constituent is known, however it is a fairly widely distributed metal. The average gallium content of the earth crust is 15 g/t. Germanit as mineral with the richest gallium content can be found in South-West Africa. Germanit contains 5 to 9 % germanium and 0.5 to 2.0 % gallium. Gallium can be found in all of the aluminium minerals so bauxite has 25-50 g/t gallium-content, too.

Gallium forms alloy with the most of metals between its melting point and 600 $^{O}$C and these alloys differ strongly from the basic metals in properties even if their gallium content is low.

Nowadays the developed industry especially the semi-conductor industry cannot stand without gallium and its cor ...

## 2.10.2 Development of gallium production

Since individual gallium mineral is not available, such technological cycles can be used for the production of gallium where it is gradually enriching in the row material. For instance

the circulating aluminate liquor of alumina industry. The gallium content of bauxite dissolves during digestion of Bayer cycle and it achieves an equilibrium concentration in sodium aluminate solution depending on the technological parameters.

Recovery of gallium from aluminate liquor was realised the first time by the French Pechiney Company the was done and a block of gallium was shown at EXPO in 1937 [1].

Important progress began in the industrial production of gallium in 1956 when P. de la Breteque published his research results. In accordance to the process he developed can be obtained from aluminate liquor by electrolysis with mercury cathode [2].

In Hungary the HUNGALU ENGINEERING AND DEVELOPMENT CENTRE and the Chemical University of Veszprém were first engaged in industrial production of gallium. Using the process of HUNGALU ENGINEERING AND DEVELOPMENT CENTRE the gallium can be obtained from Bayer liquor, choosing the current density of the cathode and the temperature of the electrolyte to deposit as much metal sodium as 0.4 times amount of gallium so that there is a really amalgam cathode during the electrolysis. Decomposing the amalgam with water the gallium deposited by electrolysis forms sodium gallate solution and the metal gallium can be obtained on the solid cathode [3].

The process of the Chemical University of Veszprém is based upon a cell equipped with rotating iron cathode disks which are coated with amalgam. So the efficiency of a given cell is substantially increased and the amount of mercury and the basic area are reduced simultaneously. It has been found the gallium can not be deposited by electrolysis only also by reduction of the sodium amalgam, too [4].

Lately researches arrive to recover gallium from Bayer liquor by non-mercury cathode for environmental considerations and to protect health all over the world. Two main trends can be mentioned:

the cementation by aluminium and the extraction from alkaline solution. In alkaline agent gallium forms complexes with β-diketone type compounds (for example acetyl-acetone and its substituted by-products) which are brought to organic solvent phase (for example : iso-butanol

or its homologouses). Characteristic of this process is that the formation of the complex and the extraction are carried out at the same time so that the watered solution of alkali is treated with the mixture of the complex forming material and the solvent [6].

## 2.10.3 Process technologies

In the Alumina Plant of Ajka Aluminiumindustrial Co. Ltd. the

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technologies of amalgam cathode and cementation by aluminium are
used on the bases of Bayer cycle. In both technologies raw
material and its preparation are the same with differences in the
method and the equipments only.

## 2.10.3.1 The aluminate liquor as basic material

To determinate the capacity of a gallium plant situated next to a
certain alumina plant it is necessary to know the quantity of
obtainable gallium.

It is known that 60 to 70 % of the gallium content of the bauxite
dissolves during digestion and it concentrates in aluminate
liquor. In literature there were no data referring to the
equilibrium gallium concentration of forming-system in a given
alumina plant. So no estimation as to the quantity of obtainable
gallium was available.

According to our tests the equilibrium gallium concentration of
precipitated aluminate liquor can be described by the following
exponential function [7]:

$$C_E^{Ga} = \lim_{n \to \infty} a * \frac{q}{1 - q} \qquad \{1\}$$

where n : number of digestions cycles,
      a : Ga mg/dm$^3$ dissolving during a digestion cycle
recalculated to the $Na_2O$ concentration of precipitation,
      q : the rate of gallium concentration in aluminate liquor
after and before precipitation.

It can be stated that the function is true for all of Bayer type
alumina production using a given technology. Changing a step of
technology the equilibrium concentration of gallium in aluminate
liquor is raising by 10 to 20 %.

Having known the equilibrium concentration of gallium and the
data of gallium balance in cycle we can calculate the amount of
obtainable gallium.

The calculated quantity of gallium is a theoretical value that
considerably depends on the impurities of aluminate liquor,
especially on $V_2O_5$.

Vanadium content of bauxite also reaches an equilibrium
concentration in Bayer liquor. This value is not indifferent to
the amount of obtainable vanadium and the minimal concentration
of vanadium that can be achieved at recovery. The former one is
raw material for production of $V_2O_5$ and the latter one has an
effect on the capacity of gallium plant (Figure 2.10-1).
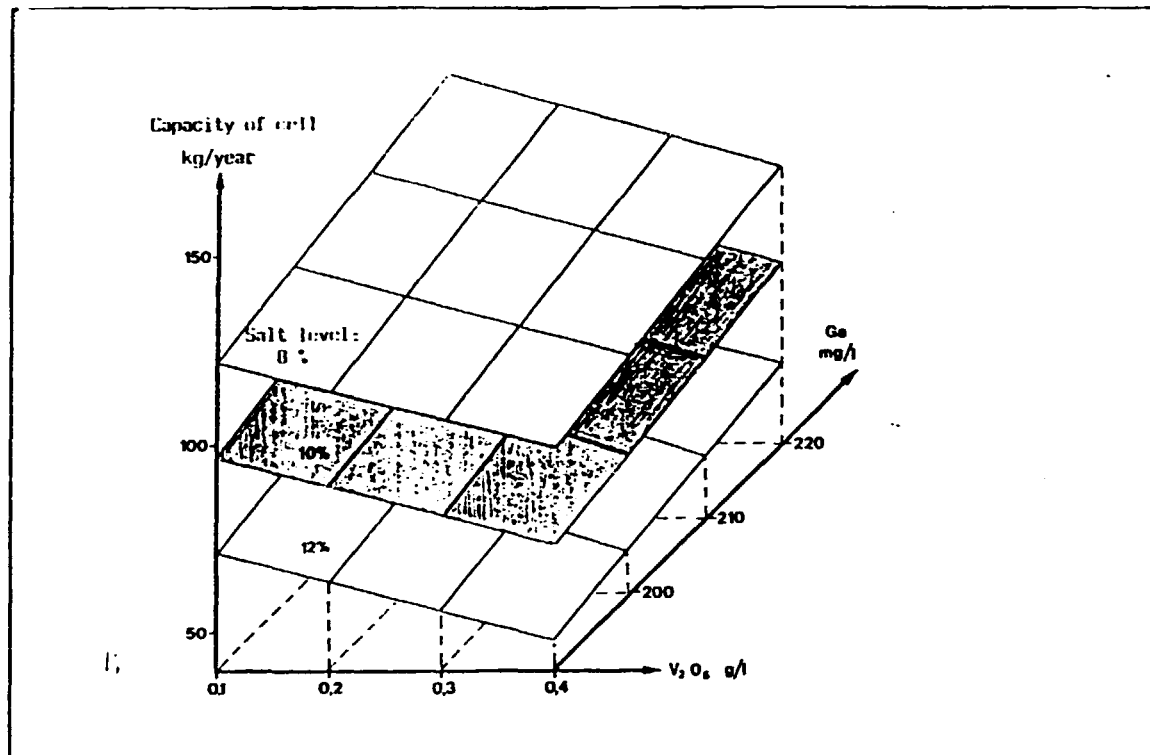
**Figure 2.10-1**
**Capacity of gallium cell in function of liquor concentration and salt level**

Recovery technologies of gallium require the $V_2O_5$ concentration to be less than 0.15 g/dm$^3$ in the aluminate liquor. To reach it the concentration of $V_2O_5$ should be increased up to 2 to 4 g/dm$^3$ by dissolving vanadium salt in boiling aluminate liquor. Before dissolving vanadium salt the aluminate liquor is oversaturated with carbonate by evaporation and/or by feeding of liquid sodium hydroxide. Under given conditions dissolving of vanadium salt is selective namely its carbonate content doesn't dissolve but its vanadium, phosphorus and fluoride content does. So the conditions of forming of vanadium-phosphorus-fluoride triple salt can be reached. Under these circumstances triple salt formed is easier to settle, filtrate and centrifuge.

Results are double, on the one hand the $V_2O_5$ content of precipitated V-salt is higher, on the other hand the V-content in the basic material of gallium production is lower than the critical level.


### 2.10.3.2 Amalgam cathode method

Using current, metallic sodium forms from sodium hydroxide solution and it produces amalgam with mercury. The electrode potential of the sodium amalgam is sufficient to reduce the gallium(III) ions to metal gallium and to deposit this gallium on the sodium amalgam. So the first step of deposition of gallium is the electrolysis with amalgam cathode method from sodium

aluminate solution having lowered vanadium and carbonate content. In the electrolytic cell the cathode is a lamella system coated with sodium amalgam. This system increases the surface of the cathode with more than one order (Figure 2.10-2.). The cells are in series connection and the sodium aluminate solution is parallel fed to each cells continuously. The sodium amalgam with the formed gallium is drained periodically in a closed system. The sodium amalgam can be decomposed with water in a stirred and indirect heated tank. In this case sodium as the most negative electrode potential metal forms and it is the solvent of gallium. So gallium content of the forming sodium gallate solution is about 100 times higher than it was in aluminate liquor.
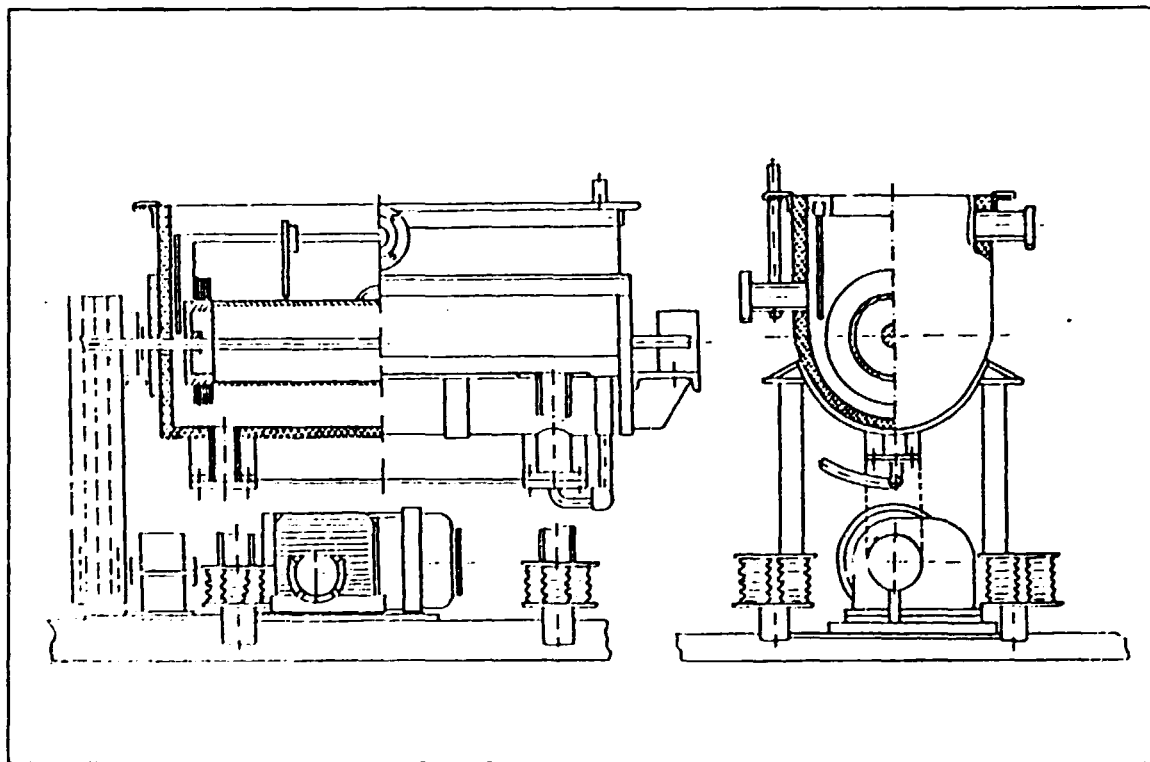


Figure 2.10-2
Electrolytic cell

After evaporation and filtration of sodium gallate solution the gallium content can be deposited by a repeated electrolysis but here a solid cathode or cementation by aluminium is used.


## 2.10.3.3 Aluminium cementation process

The gallium content of aluminate liquor can be obtained with cementation by aluminium. Gross process taking place (not considering secondary reactions ):

$$Al + [Ga(OH)_4]^- \longrightarrow Ga + [Al(OH)_4]^- \qquad \{2\}$$

Technological study of cementation requires to theoretical

analyse of gross process and the practical implications should be
taken into consideration, too. The following partial reactions
can be described, where the (Ga) marks the gallium bath.

$$Al + (Ga) \longrightarrow Al(Ga) \qquad \{3\}$$

$$Al(Ga) + 4*OH^- \longrightarrow (Ga) + [Al(OH)_4]^- + 3*e^- \qquad \{4\}$$

$$(Ga) + [Ga(OH)]^- + 3\ e^- \longleftrightarrow (Ga) + Ga + 4*OH^- \qquad \{5\}$$
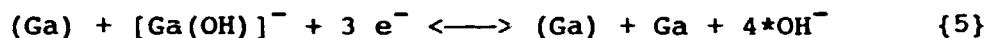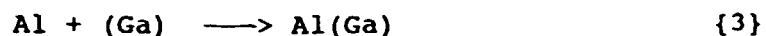
During cementation the sequence of these partial reactions is
fixed, reactions {3} and {4} being irreversible but reaction {5}
is reversible. In case when aluminium concentration is too low,
not only a reduction of the gallate ion may fail but also a
dissolution of the gallium bath may take place depending on the
value of the electrode potential [5]. Purified aluminate liquor
is loaded into a tank mounted stirrer which contains gallium bath
metal, too. This equipment is called cementator. To reach proper
aluminium concentration of bath metal, aluminium metal is fed
automatically. Electrode potential of forming gallam is
sufficient to cementate the gallium content of the aluminate
liquor and to precipitate on the metal bath. A part of
precipitated metal gallium increases the quantity of the metal
bath and the other part of it becomes metallic mud. This metallic
mud can be separated with filtration and can be dissolved in
sodium hydroxide solution. The gallium can be recovered from the
obtained sodium gallate solution with repeated cementation.

## 2.10.4 Purification of gallium

The purity of raw gallium obtained from sodium gallate solution
is only about 98 to 99 %.

Impurities - namely 1 to 2 % zinc, several tenth % aluminium and
the others - having higher electronegativity than gallium have to
be removed from at user's request. These impurities are removed
with acidic dissolution using generally hydrochloric acid in an
equipment mounted stirrer and sometimes electrodes. After acidic
treatment gallium purity is usually 99.99 %.

Higher gallium purity can be achieved by electrolytic refining.
The electrolyte is pro anal grade sodium hydroxide and the
gallium metal should be purified is connected as an anode. The
gallium passes into the solution and deposits on the cathode. The
purity of the so refined gallium achieves up to 99.9999 %.
(Figure 2.10-3.) After electrolytic refining further purification
of gallium is possible by fractional crystallization. During
crystallization impurities are concentrating in the liquid phase
and the purity of crystal goes up to 99.99995 %. If the users
need gallium with low oxygen content the crystallization is done
after a heat treatment in vacuum.
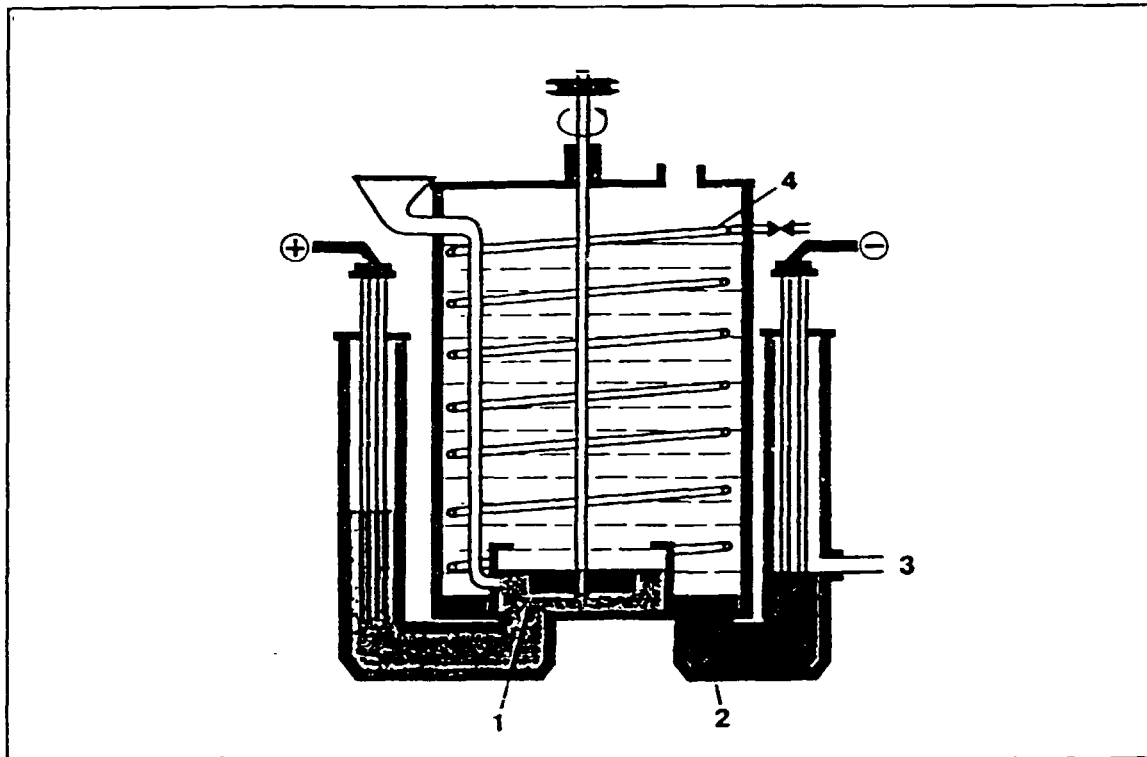
Figure 2.10-3
Refining process of gallium
1. anode space, 2. cathode space, 3. refined metal overflow 4. cooling

## 2.10.5 Production of gallium(III)oxide

Production of different gallium compounds 99.99 - 99.999 %
gallium(III)oxide is necessary as a raw material. In the applied
process gallium as the anode is dissolved in sulphuric acid and
forms gallium sulphate. Gallium is used as a cathode, too. At
electrolytic dissolution of the gallium minimum 90 % current
efficiency can be achieved and the depositing amount on the
cathode is minimal if the concentration of the sulphuric acid
electrolyte is higher than five moles. Alum type ammonium gallium
sulphate can be precipitated by means of ammonium sulphate or
ammonium hydroxide from the formed gallium sulphate solution
which can be purified by recrystallization and then it can be
decomposed to gallium trioxyde at 1000 $^{O}$C.

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# CHAPTER 3

# QUALITY CONTROL AND
MATERIAL TESTING

## 3.1 GENERAL OVERVIEW OF THE TECHNIQUES OF QUALITY CONTROL IN THE FIELD OF SPECIAL PRODUCTS

### Á. Csanády

In case of aluminium hydroxides and oxides in our terminology "special products" we are dealing partly with systems belonging to the great family of the two phase colloidal alumina-water or alumina-air systems. Not only the gelatinous aluminas, the hydroxides and oxide hydroxides, but also the transition aluminas are thermodynamically unstable forms, some types are also X-ray amorphous. The only thermodynamically stable oxide of aluminium is corundum.

It means that in most cases we are dealing with material systems which are hardly dependent on the method of preparation and which may undergo different phase transformations if the main parameters, i.e. temperature and water vapour pressure are changed.

The second important fact to be considered is the state of our solid material namely its powder form. It means that the solid phase depending on the fabricating process is present as discrete particles which may have different sizes, different structures and can be differently agglomerated etc.
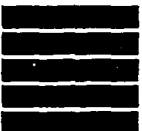
The measurements characterizing the quality of the powders have to be classified in different groups, and very often the measured properties are not independent of each other.

One can describe peculiarity of the individual particles or individual units of the powder samples. The common features of the powder particles should be considered separately. Quality control itself is mainly dealing with the functional properties of the products made out of the powder base (Table 3.1.-1).

## 3.1.1 Characteristics of the individual units of powders

### 3.1.1.1 Summary of the characteristics of individual unit of powders further their investigation methods

Table 3.1-1
Characteristics of the individual units of the powders

| Feature | Method | Electron diffraction | High resolution transmission electron microscopy | Scanning electron microscopy | Electron-probe micro-analysis |
|---|---|---|---|---|---|
| Atomic structure 1/1 | | ▬▬▬ | ▬▬▬ | | |
| Morphology 1/2 | Size shape surface roughness state of aggregation | | ▬▬▬ | ▬▬▬ | |
| Chemical composition 1/3 | | | | | ▬▬▬ |

### 3.1.1.2 Atomic structure

The atomic structure of the individual powder particles is in the $\mu$m range and below. Crystal structure and orientation of very small particles also in the range of some nanometers can be identified only by modern transmission electron microscopes, by electron diffraction technique.

In transmission electron microscopy a monochromatic beam of electrons is accelerated through a thin specimen which is usually a single crystal of $0.1 - 0.5$ $\mu$m thick or less. On the exit side of the specimen several diffracted beams are present in addition to the transmitted beam, and these are focussed by the objective lense to form a spot pattern in its back focal plane. The diffracted beam arise because the incident electrons are scattered by the atoms of the crystal and the scattered electrons are in phase (that is reinforced) in certain directions in the crystal.

The conventional types of diffraction patterns produced in

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transmission in electron microscope can be of three different
types:

1. ring-pattern of polycrystalline specimen
2. spot pattern of single-crystal region of the specimen
3. Kikuchi line pattern of single-crystal region of the specimen.

In general, spot and Kikuchi patterns will be taken from a
specific area of the specimen and are known "selected area"
diffraction patterns (SADP's). By tilting the "crystals" around
the reciprocal lattice vectors in the microscope, further by
necessary projections of these patterns, the reciprocal unit cell
can be obtained and the real crystal structure can be deduced.


### 3.1.1.3 Morphology

According to the original Greek interpretation, morphology means
a science dealing with the arrangement and connections of
particles building the material. By world morphology are meant
all spatial orders which are originated not by the relation of
atomic points but by those of   surfaces: from nm orders of
magnitude, up to the range of visible dimensions. In order to
possess scientific cognition of the morphology synthesized data
of several disciplines are required. Among these the most
important information generally used in the field of special
products are as follows:

- grain size
-- grain form and structure of the grain surface
- porosity and pore size distribution
- specific surface area

As higher the spatial resolution of the new investigation methods
as more details can be given. Recently it is well known that in
catalysis rough surfaces do chemistry. Roughness in that case is
equal to 1/packing density. Closepacked surfaces (from the atomic
arrangement point of view) has very low activity. The more open a
surface is the higher its flexibility will be, namely during
chemisorption the adsorbed molecules restructure the surface. In
the case of an oxide-metal catalyst i.e. Ni on $Al_2O_3$ all the
chemistry occurs at the oxide-metal interface (Somorjai).


### 3.1.1.4 Chemical composition

The best technique to determine the composition of individual
particles is connected to the new generation of electron
microscopes which has been specially designed to take full
benefit of the analytical signals excited by the electron beam in
the submicron samples of interest. "Analysis" refers to different
degrees of information: the most generally accepted signification
for chemical analysis consists of recognizing the specify of a
given element (iron for instance) and to evaluate its relative
concentration (% Fe) in the volume of interest. It can also

concern more refined types of information, such as valence state of the element ($Fe^{++}$ or $Fe^{+++}$), the environmental symmetry of its site (tetrahedral or octahedral....), its short or long range surroundings.

"Submicron" means some typical extension value (length, or area, or volume) with reference to a specific specimen feature; it associates scale and localization. Roughly speaking, 1 $nm^3$ of matter contains several tens of atoms and 1 $\mu m^3$ several $10^{10}$ atoms. Such an enormous reduction of the analyzed mass, down to the $10^{-20}$ g has been made possible by improvements in area localization (electron microprobe of smaller size) and depth localization (very thin specimens for thin foil studies, or small escape depth of the recorded radiation for surface studies).

In Table 3.1-2 the most important features of the powders to be determined and the methods being the most important in the characterization of the special products are shown. All these techniques will be discussed in details in Chapter 3.7 and 3.8.

### 3.1.2 Powder features

**3.1.2.1 Powder features and their investigation methods**

**Table 3.1-2a**
**Features of the powders (aerosol or gel)**

| Feature | Method |
|---|---|
| Phase structure | X-ray diffraction<br>infrared spectroscopy |
| Chemical composition | X-ray fluorescence analysis (XFA)<br><br>Atomic absorption spectrometry (AAS)<br><br>Inductive coupled plasma technique (ICP) |
| Chemical state of the surface | X-ray photoelectron spectroscopy (XPS) |
| Surface area | Gas adsorption (BET)<br><br>Adsorption of solution |
| Porosity | Mercury porosimeter |
| Chemical solubility | Classical chemistry |

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## Table 3.1-2b
### Features of the powders (aerosol or gel)

| Feature | Method |
|---------|--------|
| Strength of particles | Measurement of the Attrition index |
| Flowability | Angle of flow |
| Dusting | Artificial dusting |
| Size distribution mean size | Direct and indirect methods |
| Loss of ignition | TG, DTG. DTA |

## 3.1.2.2 X-ray diffraction (XRD)

X-ray powder diffraction is a technique which uses the diffracting power of crystals for X-ray to obtain information of a great number of individual crystals i.e. powders particles. In case of differently prepared and treated samples all the information produced by earlier measurements on monocrystals or natural or artificial "standards" further mathematical treatments have to be used in quantification of the structural observations.

## 3.1.2.3 Infrared spectroscopy

The absorption of the infrared spectral regions provides information of chemical binding state of the sample. The majority of analytical applications and so thus its application to the gelatinous aluminas are confined to a portion of the middle infrared radiation extending from 4000 to 400 cm$^{-1}$ (wave number) or 2.5 - 50 $\mu$m (wavelength). The infrared spectra of oxides and hydroxides: gibbsite, bayerite, boehmite, diaspore, corundum are well known and they can be used in the procedure of phase identification also in case of a poor crystallinity of the samples.

## 3.1.2.4 Chemical analysis by X-ray fluorescence

The main advantage of this technique is that the powders have not to be solved. XRF is one of the most widely used of all analytical methods for the qualitative identification of elements having atomic numbers greater than oxygen (>8) in addition it is often employed for semiquantitative or quantitative elemental analysis as well.

A high priority for XRF analytical technique was given also by

the International Standardization Organization (ISO)[*].

In the last years the performance characteristics of wavelength dispersive X-ray fluorescence spectrometers have been improved. Significant decreases in the detection limits of most elements normally determined in alumina have been achieved. The lower detection limits now achievable allow of adequate sensitivity when using fused beads. This technique facilitates the preparation of synthetic calibration standards using pure materials. Use of these synthetic standards coupled with virtual elimination of matrix effects provides an excellent basis of a standard procedure. The determination of $SiO_2$, $Fe_2O_3$, $Na_2O$ , CaO, $TiO_2$, $V_2O_5$, $P_2O_5$, $Ga_2O_3$, MgO, $MnO_2$, and ZnO can be carried out.

### 3.1.2.5 Atomic Absorption Spectrometry and Inductive Coupled Spectrometry

Atomic Absorption Spectrometry (AAS) and Inductive Coupled Spectrometry (ICP) are the most important analytical techniques in case of which the powder material to be investigated has to be solved.

In Table 3.1-3 a comparison of the different techniques concerning sensitivity (ngmL) for Selected Elements is given.

Table 3.1-3
Sensitivity (ng/ml)[a] for Selected Elements[b]    [1]

| Element | AAS, Flame | AAS Electro-thermal | AES Flame | AES ICP | AFS Flame |
|---------|-----------|---------------------|-----------|---------|-----------|
| Al      | 30        | 0.005               | 5         | 2       | 5         |
| As      | 100       | 0.02                | 0.0005    | 40      | 100       |
| Ca      | 1         | 0.02                | 0.1       | 0.02    | 0.001     |
| Cd      | 1         | 0.0001              | 800       | 2       | 0.01      |
| Cr      | 3         | 0.01                | 4         | 0.3     | 4         |
| Cu      | 2         | 0.002               | 10        | 0.1     | 1         |
| Fe      | 5         | 0.005               | 30        | 0.3     | 8         |
| Hg      | 500       | 0.1                 | 0.0004    | 1       | 20        |
| Mg      | 0.1       | 0.00002             | 5         | 0.05    | 1         |
| Mn      | 2         | 0.0002              | 5         | 0.06    | 2         |
| Mo      | 30        | 0.005               | 100       | 0.2     | 60        |
| Na      | 2         | 0.0002              | 0.1       | 0.2     | -         |
| Ni      | 5         | 0.02                | 20        | 0.4     | 3         |
| Pb      | 10        | 0.002               | 100       | 2       | 10        |
| Sn      | 20        | 0.1                 | 300       | 30      | 50        |
| V       | 20        | 0.1                 | 10        | 0.2     | 70        |
| Zn      | 2         | 0.00005             | 0.0005    | 2       | 0.02      |

[a] Nanogram/milliliter = $10^{-3}$ µg/ml = $10^{-3}$ ppm.
[b] AAS = atomic absorption spectroscopy;
AES = atomic emission spectroscopy;
AFS = atomic fluorescence spectroscopy;
ICP = inductively coupled plasma

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### 3.1.2.6 Strength of particles

Depending on the technology powder particles may be together as a
loose attachment or the solid particles combine forming
agglomerates. **Breakage** is the reverse of agglomeration, when a
single particle is broken into several smaller units. The term
**attrition** is used where only very small fragments are produced by
erosion of the corners, edges and protrusions of the particle.
Breakage and attrition are undesired in the practice of Bayer
process but are very important possibilities in the case of
special aluminas.

The strength of the particles can be expressed by the s.c.
attrition index. Flowability, dustiness and attrition index are
measurements not standardized yet. Procedures examined for the
determination of dustiness and attrition index have indicated
high dependence on the equipment design, materials of
construction and surface finish.


### 3.1.2.7 Particle size measurements

The **particle size measurements,** further the measurements of the
particle size distribution are possible by great many direct and
indirect techniques. A good comparison of the indirect techniques
is given by T. J. Davies in the Alumina Quality Workshop 1990
(Table 3.1-4).

The chemical state of the surface is very important in many cases
where the surface is playing an important role so is it in the
case of the powder-like materials. The topmost atomic layers are
the part of a solid which interacts with its environment and can
be very different from the material bulk. XPS, of all the surface
techniques is probably the most powerful and easy to use for
macroscopic, semimicroscopic applications. When combined with ion
etching, which enables stripping of the surface of a material,
atomic layer by atomic layer, very accurate profiles can be
obtained with sub nanometer depth resolution.

**Table 3.1-4a**
**Comparison of particle size methods for alumina and hydrate analysis[4]**

|  | Coulter Principle | Laser | Sieves |
|---|---|---|---|
| Establishment cost | ≈A$60 000 | ≈A$50 000 | ≈A$5000 |
| Productivity (No. of samples in 8 hours) | 6 - 15 | up to 80 | 8 |
| Calibration | Latex solution | Not required | Rarely done: standard glass spheres |
| Principle of operation | Volume equivalence diameter. All particles have opportunity to go through orifice | Projected area diameter. All particles must go through the cell | Physical separation Not all particles go through sieve |
| Sample size | 0.015 to 0.09 g in 250 ml electrolyte | 1.0 to 2.0 g in 350 ml water | 50-100 g dry |
| Sampling error | Large | Medium | Small |
| Range, microns | 1.5 to 180 variable - can ask for 256 channels) | 5.8 to 564 (16 fractions) | 38-150 (up to 19 fractions) |
| Precision, 2 $\sigma$ at 10 % -45 $\mu$m | 1.2 % | 0.5 % | 0.9 % |

Table 3.1-4b
Comparison of Particle Size Methods for Alumina and Hydrate Analysis
(continue) [4]

|  | Coulter Principle | Laser | Sieves |
|---|---|---|---|
| Accuracy | Reference method | Correlation with sieves diminishes above about 90 $\mu$m | Accuracy diminishes below about 75 $\mu$m. Significant variation between "equivalent" sieves |
| Features | Moderate level of operator skills. Tedious to operate | No special skills required to operate | Low skill requirement for use |
|  | Operating factor about 90 % | Operating factor 99 % | Operating factor 100 % |
|  | Not affected by: -composition -surface texture -refractive index | Affected by particle perimeter geometry: sharp edges give higher scattering |  |
|  |  | Versatile - easily adapted for other materials, e.g.. pulverised coal |  |

## 3.1.2.8 Specific surface area and porosity

Great many methods were developed for measuring  the specific
surface  area  which  is  one  of  the   most  important  powder
characteristic. Details of the main techniques namely the gas
adsorption ones and the solution adsorption methods will be given

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later. Anyway adsorption from solution appears to have great
potential, too. Different physical methods are nowadays also
available for the measurement of this characteristic.

It is obvious that pores can be understood as a dispersed failing
of material and hence the internal surfaces existing in a
material are the pores to be measured. The pores, as well as the
powder particles have mean sizes and size distributions to be
measured.

### 3.1.2.9 Chemical solubility

**Chemical solubility** is influenced by the composition, temperature
of the solute, further the agitation and heat transfer during the
process. Special case is the alumina solubility in the
electrolyte of the smelters.

### 3.1.2.10 Loss of ignition

Loss of ignition is a well standardized measurement in the
characterization of aluminas. Special aluminas may be treated in
thermo-analysers also showing the kinetic of the loss of surface
wetness.

## 3.1.3 Characterization of products - functional properties - made of powder

Table 3.1-5
Characterization of the products - functional properties - made of powders

| Adsorbers | A sorption capacity, aging |
| --- | --- |
| Catalysts | Catalytic activity, aging |
| Fillers | Wetability |
| Composites | Mechanical,thermal,optical,electrical and chemical properties |
| Ceramics | Hardness,brittleness,toughness (mechanical properties) |
| Abrasives | Electrical conductivity<br>Dielectric properties<br>Thermal expansion, thermal conductivity melting point<br>Transparency (optical properties)<br>Density, shrinkage<br>Corrosion properties<br>Biological activity |
| Different chemical products | Chemical properties |

The functional properties are partly in correlation with the powder features mainly in those cases where the powder it self is used for a given function (adsorbers, fillers etc). In other cases the technology of the product made of the powders is dependent of the physical and chemical features not only of the individual but also of the common ones.

## References

[1] Douglas A. Skoog: Principles of Instrumental Analysis Sanders College Publishing, 1985.

[2] K. Wefers, Ch. Misra, Alcoa Technical Paper No. 19, Revised Alcoa Laboratories 1987.

[3] G.I.D. Roach, J.B. Cornell, A. Antonovsky in Smelter grade alumina for the 1990's and beyond. Int. Workshop Gladstone, 1988. Sept. p. 137.

[4] T.J. Davie, ibid. p. 203.

# 3.2 PHASE ANALYSIS OF THE TRANSITION ALUMINAS

I. Sajó

## 3.2.1 Phases of the $Al_2O_3$ - $H_2O$ system

The main goal of this paper is to provide a general overview of the possibilities and limitations of phase analysis of industrially significant alumina chemicals. For this reason phases expected to encounter at room temperature and atmospheric pressure will be covered. Similarly, phase analytical methods of merely scientific importance may be touched upon, but only the ones with practical significance will be discussed.

Those who feel attracted by more exotic phases or instrumental techniques are referred to the excellent papers as [5-7].

Space limitations preclude a detailed discussion of the material covered in the lecture. For a more extensive treatment of the topic the devoted may find useful the following books:

K.Wefers and C.Misra of the Alcoa Laboratories published a thorough compilation on the subject [1]. The book by Misra [2] provides a comprehensive text with practical examples. A recently published monograph [3] is also a good source of knowledge, while Gitzen's work [4] deals with the ceramic aluminas in depth.

$Al_2O_3$ - $H_2O$ system is chemically a simple one: all the three elements exhibit a single, stable oxidation state and only stoichiometric compounds are formed. This gives three compounds with different degree of hydration: the aluminium hydroxide or alumina trihydrate [$Al(OH)_3$ or $Al_2O_3 \cdot 3H_2O$], the aluminium oxy-hydrate or alumina monohydrate [$AlO(OH)$ or $Al_2O_3 \cdot H_2O$] and the anhydrous alumina or aluminium oxide ($Al_2O_3$). But simplicity ends here. All the three compounds have several polymorphic forms. There are three well established polymorphs of aluminium trihydrate while the monohydrate is only dimorphic.

For the polymorphs of $Al_2O_3$ the better half of the Greek alphabet is used up so far, and the other half may come handy later on.

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### 3.2.1.1 Crystal Structure

**Aluminium trihydroxides**

The most frequent of the three polymorphs is the gibbsite
(=hydrargillite), the principal component of the lateritic
bauxites. In the Bayer process trihydrate is also precipitated in
the form of gibbsite. Natural gibbsite usually exhibits a
pseudohexagonal mica like tabular crystal form with excellent
basal cleavage. The crystal lattice of the gibbsite is made up of
double layers of $[OH]^-$ ions, with $Al^{3+}$ ions occupying the
two-thirds of the octahedral sites within the layers. The
aluminium ions show a hexagonal arrangement in the plane of the
layers. The hydroxyls of the adjacent double layers are situated
opposite each other with a slight displacement. Monoclinic
symmetry of the gibbsite lattice is the result of this deviation
from the hexagonal close packing of the $[OH]^-$ ions. The double
layers are held together by the hydrogen bridges formed between
hydroxyls. Sequence of the OH groups in the direction of the c
axis (i.e. perpendicular to the layer planes) is AB-BA-AB-BA.

Bayerite, an other polymorph of $Al(OH)_3$ is also characterized by
monoclinic symmetry. It is known to occur as a mineral, but a
very rare one and has no industrial significance. Synthetic
bayerite is also of lesser commercial importance. The crystal
structure of bayerite is similar to that of the gibbsite. It is
built of the same double layers but with a different stacki g
order. The hydroxyl ions of the adjacent layers fit into the
depressions between the hydroxyls of the opposite one resulting
in a layer sequence of AB-AB-AB.

Nordstrandite is a triclinic polymorph of $Al(OH)_3$, a rare mineral
and synthetic product of no commercial use. Its structure is also
based on the same double layers with the stacking order being
different from the previous ones.

**Aluminium Oxide Hydroxides**

Diaspore and boehmite, the two structural modifications of
AlO(OH) represent major constituents of certain bauxite types.

Diaspore a thermodynamically stable modification exhibits an
orthorhombic symmetry. Its structure is based on the hexagonal
close packed (HCP) sublattice of the oxygens with the aluminium
sitting in the octahedral sites.

The structure of boehmite is characterized by an oxygen
sublattice of cubic packing. Boehmite also has an orthorhombic
symmetry.

From amorphous aluminium hydroxide gel pseudoboehmite, a poorly
crystallized phase with non-stoichiometric composition can be
prepared. Its X-ray diffractogram shows broad reflections that

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coincide with the major reflections of boehmite. However it
rather seems to be an intermediate stage in the aging of the
aluminium hydroxide gels into a well crystallized aluminium
hydroxide than a poorly crystalline form of boehmite. Chemically
it is characterized with the formula $Al_2O_3 \cdot nH_2O$, where n is about
2 - 2.5.


## Aluminium oxides

The alpha-alumina (corundum) is the thermodynamically stable
$Al_2O_3$ phase. Naturally occurring corundum is used as an abrasive.
Fine coloured gem quality crystals of corundum are called ruby
(red) and sapphire (blue and all other colours) and are highly
valued gemstones. Corundum crystallizes in hexagonal-rhombohedral
system. The structure of corundum is based on the hexagonal close
packed oxygen sublattice. The relatively small aluminium ions
occupy the two-thirds of the octahedral sites of the oxygen
lattice.

All the other aluminas are metastable phases and are converted to
corundum on high temperature. The corundum structure is
maintained up to the melting point. (For a more detailed
discussion see the paragraph Thermal Transformation.) Metastable
$Al_2O_3$ phases are referred to as intermediate or transition
aluminas.

Transition aluminas fall into subgroups according to their
crystal structure, temperature of formation, degree of
crystallinity, etc.

Transition aluminas formed in the temperature range of about 200
to 600 °C are the low temperature transition aluminas and they
usually show a lower degree of crystallinity. These are the rho-,
gamma-, eta- and chi-$Al_2O_3$. High temperature transition aluminas
(usually formed between 600 and 1200 °C) are generally better
crystallized. The kappa-, kappa'-, delta- and the theta-$Al_2O_3$
fall into this class.

According to their structure two main types are known. One of
them is characterized by a more or less distorted spinel (cubic)
lattice. To this type belongs the eta-, gamma- and delta-$Al_2O_3$,
with tetragonally and the theta-$Al_2O_3$ with monoclinic deformed
spinel lattice. Chi- and kappa-aluminas, the members of the other
structure group  are supposed to have a hexagonal structure.
Rho-alumina is a nearly amorphous phase.

Before going in to a more detailed discussion, it is important to
point out that most of these structures were determined from
poorly crystallized phases from which fair sized single crystals
can not be obtained. Accordingly, these structures are highly
uncertain and not generally accepted.

Transition alumina particles are made up of a mosaic of more or
less misoriented microdomains. The coherent crystallite size of
the low temperature transition aluminas (gamma-, eta-   and

chi-$Al_2O_3$) is typically less than 10 nm, as determined from the broadening of the X-ray diffraction lines. Thus the scattering volumes are not large enough to permit classical X-ray structural analysis. According to the EXAFS studies of Larue & al. [6] the short range order of the various transition aluminas (up to 1 nm) is very similar. The structural differences do not arise from the arrangement of the first, second or third aluminium or oxygen neighbour but from differences in stacking blocks of similar structure.

The above mentioned properties give an explanation why methods of structure investigation based on long-range order as well as the ones based on short range order have problems with characterization of those substances.

### 3.2.1.2 Thermal Transformations

On heating the hydrated alumina phases start to lose water and transform to various transition aluminas. Provided the temperature is high enough they all end up as corundum. But in the meantime they follow different sequences of transformation depending on their original structure and other circumstances.

The simplest is the case of the diaspore which transforms directly into alpha-$Al_2O_3$ at about 5-600 °C. This is facilitated by its structure, as the close packed hexagonal oxygen sublattice is very close to that of the corundum, and is preserved by and large across transformation.

The cubic oxygen lattice of the boehmite is preserved in transition alumina sequence and is rearranged only at the theta $\rightarrow$ alpha-$Al_2O_3$ transformation:

boehmite $\rightarrow$ gamma-$Al_2O_3$ $\rightarrow$ delta-$Al_2O_3$ $\rightarrow$ theta-$Al_2O_3$ $\rightarrow$ alpha -$Al_2O_3$

Bayerite and nordstrandite follow a sequence similar to the route c of the gibbsite:

(bayerite/nordstr.) $\rightarrow$ eta-$Al_2O_3$ $\rightarrow$ theta-$Al_2O_3$ $\rightarrow$ alpha-$Al_2O_3$

Thermal transformation of gibbsite to alpha-$Al_2O_3$ can follow three main sequences depending on the reaction circumstances ($H_2O$ partial pressure, heating rate, particle size):

a/ gibbsite $\rightarrow$ chi-$Al_2O_3$ $\rightarrow$ kappa-$Al_2O_3$ $\rightarrow$ alpha-$Al_2O_3$

b/ gibbsite $\rightarrow$ boehmite $\rightarrow$ gamma-$Al_2O_3$ $\rightarrow$ alpha-$Al_2O_3$ $\rightarrow$ theta-$Al_2O_3$ $\rightarrow$ alpha-$Al_2O_3$

c/ gibbsite $\rightarrow$ rho-$Al_2O_3$ $\rightarrow$ eta-$Al_2O_3$ $\rightarrow$ theta-$Al_2O_3$ $\rightarrow$ alpha-$Al_2O_3$

During calcination the three process can concurrently run and compete for a share resulting in aluminas composed of

several  or nearly all of the above phases.

The structure of the transition aluminas in route 'a' (chi and kappa) is characterized by a hexagonal close-packed oxygen sublattice, similar to that of in the alpha-$Al_2O_3$. Anhydrous intermediate phases in the other two branches (gamma-, eta-, delta- and theta-) have a cubic close packed oxygen sublattice. The gamma and the eta phase share a rather similar structure, with nearly identical X-ray powder diffractogram. The only detectable difference is the <1,1,1> reflection (at 0.455 nm) being sharper for the eta and more diffuse for the gamma phase see Figure 3.2-5. The delta-$Al_2O_3$ has a tetragonal unit cell based on a spinel super lattice structure made up of gamma-$Al_2O_3$ cells. The theta-$Al_2O_3$ is known to be monoclinic, but can be regarded merely as a better ordered form of gamma-$Al_2O_3$ [8].

## 3.2.2. Phase Analysis

One can guess from the above structural characterization that transition aluminas gives  hard time for the phase analyst. And as if it were not enough, he even can't rely on elemental analysis data either.

### 3.2.2.1 Phase identification

Transition aluminas in a given branch may not be regarded as discrete phases, but points of a more or less continuous transformation path. Thus the concept of 'pure phase' is not easily applicable to them. The degree of misorientation, the size of microdomains, and the ordering of the cationic sublattice are further variables, making classification even more difficult.

Lack of reliable reference data is another source of troubles, but this is partially a consequence of the lack of well defined pure phases.

### 3.2.2.2 Quantitative phase composition

Reliable phase identification - a prerequisite of quantitative phase analysis - is next to hopeless in a complex  mixture  of transition aluminas. Reference intensities - 'constants' of vital importance - vary on a broad range with the crystallinity of  the phases. Reflections are usually broad  and  diffuse and a large proportion of them overlaps with  reflections from other phases making intensity determination unreliable or impossible. Knowing the above difficulties and limitations it is hardly surprising that not too much attempt was made for solving this question.

Bagshaw & Welch [16] published a  method  for  determination  of quantitative phase composition of aluminas. They regarded it to

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be "not fully quantitative", but it presents more serious problems, even with the "indication of trends" as well.

After all, what kind of answer can be expected to questions concerning the phase composition of alumina samples? What are the reasonable inquiries and what are the decent answers?

The discussion will be started with the X-ray powder diffraction (XRPD), as the most versatile phase analytical tool. Then other phase analytical methods will be presented to show what they can add to the results as obtained with XRPD (and for what price). According to our experiences, if the results given by XRPD measurements are not sufficient for a given purpose FTIR has the greatest potential to improve somewhat on the reliability of the data. Thermal analysis can answer only some very specific questions, and with a very low productivity (one to two measurement pro day). It is to be used only for a good reason.

## 3.2.2.3 X-Ray diffraction

After a careful investigation of the diffractograms from the pure phases (for which diffractograms are shown on Figures 3.2-1-8) the following possibilities were chosen for the identification and quantification of the transition aluminas:

**chi-Al$_2$O$_3$:** in the presence of eta- and/or gamma-alumina only the reflection at 0.211 nm can be used. Because of the poor crystallinity of the chi-alumina, minute quantities (about 10%) may remain undetected. At the same d-value the kappa-alumina also has a prominent peak. In samples containing kappa-Al$_2$O$_3$ the identification of chi-alumina (or differentiation from eta/gamma-Al$_2$O$_3$) is not reliable.

**kappa-Al$_2$O$_3$:** This phase has several reflections (at 0.62, 0.211, 0.187 and 0.164 nm) which do not overlap with reflections from other phases and therefore it is easily detectable.

**delta- and theta-Al$_2$O$_3$:** Peaks at 0.273 and 0.180 nm show their presence, while only minor reflections can help to differentiate them: at 0.51 and 0.407 nm for the delta-Al$_2$O$_3$ and 0.545 and 0.284 nm for the theta-Al$_2$O$_3$. Intensity determination for these peaks is unreliable, making the calculation of delta/theta ratio highly uncertain.

**gamma- and eta-Al$_2$O$_3$:** Because of their nearly identical powder diffractograms in samples containing both phases XRPD allows only to recognize that at least one of them is present. In the phase composition results usually only the sum of these two phases can be given. All their reflections are more or less overlapping with peaks of delta- and theta-alumina, resulting in highly inaccurate intensity determination. Extreme variability of their reference intensity values and the errors of intensity determination are so high that they are best quantified as the difference of 100% and the sum of the other phases.
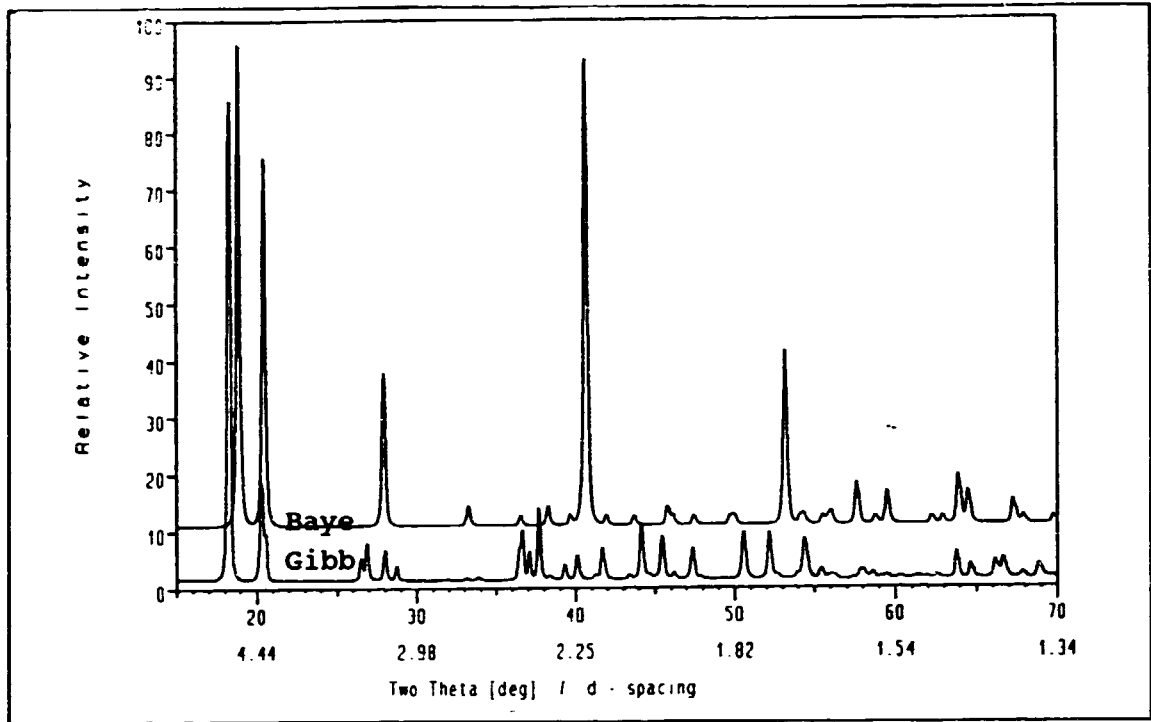
**Figure 3.2.-1**
**X-ray diffractogram of gibbsite and bayerite**
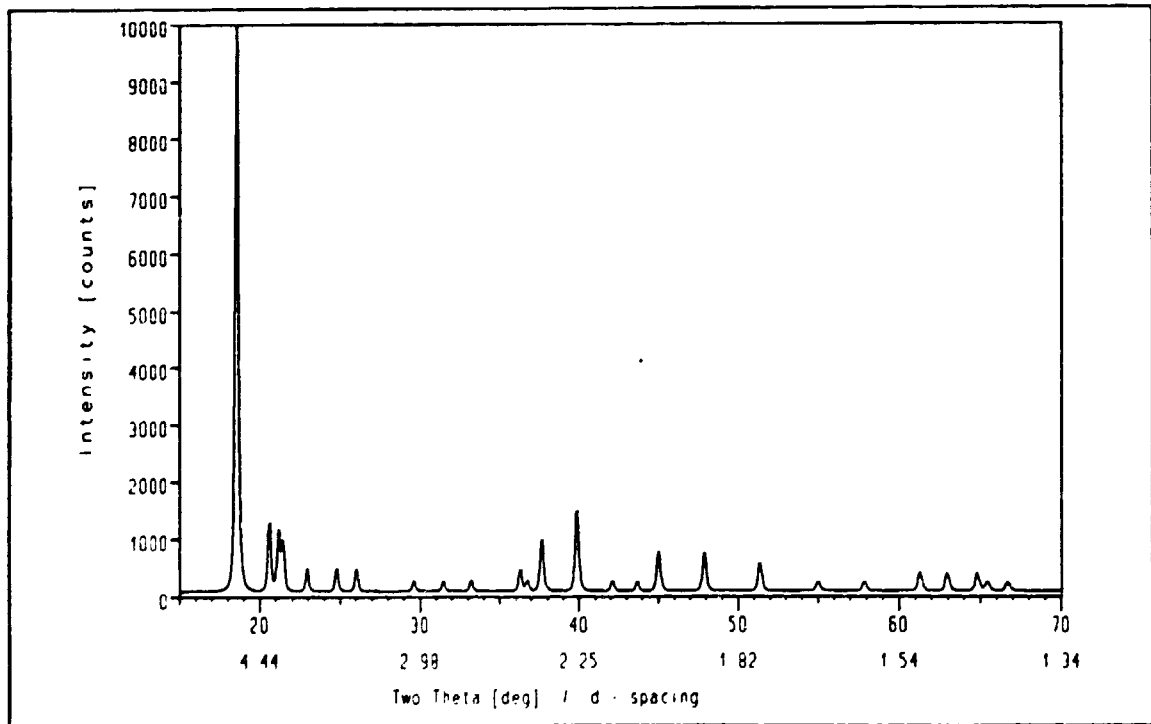


**Figure 3.2.-2**
**X-ray diffractogram of nordstrandite**
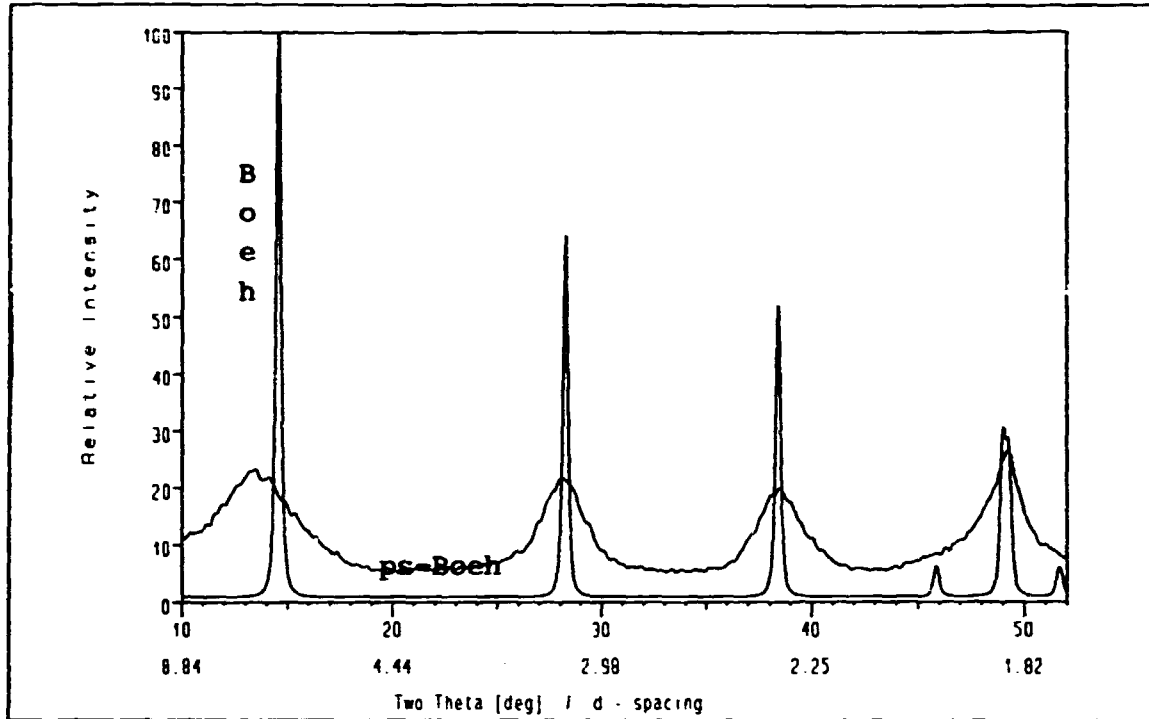
Figure 3.2.-3
X-ray diffractogram of pseudobehmite and boehmite
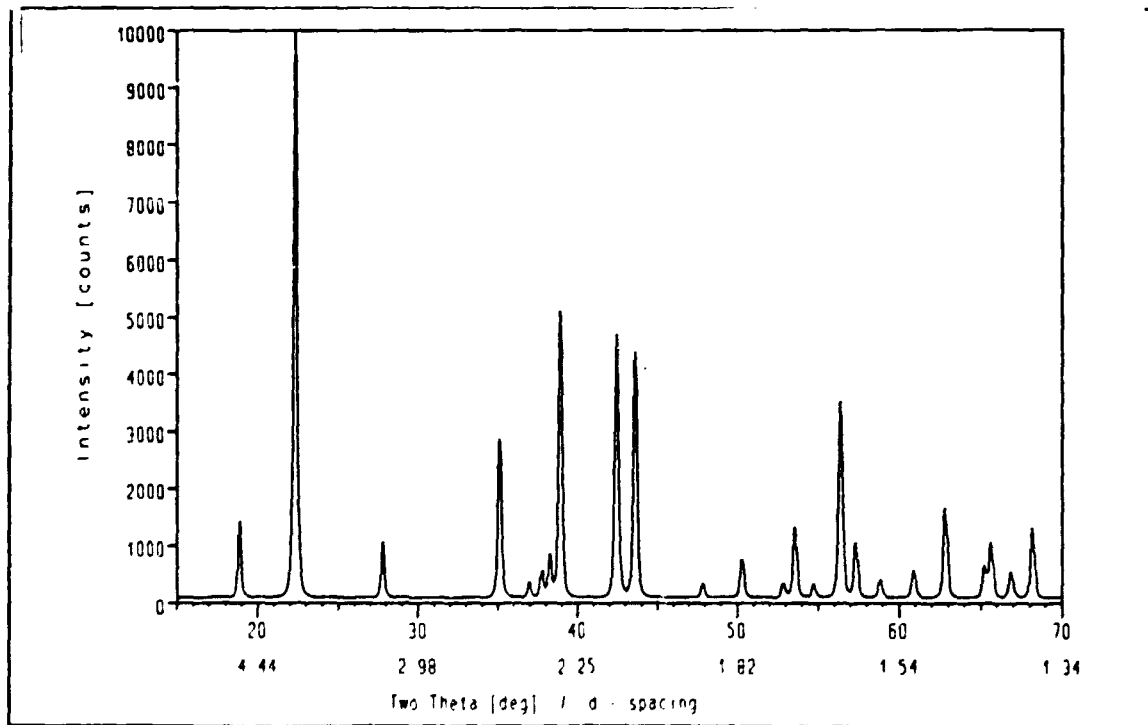


Figure 3.2.-4
X-ray diffractogram of diaspore
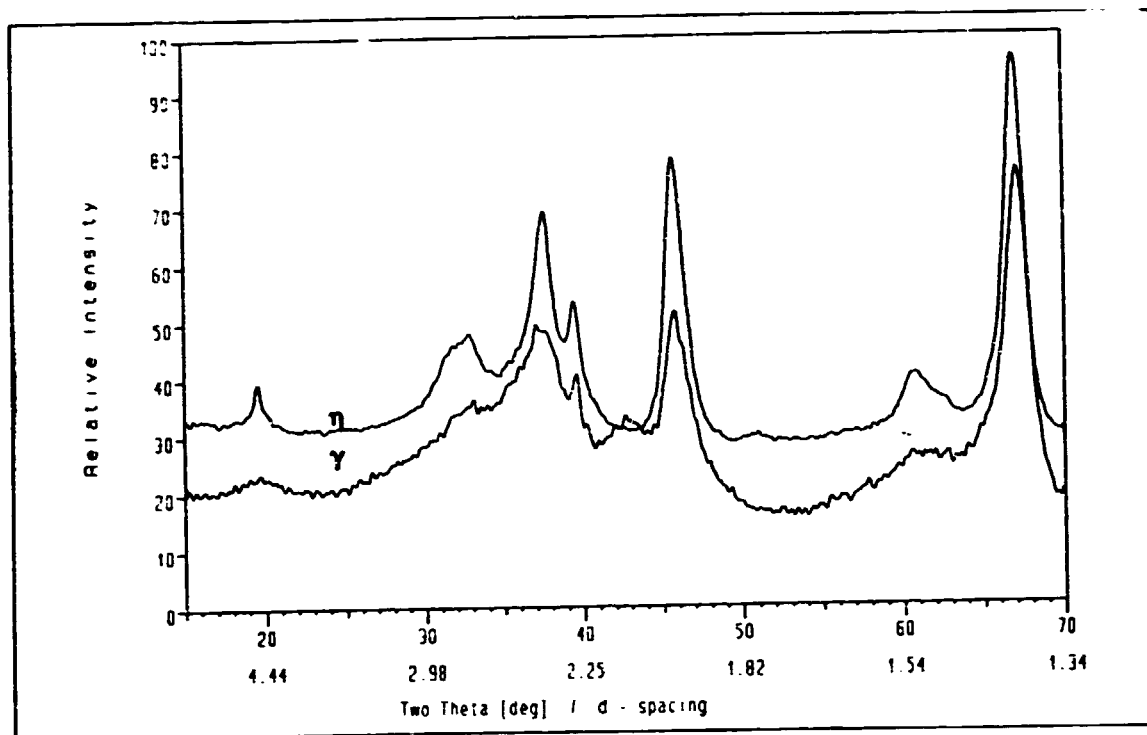
**Figure 3.2.-5**
**X-ray diffractogram of gamma- and eta-alumina**
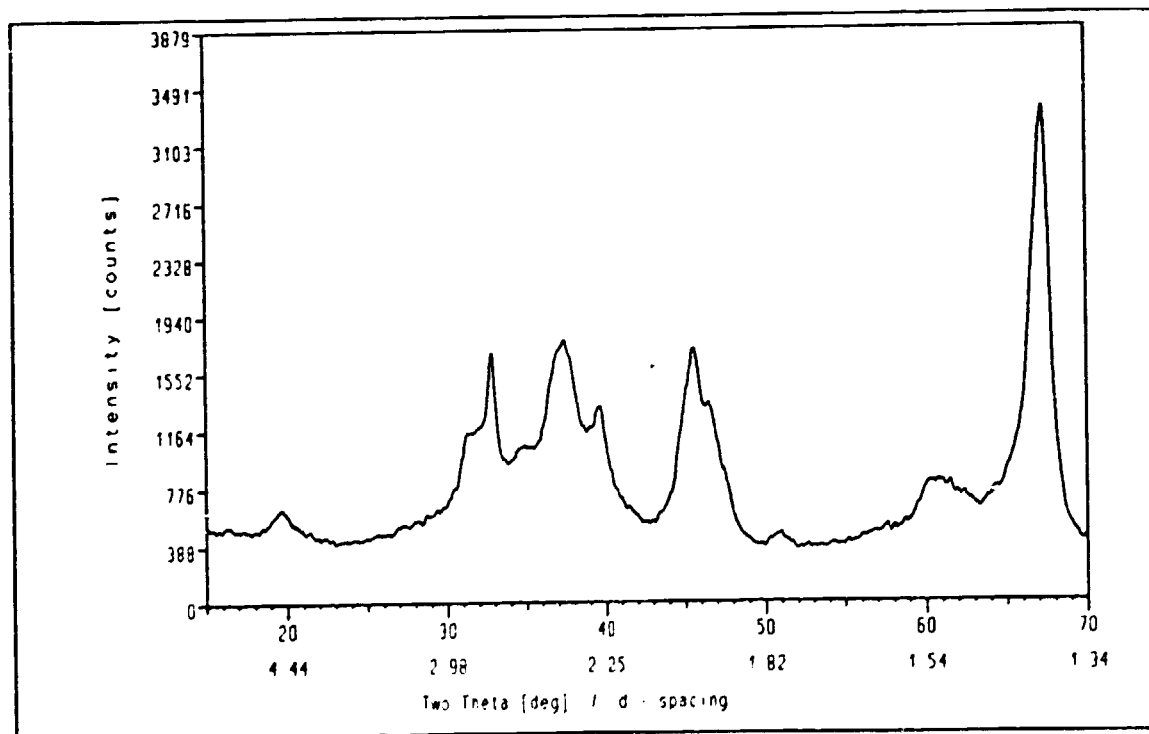


**Figure 3.2.-6**
**X-ray diffractogram of chi-alumina**
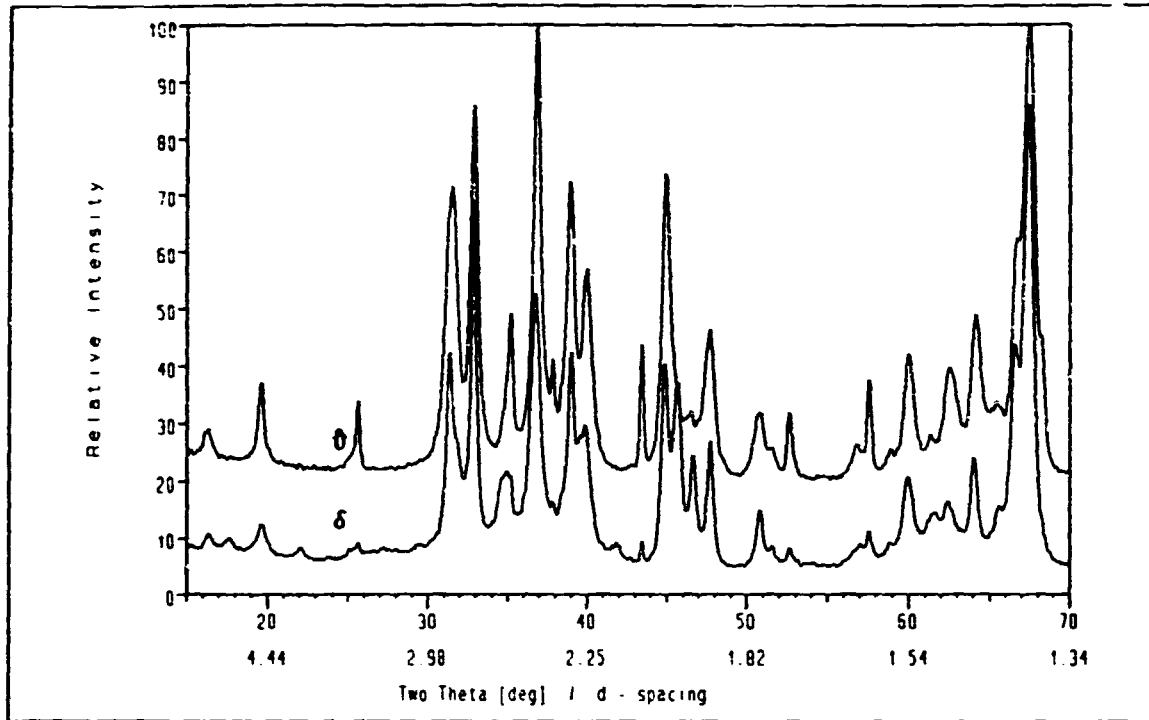
**Figure 3.2.-7**
**X-ray diffractogram of delta- and theta-alumina**
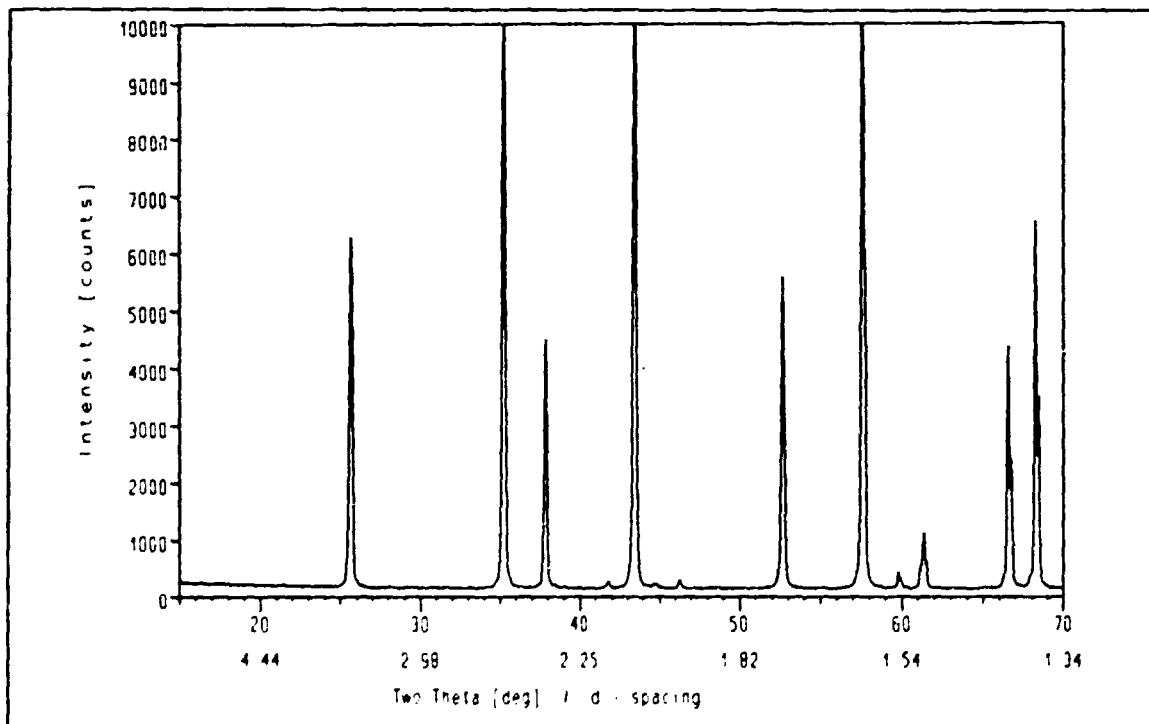


**Figure 3.2.-8**
**X-ray diffractogram of alpha-alumina**

### 3.2.2.4 Differential Thermal Analysis

The thermoanalytical behaviour of transition aluminas is rather similar. After a rapid initial period (loss of the adsorbed water; Dm is highly dependent on the specific surface area, usually in the range of -1 to -6% to 300 °C) there is a continuous weight loss up to 1400 °C with a decreasing rate (Dm about 0.6-0.8% from 300 to 1400 °C). With mass spectrometric

(QMS) detection of gaseous decomposition products it was shown that water is continuously formed over this temperature range (even above 1200 °C!).

Onset of the alpha-$Al_2O_3$ transformation is usually between 1000 and 1250 °C depending on the type of the sample, as can be seen from the DTA curves. The other phase transformations do not exhibit any DTA effect.

### 3.2.2.5 Infrared Spectroscopy

According to their infrared spectra the transition aluminas fall into two main groups: one consisting of the gamma-, eta- and chi-aluminas, while the other being formed by the delta- and theta-$Al_2O_3$. They show broad absorption bands with not too much individual details. The variability of the spectra of individual samples of a phase may be greater than differences between members of a group.

Alpha-alumina exhibits a quite different IR spectrum but this crystallographically well defined phase also shows a certain degree of variability: the intensity of the absorption band in the region of 650-800 cm depends to a high extent on the origin of the sample. (e.g. cf. the spectra published by Dorsey,[12] and Stegmann & al., [13])

The up-to-date Fourier-transform IR (FTIR) spectrometers expand the possibilities of the IR spectroscopy. They not only provide a significantly higher resolution, but can be coupled with sophisticated computerized processing of the FTIR scans.

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# 3.3 Major, minor and trace element analysis of co-products and by-products in Bayer alumina production by chemical methods

É. Kálmán

Bayer technology involves great demands on investigation and analysis. Plant control and process control in mainly based on analytical measurements, too and that is why plant operation without analytical activities is unimaginable. For that very reason it is necessary to deal in detail with the analytical problems of the alumina production. The alumina is a "raw" material and the co-products (ceramic, special alumina, electrocorundum, alumina trihydrate, aluminium-sulphate etc.) and by-products (gallium, vanadium-pentoxid etc.) are the final products in this case.

The chemical analysis provides information about the elemental composition of the material tested. From the point of view of analytical chemistry alumina substantially differs from by-products for example mullite or aluminium-sulphate because while the latter ones are multi-component materials alumina is a homogeneous one. Other elements occurring in alumina are considered as contaminants. Major contaminants of the alumina are adhesive moisture, loss of mass and finally the $Na_2O$-content. Minor and trace contaminants of the alumina are of the 0.1 to 500 ppm order of magnitude.

## 3.3.1 The elemental composition of the co-products and by-products

### The contaminating components in "raw" materials alumina

A number of contaminating components from the caustic solution segregate simultaneously with the alumina hydrate separation in Bayer alumina producing process, or they link to the large-surface precipitates (sorption) and cannot be totally removed even by washing. The contaminating components of alumina exercise disadvantageous influence on the utility of non-metallurgical special alumina, corundum, for example: $Fe_2O_3$ and $Na_2O$. Table 3.3-1 gives a survey about the contaminating components of alumina.

Examining the Table 3.3-1 it turns out that $Na_2O$ is the highest contaminating component of the alumina if we leave out of consideration the moisture content. A part of this $Na_2O$ content, the so called water-soluble $Na_2O$ originates from insufficient washing of the caustic solution. Some products, for example pseudo-boehmite and catalyst support can be characterized by low $Na_2O$ or the ceramic aluminas by low $Na_2O$, $Fe_2O_3$ and $SiO_2$ contamination.

Table 3.3-1
Contaminating components in alumina (%)

| Major impurities | Moisture 300 C° | L.O.I. 1100 C° | Na$_2$O total | Na$_2$O w.sol. | | | |
|---|---|---|---|---|---|---|---|
| range from-to | 0,5-1,5 | 0,05-0,5 | 0,2-0,5 | 0,01-0,3 | | | |
| Minor impurities | Fe$_2$O$_3$ | SiO$_2$ | TiO$_2$ | ZnO | Ga$_2$O$_3$ | CaO | SO$_3$ |
| range from-to | 0,02 0,03 | 0,01 0,04 | 0,003 0,005 | 0,01 0,02 | 0,005 0,01 | 0,005 0,02 | 0,00 0,1 |
| Trace impurities | V$_2$O$_5$ | P$_2$O$_5$ | MgO | CuO | MnO | Cr$_2$O$_3$ | NiO |
| range from-to | 0,001 0,003 | 0,0001 0,001 | 0,001 0,003 | 0,001 0,004 | 0,0005 0,001 | 0,0001 0,001 | 0,0001 0,001 |

## 3.3.2 The contaminating components in co-products and by-products

Table 3.3-2 shows the co-products manufactured in Alumina Plants of HUNGALU Rt. and their contaminating components. From the point of view of analytical chemistry co-products do not differ from alumina because all of them are Al$_2$O$_3$ matrix.

Table 3.3-2
Special co-product produced in Plants of HUNGALU Rt.

| | | ALOLT family | Ceramic aluminas | Alumina hydrates | Activated aluminas | Abrasive pastes | Electro-corundum | Fused corundum |
|---|---|---|---|---|---|---|---|---|
| SiO$_2$ | % | 0.003-0.015 | 0.01-0.035 | 0.006-0.008 | 0.025-0.035 | 0.025-0.035 | 0.05-0.15 | 0.25 |
| Fe$_2$O$_3$ | % | 0.003-0.017 | 0.01-0.045 | 0.01 -0.02 | 0.025-0.035 | 0.03 -0.04 | 0.10-0.18 | 0.07 |
| TiO$_2$ | % | - | - | 0.002-0.003 | - | - | 0.03-0.08 | 0.007-0.01 |
| V$_2$O$_5$ | % | - | - | 0.001 | - | - | - | - |
| P$_2$O$_5$ | % | - | - | 0.002 | - | - | - | - |
| Na$_2$O$_{total}$ | % | 0.0005-0.30 | 0.01-0.45 | - | 0.25-0.35 | 0.35-0.45 | 0.30-0.50 | 0.90 |
| Na$_2$O$_{w.sol}$ | % | 0-0.03 | 0.05-0.15 | 0.03-0.04 | - | - | - | - |
| CaO | % | - | - | - | - | 0.025-0.10 | 0.10 | |
| Moisture | % | 0.2 | 0.1-0.3 | 11.0 | | 0.1-0.3 | - | - |
| L.O.I. | % | 34.5 | 0.01-0.2 | 8-10 | 0.1-0.3 | - | - | |
| Al$_2$O$_3$ | % | - | 99.2-99.9 | 99.2 | 99.0 | 99.0-99 | 98.5 | |
| Al(OH)$_3$ | % | 99.5 | - | 99.5 | - | - | - | |
| a - Al$_2$O$_3$ | % | - | >90-95 | 0-3 | 92-95 | 99-99.7 | 90 | |
| Glassphase | % | - | - | - | - | - | 6 | |

Table 3.3-3 and Table 3.3-4 show the by- and co-products manufactured in alumina plants of HUNGALU Rt. and their contaminating components. From the point of view of analytical

chemistry by-products differ from alumina because they are multi-component materials.

**Table 3.3-3**
**By-product produced in plants of HUNGALU Rt.**

|  |  | Elektromullite | Zirkosit 30; 40; K | Vanadium pentoxid | Ammonium meta vanadate | Aluminium sulphate | Synthetic zeolite |
|---|---|---|---|---|---|---|---|
| $Al_2O_3$ | % | 74 | 45.3-50.0 | - | - | 17-18 | 28-30 |
| $SiO_2$ | % | 24 | 12.2-14.0 | 0.3-0.5 | 0.20 | - | 31-34 |
| $TiO_2$ | % | 0.07 | 0.08-0.10 | - | - | - | - |
| $Fe_2O_3$ | % | 0.10 | 0.08-0.10 | 0.3-1.0 | 0.10 | 0.005-0.01 | 0.025 |
| CaO | % | 0.15 | 0.35-0.40 | - | - | - | - |
| MgO | % | 0.10 | - | - | - | - | - |
| $Na_2O$ | % | 0.40 | 1.15-1.35 | 1.5-7.5 | 1.0 | - | 17-19 |
| $ZrO_2$ | % | - | 33-40.2 | - | - | - | - |
| $V_2O_5$ | % | - | - | 92-98 | 56.00 | - | - |
| $P_2O_5$ | % | - | - | 0.03-0.10 | 0.10 | - | - |
| As | % | - | - | 0.02-0.08 | 0.03 | <1 | - |
| $SO_3$ | % | - | - | 0.05-0.10 | 0.10 | - | - |
| Moisture | % | - | - | - | 25 | - | - |
| L.O.I. | % | - | - | - | - | 18-22 |  |

Table 3.3-4
Co-product produced in plants of HUNGALU Rt.

|     | Gallium 4N 99.99 | Gallium 5N 99.999 (bpm) | Gallium 6N 99.9999 |
| --- | --- | --- | --- |
| Hg  | 12000 | 100 | 5 |
| Cu  | 5000  | 100 | 5 |
| Pb  | 2000  | 50  | 1 |
| Al  | 1000  | 500 | ND |
| Fe  | 1000  | 100 | 5 |
| Si  | 1000  | 250 | ND |
| Mg  | 1000  | 10  | ND |
| Ni  | 1000  | 100 | 10 |
| Zn  | 10000 | 100 | 10 |

## 3.3.2.1 The contaminating components in sodium aluminate liquors

While the alumina, caustic and soda concentration of a wide range
of plant liquors must be continually monitored, impurities that
build up in the closed loop of Bayer circuit must also be
monitored. Anionic impurities such as chlorides and sulphates
reduce the productivity of the process liquor and oxalate makes
control of particle size in precipitation more difficult.
Impurities such as $SiO_2$, $P_2O_5$, F, $V_2O_5$, ZnO and $Ga_2O_3$ must be
monitored in the process liquor for optimum product quality
control.

## 3.3.2.2 The contaminating components in water

Water associated with the power-house boiler drums are analysed
to control impurity levels and the dosing of scale reducing
reagents. Anionic impurities such as $F^-$, $Cl^-$, $PO_4^{3-}$, $SO_4^{2-}$ must
also be monitored in water.

## 3.3.2.3 Determination of contaminating components of products

In the plants of HUNGALU Rt. modern instrumentation routinely
used for chemical analysis includes:

- Atomic Absorption Spectrophotometer (AAS)
- Automatic Titrimetric System
- Inductively Coupled Plasma Atomic Emission Spectrometer (ICP)
- X-Ray Fluorescence Spectrometer
- Ion-Chromatograph (IC)
- Gas-Chromatograph (GC)
- Leco Sulphur/Carbon Analyser
- Photographic Spectrograph
- UV-visible Spectrophotometer.

Modern instrumentation now available can readily provide accurate, precise and rapid determinations. The production of high quality special grade alumina is only possible if rapid analyses and high skilled operators are used.

Table 3.3-5 shows comparison of the various analytical methods used for routine analysis of alumina products.

Table 3.3-6 shows methods for the determination of the contaminating components of alumina.

**Table 3.3-5**
**Advantages and disadvantages of some instrumental methods for routine trace element analysis**

|  | Optical spectrography | ICP spectrometry | AA spectro-photometry | UV-visible spectro-photometry | Ion-chromatog-raphy | X-ray fluorescence |
|---|---|---|---|---|---|---|
| Capital cost | low | extremely high | low | low | low | high |
| Sensitivity | good (1-10 μg/g) | good (1-10 μg/g) | very good (1-10 μg/g) | very good (1-10 μg/g) | very good (0,1-10 μg/g) | fair (1-10 μg/g) |
| Speed of analysis | limited | unsurpassed for multi-element work | fast for single elements | fast for single elements work | fairly fast for multi element work | fast for multielement |
| Precision | average (5-10 %) | precise (2-5 %) | precise (2-5 %) | (5-10 %) | average (5-10 %) | average (5-10 %) |
| Matrix effect | considerable | considerable | slight or | slight or easily controlled | considerable easily controlled | considerable |
| Main advantage | permanent record | very high speed | ease of operation | ease of operation | ease of operation | nondestructive |

Table 3.3-6
Methods for the determination of the contaminating components of alumina

| Components | Wet * chemistry | AAS | ICP | OES | X-Ray fluorescence |
|---|---|---|---|---|---|
| $SiO_2$ | + | | | + | + |
| $Fe_2O_3$ | + | | + | + | + |
| $TIO_2$ | + | | + | + | + |
| $Na_2O_{w.sol.}$ | + | | | | |
| $Na_2O_{total}$ | | + | | | |
| $V_2O_5$ | + | | | + | + |
| $P_2O_5$ | + | | | | |
| $CaO$ | | + | + | + | + |
| $MgO$ | | + | + | + | + |
| $ZnO$ | + | + | + | + | + |
| $CuO$ | + | + | + | + | + |
| $MnO_2$ | + | | | + | + |
| $NiO$ | + | | | + | |
| $Cr_2O_3$ | + | | | + | |
| $Ga_2O_3$ | + | | + | + | |
| $B_2O_3$ | + | | + | | |
| $F^-$ | + | | | | |
| $Cl^-$ | + | | | | |
| $SO_4^{2-}$ | + | | | | |

* wet chemistry: spectrophotometry and ion-chromatography

### 3.3.3 Determination of components by classical chemical methods in alumina products

Chemical tests have to be carried out on sample prepared. International Standard Specification (ISO 2927-1973) specifies how to take the representative sample of alumina.

The dissolution or attach of the alumina does not mean an easy task. The most frequently used methods for attach can be divided into two groups:

- method by alkaline fusion
- method by acid attack under pressure.

Table 3.3-7 shows the International Standard Specifications used for the analysis of alumina.

Table 3.3-7
ISO standard methods used for analysis of alumina

| N° | Component | Principle of the determination | Method | Field of application range | ISO Number |
|---|---|---|---|---|---|
| 1. | Loss of mass at 300 °C of loss of mass | Drying of the test portion at 300 °C for 2 h and determination | | | 803-1976 |
| 2. | Loss of mass at 1000 °C and 1200 °C | Ignition of two test portions previously dried at 300 °C one at 1000 °C and the other at 1200 °C, for 2 h | | | 806-1976 |
| 3. | $Na_2O$ | Fusion of the test portion with mixture $Li_2CO_3 + B_2O_3$ or $Li_2CO_3 + Li_2B_4O_7$. Dissolution in HCl. Aspiration of the solution into a flame | Flame emission spectro- photo- metric | | 1617-1976 |
| 4. | Preparation of solution for analysis | Alkaline fusion method | | | 804-1976 |
| 5. | $Fe_2O_3$ | Alkaline fusion, reduction of iron(III) to iron(II). Formation of the iron(II)-1.10-phenanthrol-ine complex. pH 3.5-4.2. Photo-metric measurement at wavelength 510 nm | Spectro- photo- metric | >0.005 ⊕ | 805-1976 |
| 6. | $SiO_2$ | Alkaline fusion, formation of the oxidized molybdosilicate, selec-tive reduction. Photometric measu-rement at wavelength of 815 nm | Spectro- photo- metric | 0.005-0.025 0.025-0.25 | 1232-1976 |
| 7. | $TiO_2$ | Alkaline fusion test solution. formation of the titanium-di-antipyryl-methane complex. Photo-metric measurement of the coloured complex at a wavelength of 420 nm | Spectro- photo- metric | >0.001 ⊕ | 900-1977 |

Table 3.3-7
ISO standard methods used for analysis of alumina (cont.)

| N° | Component | Principle of the determination | Method | Field of application range | ISO Number |
|---|---|---|---|---|---|
| 8. | $V_2O_5$ | Alkaline fusion test solution, oxidation to V(V). Formation of vanadium N-Benzoyl-N-phenyl-hydroxyl-amine complex. Extraction of the violet coloured complex. Photometric measurement at a wavelength of 524 nm | Spectro-photo-metric | 0.0003-0.016 ● | 1618-1976 |
| 9. | $P_2O_5$ | Preparation of solution from a test portion by alkaline fusion and by dissolution in nitric acid (pH 2). Formation of the phospho-molybdic complex. Extraction by 2-methyl-propan-1-01. Reduction of the complex by $SnCl_2$ in the organic phase. Spectrophotometric measurement at a wavelength of 730 nm | Spectro-photo-metric | >0.0005 ● | 2829-1973 |
| 10. | Preparation of solution for analysis | Method by hydrochloric acid attack under pressure | | | 2073-1976 |
| 11. | ZnO | Alkaline fusion, treatment of the fused mass with $HNO_3$. Separation of the Zn in the form of thiocyanate by extraction with methyl-isobutyl ketone. Re-extraction with HCl solution. Formation of the PAN-zinc complex. Extraction of the PAN-zinc complex with chloroform and photometric measurement at a wavelength of 560 nm | Spectro-photo-metric | | R 2072-1971 |
| | | Dissolution by attack with HCl under pressure aspiration of the solution in acetylene air flame measurement c. the absorption of the 213.8 nm line emitted by zinc hollow-cathode lamp | AAS | | 2076-1976 |

Table 3.3-7
ISO standard methods used for analysis of alumina (cont.)

| N° | Component | Principle of the determination | Method | Field of application range | ISO Number |
|---|---|---|---|---|---|
| 12. | MnO (Mn) | Dissolution with hydrochloric acid under pressure. Aspiration of the solution in an air/acetylene flame and measurement of the absorption of the 279.5 nm line emitted by a manganese hollow cathode lamp | AAS | 0.00026-0.0065 (Mn 0.0002-0.005) | 3390-1976 |
| 13. | CaO | Alkaline fusion. Precipitation of the calcium in alkaline medium with naphthyl-hydroxamic acid solution. Spectrophotometric measurement of the excess of naphyl-hydroxamic acid at wavelength of 400 nm | Spectro-photo-metric | >0.01 ● | |
| | | Dissolution by attack with HCl under pressure. Addition of Na-ions to stabilize the promotion of the emission of Ca and lanthanum ions or triethanolamine to increase the sensitivity. Aspiration of the solution into acetylene dinitrogen monoxide flame and measurement of the absorption 422.7 nm line emitted by a calcium hollow-cathode lamp. CaO contents greater than 0.03 acetylene/air flame can be used | AAS | >0.003 ● | 2069-1976 |
| 14. | F | Dissolution by attack by H₂SO₄ under pressure. Separation of the fluorine by distillation. Formation of the blue coloured complex between F and alizarin complexone lanthanum chloride. Spectrophotometric measurement of the complex at a wavelength of 620 nm | Spectro-photo-metric | >0.003 | 2828-1973 |
| 15. | B₂O₃ | Dissolution with H₃PO₄, separa-tion of B by distillation as methyl borate. Formation of the red coloured complex between B and curcumin. Spectrophotometric measurement of the complex at a wavelength of 550 nm | Spectro-photo-metric | >0.0006 | 2865-1973 |

**Chemical analysis of sodium aluminate liquors**

In order to characterise the aluminate solutions their main
components and impurities have to be analysed. Caustic soda
($Na_2O_{caust.}$) aluminium ($Al_2O_3$) content and the caustic molar
ratio are determined by thermometric method. Thermometric
titrimeter (THERMATIC) has been developed in ALUTERV-FKI. The
instrument perceives the thermal effect following the chemical
reaction and makes use of it to indicate the end point of
titration. From among the impurities of the aluminate liquors the
determination of iron, fluorine, vanadium, phosphorus, gallium,
zinc, sulphate, chloride and the organic material is of
importance because Bayer process is cyclic, soluble impurities
accumulate in the process liquor stream. Cationic components can
be analysed by spectrophotometric and AAS methods, **while the
anionic components** by classical and chromatographic methods.
Conventional analysis requires different techniques for each of
the anions, the major advantages of these methods are that
usually the equipment is not expensive and the cost per test is
low. The disadvantage of each technique is that it takes   long
analysis time. Ion-chromatography offers a fast technique for the
analysis of inorganic ($F^-$, $Cl^-$, $SO_4^{2-}$ etc.) and organic (oxalate,
formate, acetate, malonate and succinate etc.) ions. Many of the
ions can be analysed simultaneously. The problems to overcome are
associated with the solubility of the samples in the eluents used
for the resolution of all required compounds in complex matrices.

In addition  individual organic components may also be measured
by means of  gas chromatography. Gas chromatography provides a
rapid, accurate method. Sample preparation is labour intensive
and the equipment needs a very good expert to handle.

### 3.3.4 Anions in the Bayer process determined by ion-chromatographyc methods

The term ion-chromatography (IC) means an analytical technique
for separation, detection and quantization of ionic species. The
determination are faster than conventional methods. Ion-
chromatography is a separation technique: analytes of interest
are separated from each other and from most interfering
substances, before quantization, so major ions can often be
analysed sequentially in one run. The sample injected into the
ion-chromatograph and carried through an ion exchange separation
column by an ionic solution termed the eluent. A precision pump
maintains constant flow rate. After separation the ions are
carried by the eluent into a detector which responds to the
amount of each component. The resultant "chromatogram" identifies
each component by retention time and quantization is based on the
magnitude of the response. The most common detection mode being
the measurement of the changes in ionic conductivity of the
eluate.  In ALUTERV-FKI Ltd. there is a Bio-Rad HRLC system as a
non-suppressed ion-chromatograph, used in "isocratic" mode. Ion-
chromatography is now in routine use in our laboratory to analyse

# 3.4 X-RAY FLUORESCENCE SPECTROMETRY

J. Vitéz

## 3.4.1 X-ray fluorescence spectrometry

Following the discovery of X-rays in 1895 by Wilhelm Conrad Röntgen the new type of radiation gained importance in various fields of analytical and materials science. X-ray emission spectroscopy, one of its major applications is a widely accepted method of instrumental elemental analysis. When an element is bombarded with an ionizing radiation, vacancies are generated in its inner electron shells. As the vacancies are refilled with electrons from the outer shells, characteristic X-rays are emitted. X-ray emission spectroscopy is based on the information carried by the wavelength and intensity distribution of this secondary radiation.

### 3.4.1.1 Production of characteristic radiation

For the generation of characteristic X-rays the following methods are commonly used:

- The sample is excited by a focused high energy beam of electrons (*Electron Probe Microanalysis*, EPMA). Useful for the elemental analysis of selected small areas, thus primarily serves research purposes. With the *Particle Induced X-ray Emission* (PIXE) the energy spectrum generated by a particle beam is analyzed. Present nuclear microprobe facilities are not simple and rugged enough for routine analytical use.

- X-rays can be generated by gamma-radiation from radioactive isotopes (e.g. $^{55}Fe$, $^{241}Am$) as well. This method can be applied in portable instruments if only a few predefined elements are to be determined.

- When multicomponent samples are to be analyzed with a higher accuracy, for the excitation of the sample the radiation from an X-ray tube is applied. This method is referred to as the *X-ray Fluorescent Spectrometry* (XRF).

X-ray sources for the use in XRF spectrometry should conform to the following requirements:

- the wavelength of the primary beam has to be shorter than that of the characteristic radiation of all the elements to be analyzed

oxalate, formate and acetate in sodium aluminate liquors.

### 3.3.5 Quality assurance in analytical chemistry

A quality assurance is an analytical protocol. However, there is
a clear need for its wider use by analytical chemists engaged in
analytical measurements. The samples analyzed must be valid if
the results obtained for them are to be intelligently
interpreted. Expressed results should include the average
measured value written with the standard deviation. The
reliability and acceptability of chemical analytical information
depend upon the rigourous completion of all the requirements
stipulated in a well-defined protocol. Such protocols will
describe the documentation requirements of the study including
sampling procedures measurements, confirmation and validation.
Today it is necessary to communicate the results of such
measurements in a way that permits open inspection of their
intrinsic weaknesses and strength. Attainment of a state of
statistical control of the measurement system must be
demonstrated by the analyst. The key role of reliable reference
materials in the validation of analytical measurements cannot be
over-emphasized. There is international standard specification
(Nr. 5725-1981) to determine repeatability and reproducibility
of applied analytical procedures. Cochran's maximum variance test
and the Dixon's outlier test should be carried out to detect and
correct problems.

- high long term stability (usually better than 0.1%) is required

- allow a high voltage operation (at least 60 kV) to achieve high intensity

- primary beam may not contain characteristic radiation

### 3.4.1.2 The spectrometer

The construction of X-ray spectrometers follow two basic design types, the *simultaneous* and the *sequential*. The simultaneous or multichanel spectrometers are equipped with separate channel (*"monochromator"*) for each element to be analyzed. They are characterized by:

- high counting efficiency
- high resolving power
- high long term stability
- high sample throughput.

The sequential spectrometers have a single channel which is tuneable to any of the elements within its detection range. The advantage of this arrangement is the higher flexibility and lower capital cost.

## 3.4.2 Quantitative analysis

Reliability (i.e. accuracy and reproducibility) of the quantitative analysis with XRF spectrometry basically determined by the sample preparation and calibration. These areas deserve a closer look for a better understanding - and a tighter control - of the reliability of the results.

### 3.4.2.1 Sample preparation

Techniques suitable for sample preparation are determined by the physical and chemical characteristics of the sample and the required accuracy of the analytical results. For this reason the contents of this paragraph will be restricted to a general summary of the problem and only the techniques important for the preparation of alumina samples will be discussed in depth.

Techniques available for preparing samples of minerals and ores fit into three main categories:

- powder pellet pressing
- fusing and bead casting
- dissolution.

The main features of this techniques are summarized in Table 3.4-1.

Table 3.4-1
Sample preparation

| | sample quantity [g] | Preparative steps | weigh in | XRF-SPECIMEN additives | preparative steps |
|---|---|---|---|---|---|
| alumina | 25 | ignition 1100 °C 1.5 hour | 6 | boric acid 3 g | pressing 300 MPa 2 min. |
| aluminium hydroxide | 25 | drying in steps ignition 1100 °C 6 hour | 6 | boric acid 3 g | pressing 300 Mpa 2 min |
| zeolite | – | – | 0.8   6.4 g | $Na_2B_4O_7$ $Na_2NO_3$ KI | digestion 1260 °C 9 min |

It is difficult and time consuming to dissolve bauxite and red
mud samples. However they are easily pressed into pellets without
the addition of binding agents. The strength and surface
characteristics (surface finish) of these pellets are suitable
for XRF spectrometry but the mineralogical effect (matrix
interference) prevents their use. This is caused by the
inhomogenity of the sample: the specimen consists of grains of
different chemical composition and crystallographic structure,
which may influence the absorption of the primary beam and the
emission of the fluorescent X-rays. Therefore reliable intensity
measurement can be expected only from amorphous (fused) specimens
of bauxite and red mud. When preparing fused disks as specimens
for analytical purpose, the following factors are to be
considered:

- the physical characteristics of the sample: grain
  size, ignition losses
- the type of the fusing agent (e.g. lithium or sodium tetra-
  borate)
- the sample to fusing agent ratio
- temperature and duration of the annealing
- storage of the fused beads.

For the preparation of the fused beads laboratories are equipped
with automated instruments.

When analyzing alumina for the minor (contaminating) components,
one may regard it as a chemically homogenous powder. Because of
the low concentration of the contaminants any unnecessary
dilution of the sample is to be avoided. Thus the only acceptable
technique for preparing alumina samples is the pellet pressing.
Pressed pellets of acceptable mechanical stability can not be

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prepared from alumina without the addition of a binding agent.
The use of boric acid as a binder results in pellets of
appropriate strength.

For preparation of pressed pellets the following factors are of
vital importance:

- the physical characteristics of the sample (grain size, crystal
  structure)
- the type and purity of the binder
- the sample to binder ratio
- pressure and duration of the pellet pressing.

For the analysis of aluminium hydroxides and aluminium hydroxide
based products there is a choice of two possibilities:

- pelletized specimens are prepared similarly to the alumina    s
  amples and analyzed using a different analytical program
- the samples are ignited to alumina and then analyzed
  identically.

The second option provides several advantages. First of all, only
one analytical procedure is needed. On the other hand, as the
water is driven out of the samples, the sensitivity of the
analysis improves as the concentration of the contaminants is
elevated.

The sample crystallinity was shown to exert the highest impact on
the XRF analysis results of alumina and aluminium hydroxide type
of materials. The intensity of silicon, titanium, vanadium and
calcium fluorescence varied as a function of $\alpha-Al_2O_3$ contents of
the samples. Therefore specimens of unknowns and standards with
identical crystallinity are to be prepared using appropriate heat
treatment.

No grain-size effect was detected, but the boric acid binder
enhances (e.g. P, Si) or reduces (e.g. V, Mg) the intensity of
some elements. A constant binder-to-sample ratio is to be adhered
accordingly.

Synthetic sodium aluminium silicates, produced at a number of
alumina plants, can also be regarded as chemically homogenous
powders. However they are analyzed for major components, not for
contaminants. Thus dilution of the matrix is not only acceptable
but favourable. Bead casting is the best choice for these
samples.


### 3.4.2.2 Methods of concentration determination

If a flat sample with a thickness higher than the critical is
presented to a primary beam of X-rays with intensity of $I_o$, the
$I_i$ intensity of the fluorescent $K_\alpha$ radiation from the element $i$
is given by the Equation {1}:

$$I_i = C_i - I_o - G_i \qquad\qquad \{1\}$$

where    $C_i$ is the concentration of element $i$
         $G_i$ is the 'excitation coefficient'

The *excitation coefficient* is a function of the absorption coefficient of the matrix for the exciting and for the fluorescent ($K_\alpha$) radiation as well, along with the probability of the $K_\alpha$ generation. This shows that mathematical models based on fundamental parameters (i.e. using calculated $G_i$ values) are beyond reach for routine analytical work.

As far as the composition of the sample is known, or it contains an internal standard of known concentration, the value of the $G_i$ or the ratio of the $G_i$ values can be determined and then the concentrations calculated. However these methods are not widely used for routine analytical purpose.

Typically a series of standard samples of known chemical composition is used for the determination of calibration curves covering the required range. This approach in combination with the high long term stability of the up-to-date instruments ensures appreciable results, but it should rely on reference materials with known composition satisfying the following requirements:

- standard reference samples with appropriate documentation
- round-robin analyzed according to international standards
- display a long term stability
- their chemical composition and physical properties should correspond to that of the samples to be analyzed.


### 3.4.2.3 Reliability of the results

Reproducibility of the analytical results is characterized by the *standard deviation* ($\sigma$). $\sigma$ is a measure of the statistical fluctuations of the results for a given type of analysis, chemical element and concentration:

$$\sigma = SQR \frac{\Sigma(C_i-C)^2}{n-1} \qquad M,Z,C = const. \qquad \{2\}$$

where M = matrix
      Z = atomic number
      C = concentration


The standard deviation is influenced by the concentration as follows:

$$\sigma = k_i - C^{k2} \qquad M,Z=const. \qquad \{3\}$$

According to our experience the value of the constant $k_2$ can show

fairly high deviation from 0.5, its accepted value. When the effect of the matrix on the standard deviation is to be considered, the average atomic number of the matrix ($Z_M$) can give the clue:

$$\sigma = \frac{1}{Z_M^2} \ k_i \ c^{k2} \qquad\qquad Z = \text{const.} \qquad\qquad \{4\}$$

The effect of the atomic number on the $\sigma$ is given by the formula:

$$\sigma = k_1 \frac{1}{Z^2} + k_2 \qquad\qquad M,C = \text{const.} \qquad\qquad \{5\}$$

Statistical characteristics and calibrated concentration ranges for the analytes of interest are given in Tables 3.4-2 and 3.4-3.

### Table 3.4-2
**Characteristics of the XRF-tests for alumina and aluminium hydroxide**

| | Calibrated concentration range (%) | Standard deviation of the determinations (*) (± abs. %) | Deviation from the results from the classical analytical methods (**) (± abs. %) |
|---|---|---|---|
| $SiO_2$ | 0.010 - 0.028 | 0.0015 | 0.003 |
| $Fe_2O_3$ | 0.018 - 0.060 | 0.0008 | 0.001 |
| $TiO_2$ | 0.002 - 0.011 | 0.0007 | 0.0005 |
| $V_2O_5$ | 0.002 - 0.012 | 0.0007 | 0.001 |
| $P_2O_5$ | 0.0002 - 0.0008 | 0.0003 | 0.0005 |
| CaO | 0.008 - 0.036 | 0.005 | 0.003 |
| MgO | 0.0025 - 0.0037 | 0.0005 | 0.0005 |
| CuO | 0.0008 - 0.0012 | 0.0001 | 0.0005 |
| ZnO | 0.010 - 0.028 | 0.0002 | 0.001 |

\* = at the middle of the concentration range
\*\* = based on comparative series analysis

### Table 3.4-3
**Characteristics of the XRF-tests for zeolite**

| | Calibrated concentration range (%) | Standard deviation of the determinations (± abs. %) | Deviation from the results from the classical analytical methods (± abs. %) |
|---|---|---|---|
| $SiO_2$ | 30-40 | 0.08 | 0.3 |
| $Al_2O_3$ | 18-30 | 0.3 | 0.5 |

# REFERENCES

[1] Jenkins, R.: *X-Ray Fluorescence Spectrometry*; John Wiley & Sons, New York, 1988.

## 3.5 MINOR AND TRACE ELEMENT ANALYSIS OF CO- AND BY-PRODUCTS IN BAYER ALUMINA PRODUCTION BY ATOMIC ABSORPTION SPECTROMETRY

**M. Borsodi**

Atomic Absorption Spectrometry (AAS) as an analytical technique developed in the last  fifties has been introduced in alumina industry quite rapidly for its relatively low expenses and simple sample preparation (in some cases solution of sample can be used directly without any other separation procedure). This technique can be applied mainly if analytical problems need complicated procedures, i.e. determination of Mg, Zn, Na.

### 3.5.1 Working Principle of AAS Units  [1, 2]

The AAS technique is based on measuring the "peak absorbance" of a spectral line by using a spectral light source emitting a sharp line. The absorption coefficient, the total absorption and the absorbance quantities are used to relate phenomenon observed in practical measurement of atomic absorption as relationship between concentration and energy absorbed.

*Absorption coefficient, $k_v$*

The absorption coefficient at a discrete frequency, $v$, is defined by the equation:

$$I_v = I_v^{o} e^{-kvL} \qquad \{1\}$$

where, $I_v^{o}$ and $I_v$ are the initial and final intensities of radiation of frequency $v$, passed through an absorption cell of length $L$. (A plot of $k_v$ against frequency represents the profile of the absorption line.)

*Total Absorption Factor, $A_T$*

It is defined in terms of the total amount of light passing through the cell at a particular spectral line. The intensities used are integrated with respect to the complete absorption line, and are given by :

$$A_T = \Delta I/I_o \qquad \{2\}$$

where    $\Delta I = I_o - I$, and I is the amount of radiation leaving the

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cell. The term percent absorption used in atomic absorption is
defined as [( $\triangle I/I_o$) x 100].


*Absorbance, A*

It is defined as:

$$A = \log_{10} (I_o/I) \tag{3}$$

where $I_o$ and $I$ are the incident and transmitted intensities at
the absorption cell.

The principle of operating an AA spectrophotometer is that
hollow cathode lamp is used as resonance line source. The light
beam from this source consists of resonance radiation. (The line
that represents a transition between the ground state and a
higher state is known as resonance line.). This resonance
radiation, which is electronically or mechanically pulsed, passes
through the atom reservoir (flame or furnace) where they may be
absorbed by atomic vapour. Analyte atoms are produced thermally
in the atom reservoir. The ground state atoms, which predominate
under the experimental conditions, absorb resonance radiation
from the lamp, reducing the intensity of the incident beam. A
monochromator isolates the desired resonance line and allows to
fall on a photomultiplier tube. An electrical current, whose
magnitude depends on the light intensity is produced. The
electronics of the unit are designed to respond selectively to
the pulsed radiation from the radiation source, and measure the
amount of light attenuation in the sample cell, and convert these
readings to the actual sample concentration.

Since the light source provides the resonance line of a single
element, in general, this is not a multielement method.
Development of simultaneous multielement AA equipment has been
hindered by problem with optical alignment of components, the
need for different operating conditions for many elements, and
relatively short linear range of calibration curves.

Due to the small number of resonance lines, spectral interference
has to be consider only rarely in AAS.

## 3.5.2 Instrumentation [1, 3, 4]


In every photometer intended for AA, the following instrumental
systems may be distinguished.


*Emission system*

Basically, the system consists of  a source. The most common
source for AA measurements is the **hollow cathode lamp**, which
consists of an tungsten anode and a cylindrical cathode sealed in

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a glass tube that is filled with neon or argon at a pressure of 1-5 torr. These lamps can produce resonance radiation of narrow linewidth typically <0.01 A, the cathode constructed from the metal or an alloy of the element being determined. If the cathode consist of a mixture of several metals such lamp permits the analysis of more than a single element with it (multielement lamp). In routine operation of an AA spectrophotometer the use of multielement lamp is convenient, easy and economical.

For certain elements (As, Se, Te, Sn, Pb) higher intensity of emitted light can be achieved when applying **electrodeless discharge lamps**. These lamps are constructed by sealing a small amount of the pure metal or pure metal salt of element interest into a silica bulb together with an inert gas at low pressure. This bulb is placed in the cavity of radio frequency coil powered at 27 MHz. The components are than built in a lamp body of size similar to hollow-cathode lamp. The electrodeless discharge lamps provide radiant intensities that are usually one or two orders of magnitude greater than their hollow-cathode counterparts.

Sodium and potassium hollow-cathode lamps are often unsatisfactory. The **vapour discharge lamps** are available for these elements.

With the modern equipments using modulation of the heating currents of lamp so that intensity fluctuates at constant frequency, a long-life lamp (about 2000 working hours) can be achieved and the interferences caused by emission of radiation from flame can be eliminated.


*Absorption system*

The main component of this system is the *atomic vapour* which is to exercise its absorption on the beam of radiation from the source. The absorption system thus comprises all the instruments and accessories that are involved in generating the atomic vapour, starting with the means of introducing the sample; in these parts it is necessary to preserve a constant ratio between the concentration of the analyte in the sample and that of the atomic vapour.

- In the case of photometers that **use a flame**, the absorption system consists of the flame, the burner that supports it, the sprayer, capillaries, tubes or injection system for introduction of the sample, flowmeters to control the gases, turning mechanisms for rotating the burner, devices for adjusting the height of the burner. Apart from viscosity of the solution to be tested and material quality of component and matrix to be measured the efficiency of atomization additionally depend on the designe of atomizer, the rate of atomization, the temperature depending on the chemical composition of the flame and the character of the flow of the flame (construction and shape of the burner head). The atomizing gas burner system is of decisive importance concerning the accuracy of the measurement.

- If photometers that **do not use a flame** than resistance heated graphite tube, heated carbon rod or filament furnace (ETA), flash-heating chamber or electrodes in spark-in-spray techniques generate the atomic vapour.

The ETA and later techniques are generally used for trace analysis.

Further advantage of these is that small amounts of material are required.

The auxiliary optical components, such as lenses for collimating the beam, mirrors for the multi-path devices are also included in the absorption system.

*Selection system*

This refers only to the equipment for spectral selection. The system includes both the optical devices for spectral selection (filters, monochromators with prism or grating) and mechanical accessories (slits, turning mechanisms, and means for reading wavelength settings and slit widths).

*Photometric system*

The measurement of light intensity is performed with a photomultiplier. The system includes all the electronic equipment necessary for supplying the photomultiplier, amplification, rectification, direct reading, scale expansion. The photometric system is capable of discriminating between the modulated signal from the source and the continuous signal from the flame.

These devices produce signals $I_o$ and $I$ proportional to pulse heights of the respective signals. Log amplifiers are used to process the signal which is fed into the differential inputs of an operational amplifier, which performs the required subtraction,

$$A = \log (I_o/I) = \log I_o - \log I \qquad \{4\}$$

and a readout in absorbance is obtained.

Modern devices, in general, provided digital or screen display of extinction and in that time enable auto-zero setting and measurement under various integration times. Direct electronic display of concentration and curve correction possibility required from time to time is also ensured.

The AA-instruments generally can also be used in emission mode as flame photometers. The instruments for flame emission work are similar in design to flame absorption instruments except that the flame now acts as radiation source (the hollow-cathode lamp and chopper are therefore unnecessary). For emission flame

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photometry, use is made of radiation emitted by a sample introduced into the flame and excited in it. The most important uses of flame photometry have been in the determination of sodium, potassium, and lithium.

There are two basic types of AA spectrophotometers: the single-beam and double-beam.

## 3.5.3 Sample preparation for AA-measurement [4 - 6]

Samples arrive in analytical laboratory usually either as solids or liquids and the analyst is required to determine the concentration of one element or series of elements. The sampling procedure is usually out of the analyst's control but is very important and if incorrectly carried out it can lead to errors in the final results. That is why it is recommended as far as possible to make sure that the analysed sample is homogenous, uncontaminated and representative of bulk material.

A disadvantage of flame AA-method is the requirement that the sample be introduced into the excitation source in form of solution, most commonly an aqueous one. Unfortunately many materials of interest, such as minerals or i.e. the co-, and by-products in Bayer alumina production are not directly soluble in common solvents, and extensive preliminary treatment is often required to obtain a solution of the analyte in a form ready for atomization.

Indeed the decomposition and solution steps are often more time-consuming and introduce more errors than the AA-measurement itself.

One of the advantages of electrothermal atomization is that some materials can be atomized directly thus avoiding the solution step. For example liquid samples as aluminate liquors can be pipetted directly into the furnace for ashing and atomizing. Moreover some of solid samples (i.e. alumina) can be weighed directly into cup type atomiser or into tantalum boats for introduction into tube type furnaces or can be pipetted into the furnace in suspension form.

**Liquid samples** are relatively easy to analyse. The aqueous solution can often be analysed without any further treatment provided that the total dissolved solid content does not exceed about 2% w/v.

- If the concentration of the analyte element is too high for accurate measurement then simple dilution with an appropriate solvent to reduce the analyte concentration within the analytical range of instrument is usually sufficient. In certain cases, for example, determination of zinc content of aluminate liquor after aciduating the sample can be directly atomized in the AA-unit.

- If the element of interest is present in a concentration too low for measurement than some kinds of preconcentration may be necessary.

- If the sample matrix interferes in the determination than it may be necessary to separate the analyte from the matrix before the measurement is carried out.

**Solid samples** will require some form of dissolution procedure prior to measurement. The requirements for dissolution procedure will depend on the type of sample and of elements to be determined. Therefore total dissolution of the sample may not always be necessary, for example in the case of "quick" sodium content determination of red mud.

- In the simplest case for water soluble salts (i.e. aluminium sulphate) distiled water can be used as solvent.

- At the other extreme, fairly drastic techniques must be used such as pressure dissolution or fusion for refractory compounds (alumina, zircondioxide).

Generally, the simplest possible procedure for that particular sample should be employed.

The following types of dissolution procedures are usable for solid co- and by-product samples :

- Aqueous dissolution: for aluminium sulphate

- Dilute acids (HCl, $HNO_3$ or $H_2SO_4$) dissolution: for some kinds of aluminium hydroxide, and vanadium pentoxide

- Mixed acids /conc.acids ($HCl+H_2SO_4$) dissolution: for gallium and vanadium pentoxide.

- Pressure dissolution :

= in teflon lined bomb with mixture of hydrochloric and sulphuric acid for alumina

= in microwave oven a specially designed microwave digestion vessel with a mixture of suitable acids for some kinds of alumina, zeolites,

= wet ashing (HF and $H_2SO_4$ mixture) for some kinds of aluminium hydroxide, zeolites, zircosites, mullites

- Fusion dissolution :

the sample fused with an alkaline carbonate or hydroxide is usually mixed with borate to act as flux. The type of flux depends on basicity of the sample. NaOH or $Na_2CO_3+H_3BO_3$ or $Li_2B_4O_7$ can be used for different kinds of alumina, aluminosilicates, ziconiumdioxide and vanadiumpentoxide.

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Though fusions are the easiest and the most successful way of
achieving dissolution of the sample,  the extra salt content
introduced by the flux can pose problems. In flame AA it is
desirable to keep the salt content below  3% w/v and in furnace
AA the salt content is even more critical. If these requirements
can not be met by the fusion process, than it may be necessary to
use another dissolution method.

Although in most cases the sample is in solution, all that
remains is to make the sample up to an accurate volume with a
suitable solvent, yet sometimes further treatment is necessary.
These cases are when interferences occur. Interferences can
occasion problems in AA analysis especially when graphite furnace
is used. Consequently it may be necessary to separate the analyte
of interest from the sample matrix.

Available separation techniques can be described as follows

- Coprecipitation of the analyte with collector. The principle of
  this technique is based on the fact that certain elements
  precipitate selectively and qualitatively at particular pH. The
  analyte of interest is precipitated with a suitable collector
  and they are both filtered and dissolved in acid (i.e. gallium
  on aluminium-hydroxide from aluminate liquore)

- Use of ion-exchange chromatography. Various anionic and
  cationic resins are commercially available and are relatively
  straightforward to use.

- Solvent extraction. The most commonly used solvents are MIBK,
  and APDC because a wide range of metals can be chelated and
  extracted with high degree of efficiency.

In most cases the above listed methods can be used both for
separation and preconcentration techniques.

In the course of all possible kinds of applied treatments
(dissolution, fusion, separation or preconcentration) the samples
may be contaminated by the reagents used in respect of analyte.
Contamination must be avoided and the acids and all reagents used
must be of AnalaR grade. For some trace elements it may be
necessary to use Suprapure grade reagents.

### 3.5.4 Methods of concentration determination. [2, 3, 5]

*Measurement*

The solution of adequately prepared sample are atomized in the
burner head by use of different gas streams depending on the
component to be tested. Gas mixtures frequently used for the
investigation are

- air / acetylene

- $N_2O$ / acetylene.

The magnitude of the absorption for given concentration in the sample supplied to the instrument depends upon an aggregate of experimental conditions. Various factors greatly affect the magnitude of absorption. The selection of instrumental and operational conditions can, within certain limits, reduce or increase the response obtained. A change in response is produced by variation of any the instrumental or operational conditions (current supply to emitter unit, pressure and flow-rates of the gases feeding the flame, the path of the beam through the flame, sample flow-rate etc.).

*Evaluation*

In qualitative work a linear relationship is used which, in its simpler form can be expressed as:

$$A = m * C \qquad\qquad \{5\}$$

where A is absorbance, C is amount of the absorbing species in the light path.

The relationship between the absorption indicated by the instrument and the concentration of the analyte element, which produces it, is established in the calibration procedure.

Normal procedure using *calibration curve*. A calibration curve covering the range of concentrations found in the sample should be prepared. Usually a series of two to five known standard solutions of the element to be determined must be prepared. This method is used in the absence of interferences and under control conditions. Since the working curve changes from day to day, the instrument should be calibrated for each set of samples. It is generally preferable that calibration solution be prepared in a way that they have same relative concentrations of reagents used for dissolution (if any) and similar concentrations of the major components of the solution, because the maximum accuracy can be obtained by matching the matrix of samples and the standards. Viscosity of sample and calibration solutions must be similar so that both types of solution give the same uptake rate.

*Standard addition method* widely used in AAS. This method is **applied only** when the calibration curve is linear over the region of interest and background correction is made. This method compensates for physical and chemical interferences of the sample matrix by addition of known quantity of standard to the sample. Absorbance is measured for the sample first and then for the sample with added aliquots of standard. Three or four measurements are sufficient to provide greater accuracy. The main advantage of this method is that matrix matching is achieved automatically. This method should be used for the unknown sample matrix and for samples containing a low concentration of analyte elements in a large amount of varying matrix constituent. In a

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usual standard addition method, the first sample aliquot is
diluted to volume, while the second and third ones are spiked
with a standard solution and then diluted to a similar vclume.
Samples should be spiked in such a way that the second solution
has a concentration of approximately twice that of the unknown
and the third, three times that of unknown. The absorbance of
each solution is plotted on a calibration curve and the
concentration of the sample is graphically derived by
extrapolation to zero absorbance on the negative X axis.

### Internal standardization method

The usual procedure is to add tc each of the sample and standard
solutions a known amount of an internal standard element and
measure the absorption signals for both simultaneously. The ratio
of the signal intensities is then measured as a measure of
analyte concentration. This method permits similar compensation
for errors caused by variation in nebuliser and flame
characteristics.

## 3.5.5 Sensitivity, detection limit and accuracy in AAS [2, 4]

Atomic absorption spectroscopy is a sensitive means for the
quantitative determination of more than 60 metals or metalloid
elements.

### Analytical sensitivity

The analytical *sensitivity* for determination of an element by AAS
with given instrument is defined as the concentration of the
element ($mg/dm^3$) which produced a 1% absorption signal (0,0044
absorbance) under optimum conditions. The analytical sensitivity
depends on absorption path length and nebulisation/atomization
efficiency.

### Detection limit

This term is used to define the lowest detectable concentration
of the element in the sample solution and depends on the
instrumental stability. Detection limit may vary from instrument
to instrument and from one type of sample matrix and solvent to
another for the same element. Fluctuation can result due to
source, flame, and detector noise.(The source noise is negligible
in double beam instruments).

For many elements, detection limits for AAS with *flame*
atomization lie in the range of 1 to 20 $ng/cm^3$ or 0,001 to
0.020ppm; for *electrothermal* atomization 0.002 to 0.01 $ng/cm^3$ or
2x10-6 to 1x10-5 ppm. In a few cases, detection limits well
outside of these ranges are encountered.

*Accuracy*

In quantitative measurements there are two types of errors :

1. Random errors, which are indeterminate and caused by uncontrollable variables. A measure of random error is given by precision of a measurement.

2. Systematic errors, which are determinate and attributable to a definite cause. These errors can be constant from sample to sample, proportional to the size of the sample, or may vary in a complex way. The accuracy of measurement is determined by systematic errors.

Under usual conditions, the relative error associated with flame AA is of the order of 1-3%. With special precautions this can be lowered to a few tenth of one percent. In casess of nonflame atomization the accuracy usually exceeds those for flame atomization by factor of 5-10.

# References

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# 3.6. ANALYTICAL SPECTROSCOPY

A. Farkas

The analytical spectroscopy uses of outgrowths of interaction between the matter and the electromagnetic radiation for the determination of the qualitative and quantitative composition of a sample. Groups of clustering are emission, absorption, reflection and fluorescent spectroscopy. Clustering by the sensors are spectroscopy, spectrography, spectrometry.

An **excited atom** tends to assume lowest energy level by the radiation of a photon. Photon is a quantified pocket of energy.

Exciting the core shells the emission is in the range of XRF, exciting the valence shells it is in VIS, UV and VUV range. In the optical range the following materials absorb the light below the wavelength given here:

- glass    < 310 nm
- air      < 180 nm
- silica   < 160 nm.

The optical path must be filled with a non absorbing gas or vacuum for working below 190 nm . The different instrument-names e.g. quartz spectrograph or vacuum spectrometer show the optical range.

## 3.6.1. Excitation

The analyte is in the spectroscopic source like an **"atomic vapour"**, however the samples are in solid, powder, liquid or rarely gas state.

**Solid samples** can be transported to source and excited by:

- Spark and arc stand
- Laser atomisator
- Conductive solid nebuliser
- Glow discharge lamp
- Electro - Thermal Atomizer
- Special methods for solid or slurry sample  intake.

The **solutions** have to be nebulized, desolvated, atomized and then excited. Nebulisers may be:

- Meinhard concentric (Figure 3.6-1)
- Babington grooved (Figure 3.6-2)
- Ultrasonic

- Thermospray
- High pressure
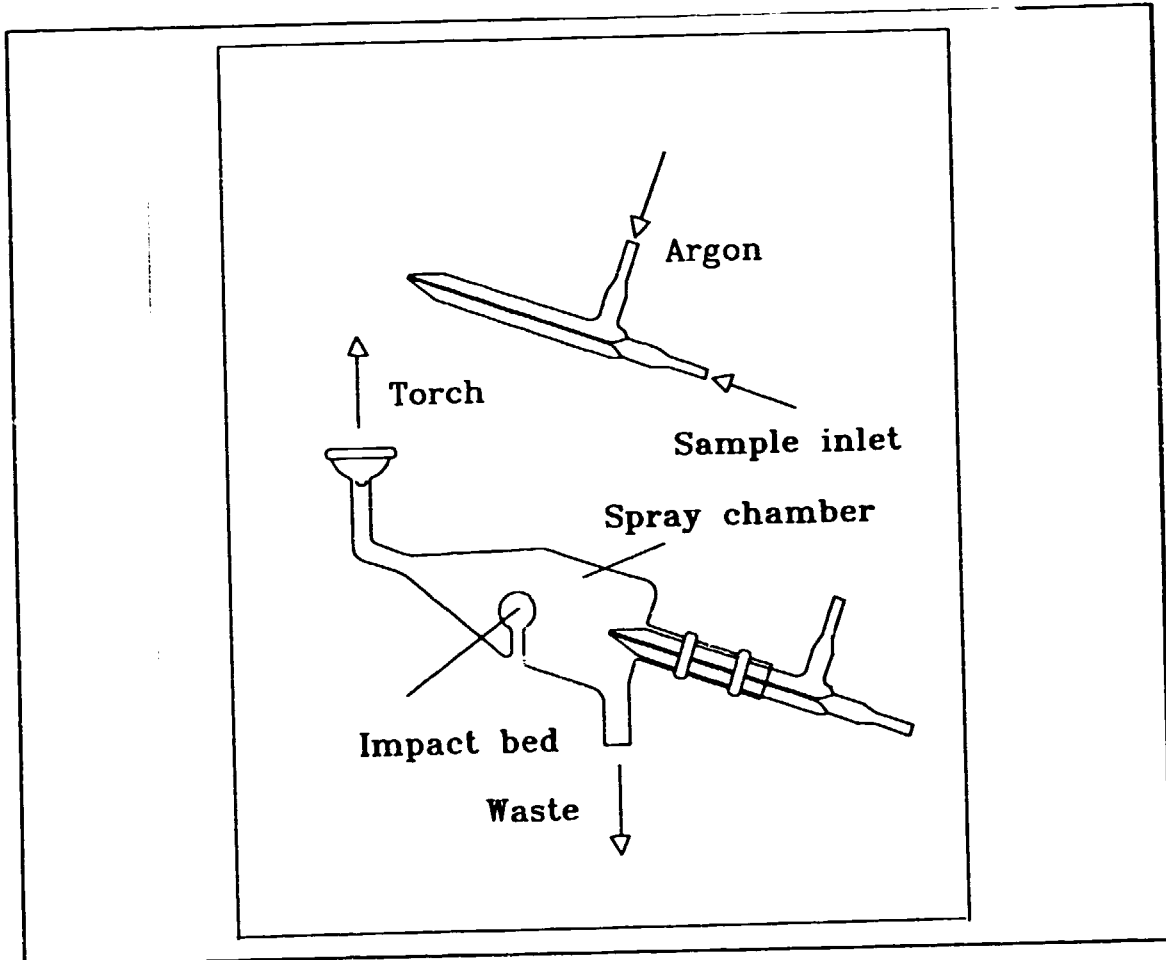


Figure 3.6-1
Meinhard nebuliser
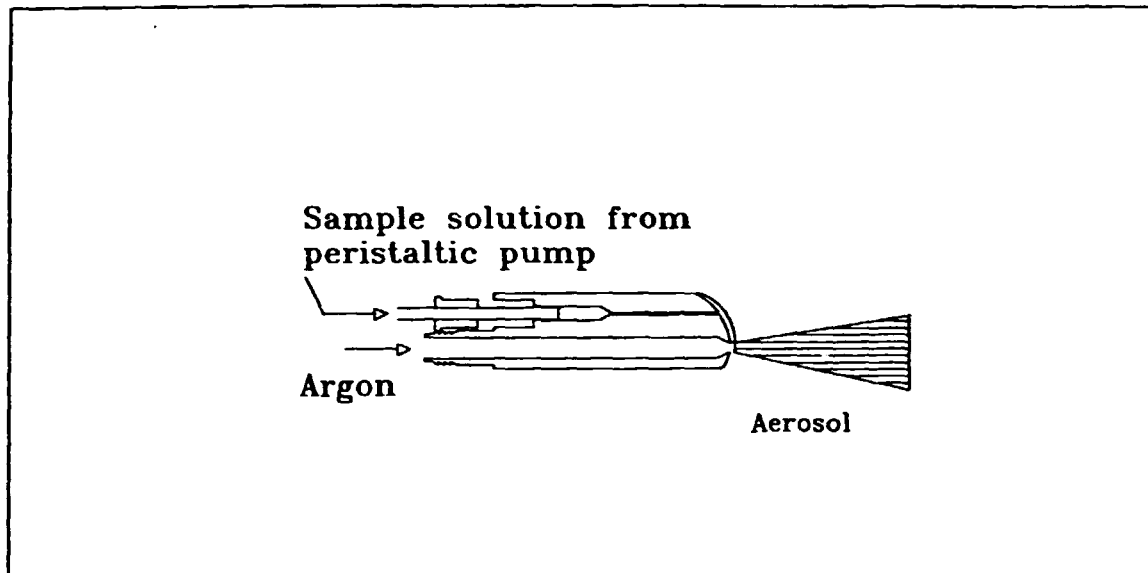
**Figure 3.6-2**
**Babington grooved nebuliser**

A special tool for the determination of hydride producing elements is the hydride generator in which case the analytes are in **gas** state (Figure 3.6-3).
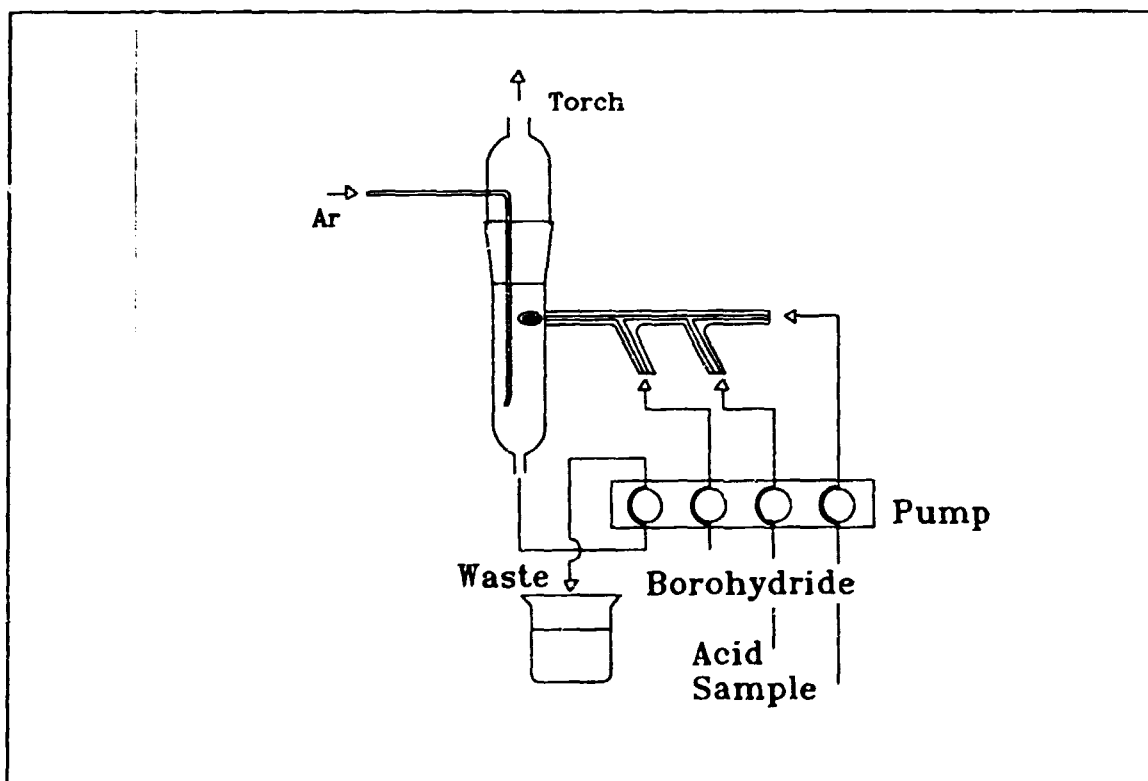


**Figure 3.6-3**
**Hydride generator**

The **plasma** in arc, spark and ICP torch is for desolvating,
atomizing and exciting. ICP torch can be seen in (Figure 3.6-4).
The plasmas differ from each other in excitation and ionisation
degree due to different temperature, gas and live time.
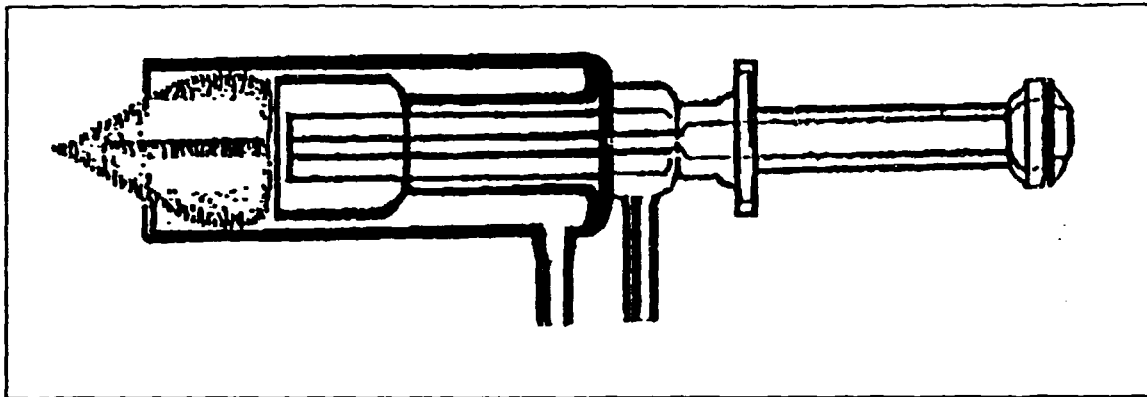


Figure 3.6-4
ICP torch

Increasing the degree of ionisation the number of spectral lines
becomes greater. The atomic and ionic spectra of a given element
are compared to each other and the ion spectra contain more lines
then the atomic spectra. The intensity of the former is much less
than that of the latter [1].

At a given photon energy, i.e. at a given wavelength, the
intensity depends on the number of photons produced during a
unite of time. The number of photons is a function of the number
of analyte particles present in an unit volume of plasma.

$$I = f(c) \qquad\qquad \{i\}$$

The intensity quantifies the concentration. As the relationship
is extremely complex to be derived theoretically, in practice it
is established empirically with the aid of samples of known
composition (Figure 3.6-5). The process is the so called
**calibration.**
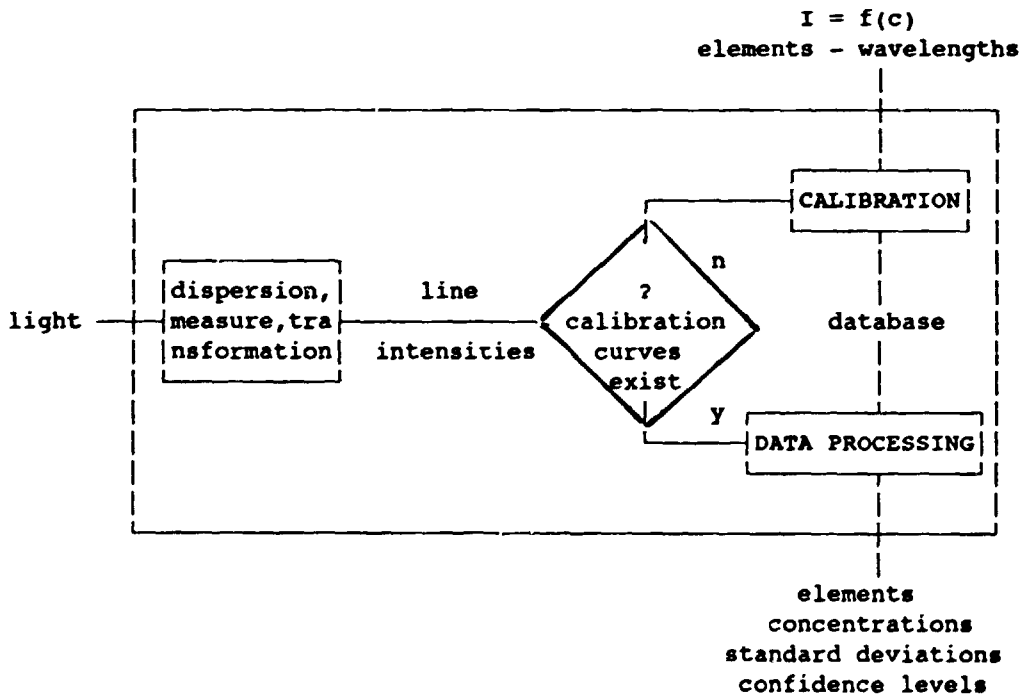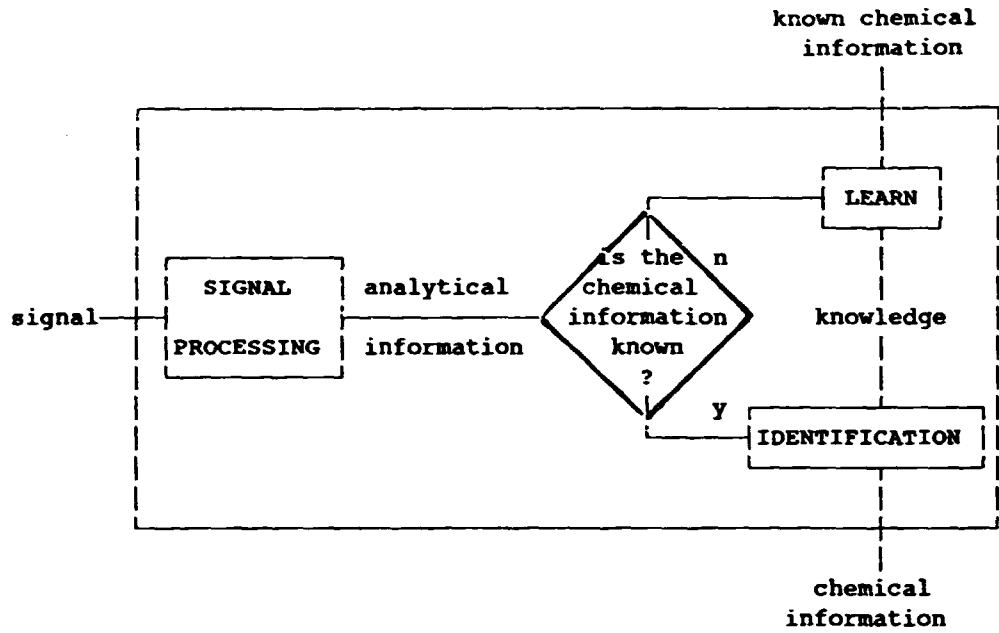
Figure 3.6-5
Producing Chemical Information

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## 3.6.2. Dispersion of the light

The light produced by excitation is composed of rays of different
wavelength. Mono- and polychromators resolving the light into
components are called dispersion devices. The devices are based
on three different principles:

-- refraction of light ( Prisms )
-- interference due to light diffraction ( Grating )
   absorption of light ( Filters )

The angle dispersion of a grating is:

$$m\lambda = b \ (\sin \alpha + \sin \beta) \qquad \{2\}$$

where   $m$    spectral order
        $b$    grating constant
        $\alpha$    incident angle
        $\beta$    diffraction                              angle
        $\lambda$    wavelength

Known the focal length of the optical system the linear
dispersion can be calculated. It is an important parameter
choosing a spectrometer.

## 3.6.3. Detection

The **spectroscopy** means comparing similar (or homologous) line
pairs by visual observing.

In a classical **spectrography** the spectrum is recorded onto a
photo-plate or film. It is possible to make qualitative analysis
from the recorded spectrum by the help of a wavelength standard
spectrum.

Quantitative results can be determined from measured blackening
by a micro-photometer. The method uses Standard Reference
Materials for the calibration. There is not a linear function
between the intensity of a spectrum line and blackening. There
are some evaluation methods for the linearization [5].

**Spectrometry** is the electronic measurement of the intensity of
spectrum lines by photoelectron multipliers (Figure 3.6-6) or
photo-cells, photo-diodes or other semiconductor materials.
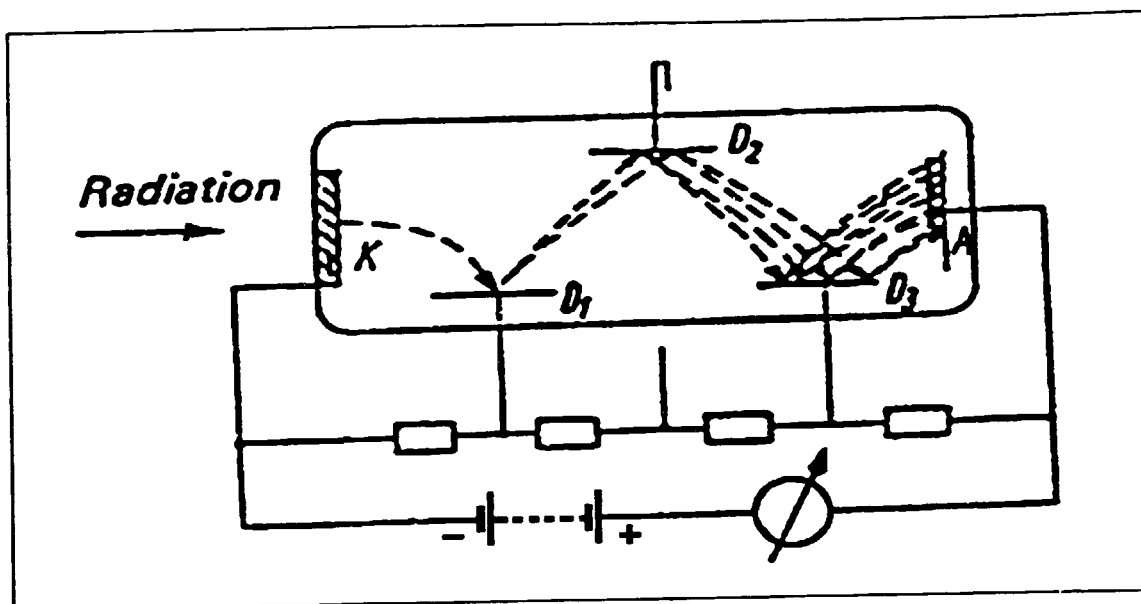
Figure 3.6-6
Photoelectron multiplier tube

## 3.6.4. Data acquisition

In **quantometer**s the analog-to-digital conversion, digital signal processing, calculations, recording and handling measured data are controlled by a microprocessor or computer. They carry out automatic quantitative analysis and yield concentrations if it has been calibrated.

## 3.6.5. Spectrometry in alumina plants

Analytical emission spectrometry is series of high performance methods. The performances of methods are comparable with regard to the analitical task only.

### 3.6.5.1 Spectrography

The method is used for the determination of main and trace elements of :

- bauxite
- red mud
- alumina
- corundum
- hydrate
- aluminate liquor
- chriolite and $AlF_3$

- ash of anodic mass
- aluminium
- high purity aluminium
- aluminium alloys
- gallium and high purity gallium
- qualitative analysis of environmental samples
- qualitative analysis of unidentified materials.

The advantage of the technique is the spectrum recorded for ever. The disadvantages are, that the photographic plates have to be stored in proper circumstances, they have to be developed, blackening to be measured and the concentration calculated [1-4].

The spectrographs work with electric arcs and sparks. The electric spark or arc needs conductive materials. The explanation for nonconductive matrixes is the mixing with high purity graphite or using "well-type" electrodes. The suitable exciting mode for a given matrix can be chosen on experimental way or from tables (e.g. see Table 3.6-1). Spectrographic quantitative analysis based on self-made synthetic calibration specimens or Standard Reference Materials.

**Table 3.6-1**
**Excitation modes for different needs [1]**

| Excitation modes | reprodu- cibility | detection limit | duration of discharge |
|---|---|---|---|
| a.c. Arc continuous | | | $10 - 10^2$ |
| a.c. Arc interrupted | | | $10^{-1} - 1$ |
| d.c. Arc continuous | | | $10^{-3} - 10^{-2}$ |
| d.c. Arc interrupted | | | $10^{-3} - 10^{-2}$ |
| spark low volt high selfinduction | | | $10^{-4} - 10^{-3}$ |
| spark low voltage L=0 | | | $10^{-5} - 10^{-4}$ |
| spark medium.volt.high selfinduct | | | $10^{-5} - 10^{-4}$ |
| spark medium voltage L = 0 | | | $10^{-6} - 10^{-5}$ |
| spark high.volt.big selfinduct | | | $10^{-6} - 10^{-5}$ |
| spark high.volt. | | | $10^{-7} - 10^{-6}$ |

For the recording of spectra three-grade filters can usually be used, because of the sensitivity of photoplates. The composition, the temperature and the duration of the development, together with the type of the photo-plates should be constant.

The evaluation of the plates can be divided into three phases: measuring of blackening, calibration of emulsion, determination of concentrations.

### 3.6.5.2. Optical Emission Spectrometry

The OES method involves burning a small quantity of a sample using electric spark and measuring the intensity of the light produced at specific wavelength. In order to obtain this analysis

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the spectrometer has to be first calibrated by burning standards.
The spectrometers build for certain job or jobs. Generally one or
a couple of limited excitation modes are built in a spectrometer.

Spectrometers are used for analysis of various metals and ores
similar to spectrographs. Analysis of ores oscillatory type spark
is needed with graphite electrode [6]. A simplified block diagram
of a spectrometer can be seen in Figure 3.6-7.
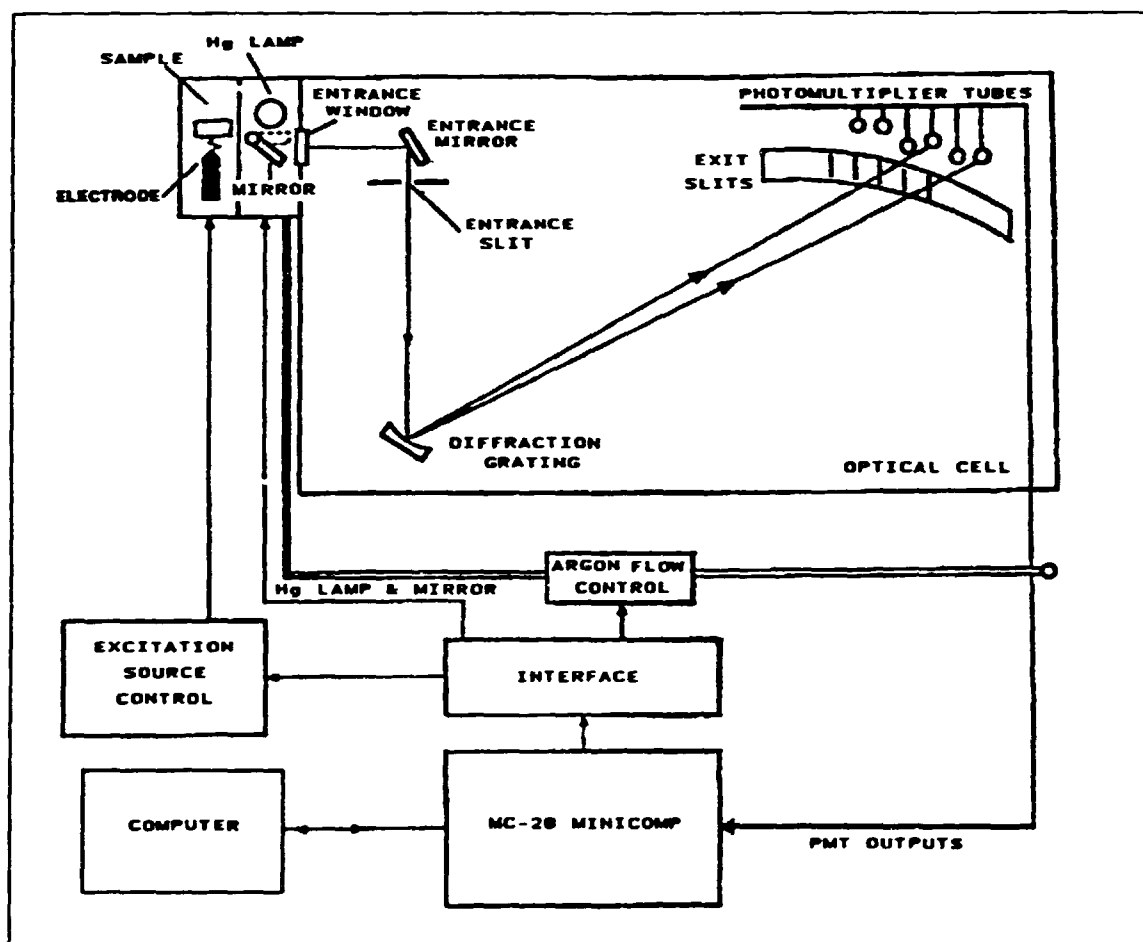


Figure 3.6-7
Optical system of a spectrometer

## 3.6.5.3. ICP optical emission spectrometry

Inductively coupled plasma spectrometers are used mainly for
analysing solution samples. Different nebulisers are used with
forced or self fed in a spray chamber with an impact bed to
separate the bigger particles from the sample spray. The inner
(or sample) gas purge the vapour to the centre of the torch where
the argon plasma is on. The emitted light can be treated in
similar way like spark spectrometry. Due to continuous sample
inlet line-intensities can be measured by simultaneous or
sequential spectrometers.

The ICP instruments can be used properly for analysis of:

- Bauxite
- Alumina
- Alumina hydrate
- Aluminium sulphate
- Aluminium
- Aluminium alloys
- High purity gallium
- Other samples

Analysis of bauxite and high purity metals are developing. Arsenic in aluminium sulphate is determined by a method of hydride generation. Important step before the hydride generation is the reduction of ions existing in III and V valence state as well. For the determination of trace elements in high purity Ga an enrichment technique was developed on Hyphan-cellulose ion exchanger. Analysing of traces in water can be analysed by the aid of a ultrasonic nebuliser.

For the analysis of an unknown or new material an apropriate method and spectral line have to be selected first. The chosen line must be checked to avoid coincidences and other disturbing processes.

### 3.6.6. Disturbing interferences

**Spectral coincidence** is a source of analytical error. Judicious choice of interference-free lines and the application of interference correction techniques ensure the accurate, precise and rapid elemental analysis in a broad range of sample matrixes. Types of interferences other than the simple **overlap** are also important but they are not covered in the existing tables. A type of spectral interference (e.g. Al) leads to **systematic biases** of analyte line intensities unless corrective strategies are applied. In this case computer aided - or other - background correction is suggested, however in other cases not only the bias level is moved but the **peak is suppressed.** In this case an interelement correction ensures the proper result. Complex interelement correction algorithms can identify and evaluate two or more peaks.

A further **overlap** is the interference **with higher spectral order.**
    e.g.        P    178.287*3 = 534.861nm
                Mo   267.43 *2 = 534.86 nm

The wavelengths of the two lines differ from each other, but the positions are the same. **Order filters** can be used for separation. The absorbance of a particular filter is a value, not endless, so the filters may be practically good or not.

High concentration of an analyte in the outer part of the plasma decreases the radiation coming from the centre. Due to the **self-**

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**absorption** the peak is collapsed on its top, the intensity of the line is not proportional to the concentration.

Brightening reflexes cause **stray or unwanted lights** in the optical chamber and light path.

Stabilized power supply and internal standard helps for the simultaneous measurement to compensate the **generator output fluctuation.**

Valuable alkaline concentration or high radio frequency power causes changes in signal of analyte by **ionisation effects.**

The sequence of the samples need any intermission for flushing after a sample with high concentration to prevent the **memory effect.**

The differences among density and viscosity of samples and calibration standards cause **disturbances in sample intakes.** Standard addition, internal standard and precise simulation of samples are the best suited to resolve the problem.

## 3.6.7. Calibration

### Calibration without any correction

In ICP technique linear response range is said to be about thousand times of its background. According to the opinion of other authors it is linear through six order of concentration.

### Calibration with background correction

To define the sharp position of the background a part of the spectrum have to be scanned. In different spectral order the distances differ between the peak and the background measurement position.

### Calibration with internal standard

Synthetic solutions, matrix element or additives are to be used for normalisation since Standard Reference Materials are expensive. The signal of analytes are compared with the signal of internal standard. It is added in the same concentration to every sample and synthetic standard. (Tables 3.6-2 and 3.6-3). Changing plasma parameters due to burning causes the same reaction on the line of analyte and on the nearest line of internal standard. It is valid in case of solid bauxite and the nebulized bauxite solution as well. We add the same amount of Co to the bauxite samples as well to calibration standards. Determining trace elements in alumina or high purity aluminium the internal standard is the matrix.

Table 3.6-2
The pair of spectral lines for analysing of bauxite

| Component | Line pair | | | | Range of the concentration [%] |
|---|---|---|---|---|---|
| Al$_2$O$_3$ | Al | 309.27 / | Co | 307.23 | 0.5  -30 |
|  | Al | 266.03 / | Co | 253.22 | 30    -60 |
| SiO$_2$ | Si | 251.61 / | Co | 253.22 | 0.5  -90 |
| Fe$_2$O$_3$ | Fe | 259.94 / | Co | 263.22 | 0.1  -40 |
|  | Fe | 275.57 / | Co | 263.22 | 0.5  -50 |
| TiO$_2$ | Ti | 308.80 / | Co | 307.23 | 0.05 - 5 |
| CaO | Ca | 317.93 / | Co | 307.23 | 0.1  - 5 |
|  | Ca | 315.89 / | Co | 307.23 | 5     -50 |
| MgO | Mg | 279.08 / | Co | 263.22 | 0.05 -25 |
| MnO | Mn | 293.31 / | Co | 263.22 | 0.1  -10 |
| ZnO | Zn | 334.56 / | Co | 307.23 | 1     -25 |
| V$_2$O$_5$ | V | 310.23 / | Co | 263.22 | 0.1  - 5 |
| CuO | Cu | 327.40 / | Co | 307.23 | 0.01 - 0.5 |

Table 3.6-3
The pair of spectral lines for analysing of alumina

| Component | Line pair | | | | Range of the concentration [%] |
|---|---|---|---|---|---|
| SiO$_2$ | Si | 251.61 / | Al | 266.93 | 0.005 -0.1 |
|  | Si | 288.16 / | Al | 306.43 | 0.003 -0.1 |
| Fe$_2$O$_3$ | Fe | 259.84 / | Al | 266.93 | 0.005 -0.1 |
|  | Fe | 275.57 / | Al | 306.43 | 0.005 -0.1 |
| V$_2$O$_5$ | V | 318.40 / | Al | 306.43 | 0.001 -0.5 |
| TiO$_2$ | Ti | 334.90 / | Al | 306.43 | 0.001 -0.1 |
| ZnO | Zn | 334.50 / | Al | 306.43 | 0.10  -0.5 |
| CuO | Cu | 324.75 / | Al | 306.43 | 0.001 -0.05 |

## Standard addition

In unknown matrix with measurable blank or background correction standard(s) is/are added to the sample.

## 3.6.8. Statistics for analytical spectrometry

Guiding principle is that no quantitative results are of any value unless they are accompanied by some estimates of the errors in them.

Least square method is a frequently used method for evaluate of the calibration curve. The shape of calibration curve, the number of calibration points and the confidence level of "fixed" values

have to be carefully checked time by time. The calibration of an
instrument needs primary **Standard Reference Materials.** To correct
the calibration curve parameters we use well known quasi
homogeneous type standards.

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# 3.7 SURFACE ANALYSIS AND MORPHOLOGICAL STUDIES OF SPECIAL PRODUCTS

Á. CSANÁDY, A. CSORDÁS TÓTH

## 3.7.1 Surface analysis of special products

Progress in development of new materials and their technology depends mainly on the scientific knowledge of property-composition relationships, which is based on a detailed characterization on a microscopical scale. Many important material properties are governed by local variations of the chemical composition.

The experimental effort in studying solid-gas and solid-solid interface is more and more extensive also in case of materials used for practical applications. Understanding of nucleation and condensation, catalysis, adhesion, surface diffusion, sintering, corrosion etc. will all be enhanced by the determination of the chemical composition of the interfaces. A realistic view of the boundary at a solid surface is not the obvious ideal infinite plane. On atomic scale, the boundary includes crystal faces having composition, extent, and orientation that are fixed by the pretreatment of the solid. In an applied sense, almost everything that is interesting seems to happen on a surface or requires a surface reaction. The most common compositional analysis methods are summarized in Table 3.7-1.

EELS, FIM-AP and ISS techniques are less convenient and versatile than others therefore they are not discussed in details as it is shown in Figure 3.7-1.

**Table 3.7-1**
**Survey of the most distributed compositional analysis methods based on physical phenomena**

(Only methods for which commercial apparatus is on the market are listed)

| | | Excitation | | | |
|---|---|---|---|---|---|
| | | h | e | ions | E |
| **E M I S S I O N** | h | X-ray fluorescence analysis (XRF) | electron micro-probe analysis (EPMA: WDX, EDX) | | |
| | e | Electron spectroscopy for chemical analysis (ESCA) or soft X-ray photo-electron spectroscopy (XPS) | Auger electron spectroscopy (AES) (Electron-loss spectroscopy (EELS)) | | |
| | ions | | | Ion micro-probe or secondary ion mass spectroscopy (SIMS) (Ion scattering spectroscopy (ISS)) | (Field ion mass spectrometry and microscopy (FIM-AP)) |
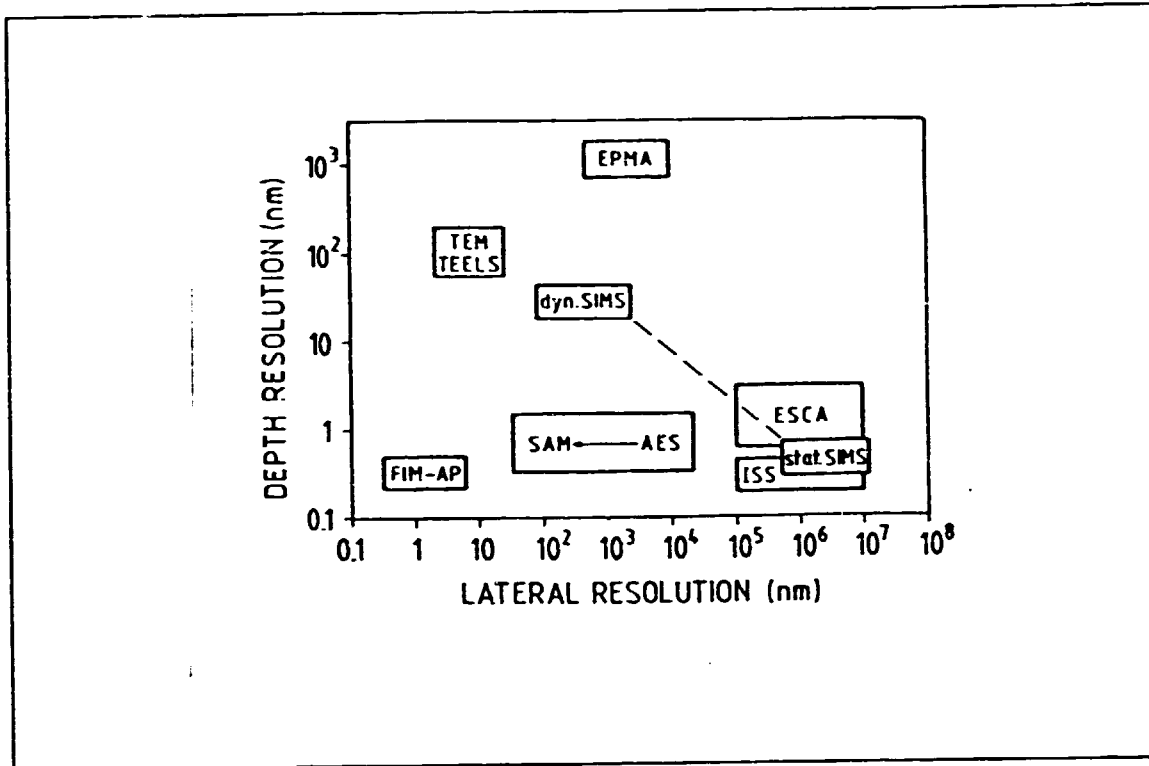
**Figure 3.7-1**
Comparison of typical lateral and depth resolution ranges of the most
important surface and thin film analysis

## 3.7.2 Electron beam excited analytical methods

The characteristic information used for chemical analysis is a
consequence of the interaction of the incident electrons with
atomic levels in the target e.g. in the sample as schematized in
Figure 3.7-2.

The two methods (EPMA and AES) are complementary for several
reasons. Their relative probability is governed by yield factors
$w_X$ and $w_A$ which sum to 1 for a given primary hole. X-ray analysis
is generally recognized for characteristic energies $\geq$ 1 keV while
Auger analysis is more efficient for lower energies.
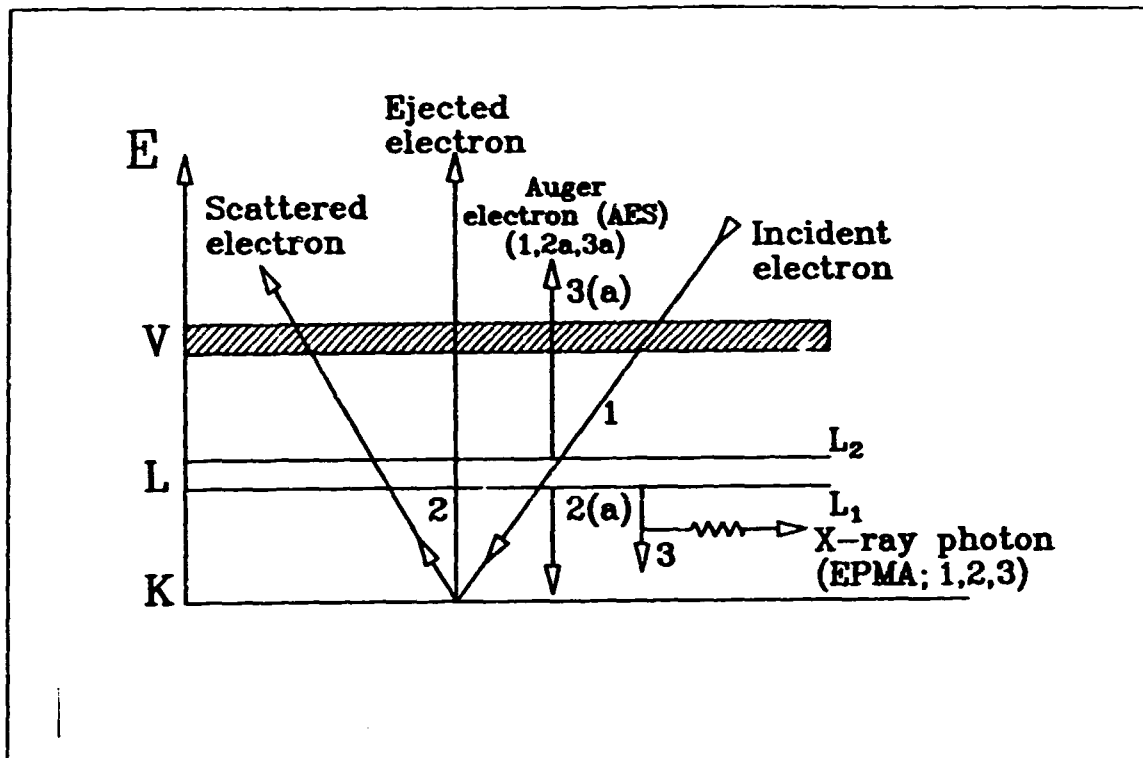
**Figure 3.7-2**
**The interaction of the incident electrons with atomic level**

### 3.7.2.1 EPMA

**Electron microprobe analysis (EPMA: WDX, EDX)** is the most widely
distributed analytical technique [2] based on the electron beam
excitation of the material in an electron microscope, i.e. in a
vacuum system.

Energy of the X-ray photons is characteristic of the elements
emitting them. As they come from a few $\mu$m thick layer of the
surface to get information of thinner layers, special preparation
and investigation techniques have to be used (e.g. slantwise
polished samples or surfaces inclined by sputtering). There is a
good possibility to follow the Na contamination of $Al_2O_3$ products
originating from the Bayer process by WDX.

The X-ray photons can offer elemental distribution of an element
of interest, line profile analysis and point analysis can be
performed by detecting these photons by wavelength dispersive
spectrometers which apply crystal spectrometers. This method is
called **wavelength dispersive microanalysis (WDX)**. **Energy
dispersive microanalysers** make use of solid state detectors
**(EDA/X)**. The main differences between the two techniques are
shown in Table 3.7-2.

**Table 3.7-2**
**Comparison between WDX and EDA techniques**

| Detection limit | WDX | EDA(X) |
|---|---|---|
| Range of detected elements | B-U | Na-U |
| Detection limit (at%) | 0.01-0.1 | 0.1 |
| Energy resolution (eV) | 10-20 | 146 |
| Type of data collection | sequential | simultaneous |
| Time requirement of analysis | fairly long | short |

The data are only valid in case of the instruments used in ALUTERV-FKI Ltd. i.e. they depend on the type of the instruments to be used.

### 3.7.2.2 AES

One of the most versatile and convenient techniques for microlocal elemental analysis is AES, particularly in its more recently developed instrumental configurations, high resolution scanning Auger electron spectroscopy (SAES) or scanning Auger microscopy (SAM).

It is used to observe: segregation, diffusion, contamination, adsorption, oxidation, etc. i.e. sintering, adhesion, catalysis, corrosion etc. processes.

Auger electron emission occurs when an inner shell of an atom is ionized e.g. by electron impact excitation in AES, that is followed by a radiation less Auger transition and the escape of the Auger electron into the vacuum. The kinetic energy of an Auger electron $E_{wxy}$ for an ionized level of binding energy

$E_w$ and the interacting outer levels with energies $E_x$ and $E_y$ is given by:

$$E_{wxy} = E_w (Z) - E_x (Z') - E_y (Z') - \Phi_A \qquad \{1\}$$

where $Z' = Z + \frac{1}{2}$, and $\Phi_A$ is the analyzer work function. The Auger electron energy is independent of the primary electron energy $E_p$ if $E_p > E_w$ and a unique function of the atomic number Z for a given transition (Figure 3.7-3). Thus a qualitative analysis becomes possible in comparison with "fingerprint" spectra which are compiled in reference books. All elements can be detected with the exception of H and He (and atomic Li) because of three electrons participate. A suitable choice of transitions (KLL, LMM, etc.) provides an elemental detection in the energy range 20 - 2500 eV with an optimum sensitivity of about 0.1 to 0.5 at%. The electron escape depth is about 0.5 to 3 nm in this range and is the cause of the surface sensitivity of AES.
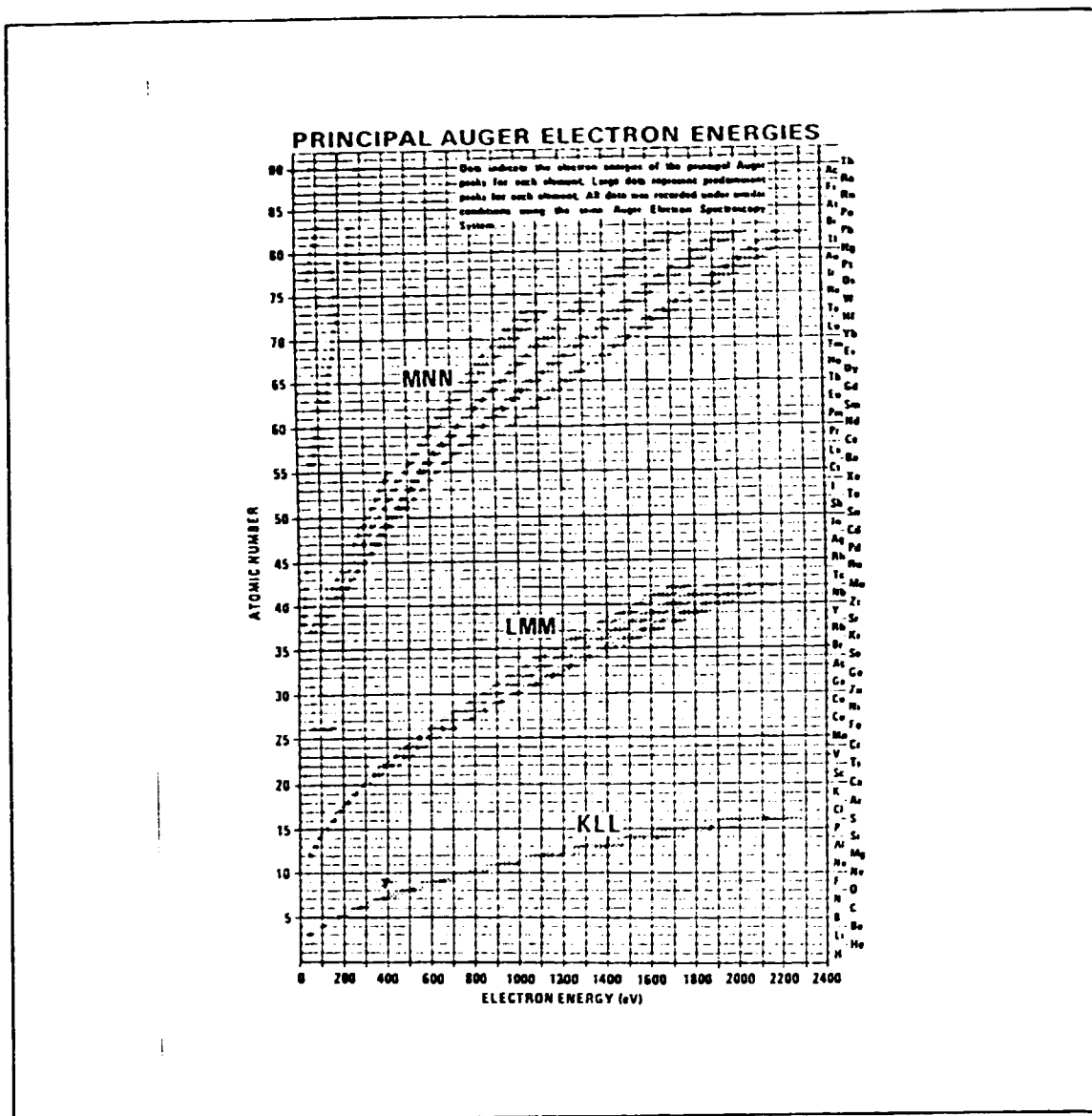
**Figure 3.7-3**
**Most prominent Auger transitions observed with atomic levels**

Chemical bonding results in a change of the binding energies involved. Generally large effects occur for transitions from valence bonds. For example the energy shift of the LVV transition is - 15 eV in $Al_2O_3$ with respect to Al. The secondary emission spectrum contains additional features which can be used for analytical information.

By ion etching (sputtering) in depth profiles can be achieved. An example of depth -- composition profile analysis of a thin film metallization system is shown in Figure 3.7-4. This particular composite is made up of three separate metallic layers bonded to alumina (Thin layers of chromium and titanium are typically used to promote gold adherence to ceramic surfaces).
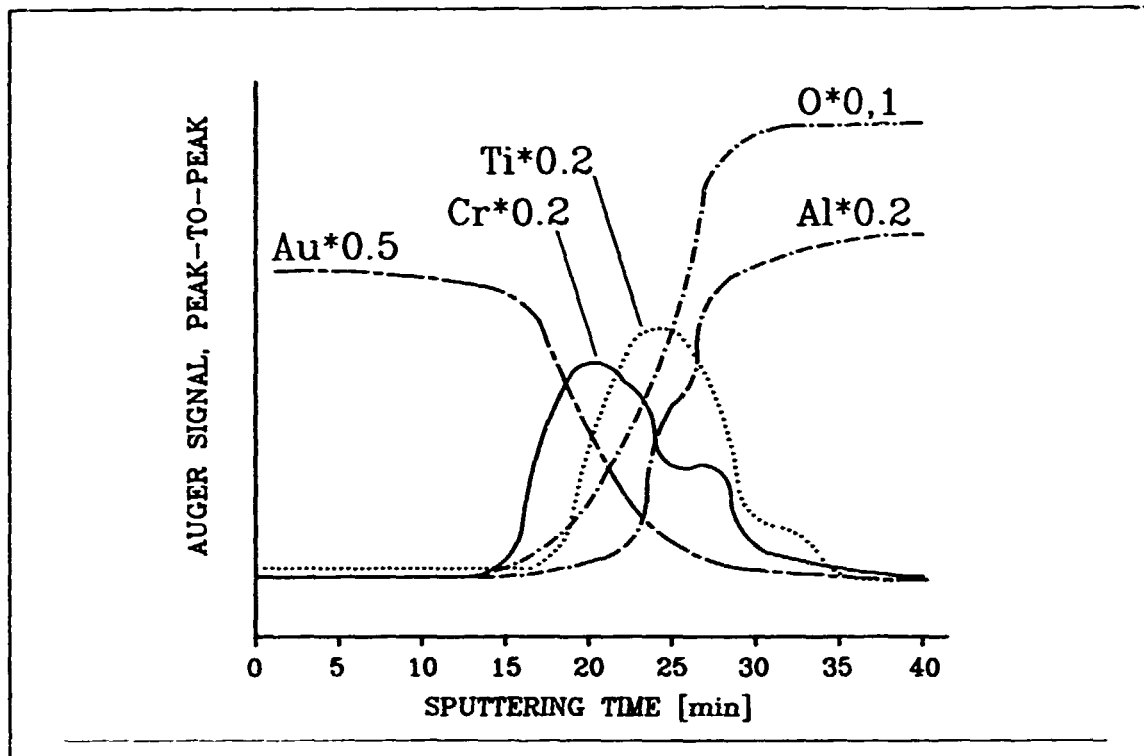
**Figure 3.7-4**
**Depth composition profil of Au, Cr and Ti metallization system on Al$_2$O$_3$**

### 3.7.3 X-ray excited method: Photoelectron Spectroscopy (XPS)

There is an other acronym **ESCA** which describes the same technique "X-ray Photoelectron Spectroscopy" or "Electron Spectroscopy for Chemical Analysis" which can be similarly used.

The basic ESCA experiment is shown schematically in Figure 3.7-5 for a free atom in the gas phase. X-ray photons, **hv**, from a nearly monoenergetic beam are directed onto the sample. The photons are absorbed by sample atoms with each absorption event resulting in prompt emission of an electron. Electrons from all the orbitals of the atom with a binding energy, $E_b$, less than the X-ray energy are excited, but not with equal probability. Thus some peaks are more intense in the spectra than others. Since energy is conversed, the kinetic energy, KE, of the electron plus the energy required to remove it from its orbital to the spectrometer vacuum must equal the X-ray energy. If the X-ray energy is known and the kinetic energy is measured with the electron spectrometer, the binding energy of the electron in the atomic orbital can be obtained. In practical solid state experiments, a correction for the spectrometer work function, $\phi_S$, must also be applied, normally as a part of the spectrometer procedure. Thus one obtains

$$E_b = hv - KE + \phi_S \qquad \{2\}$$
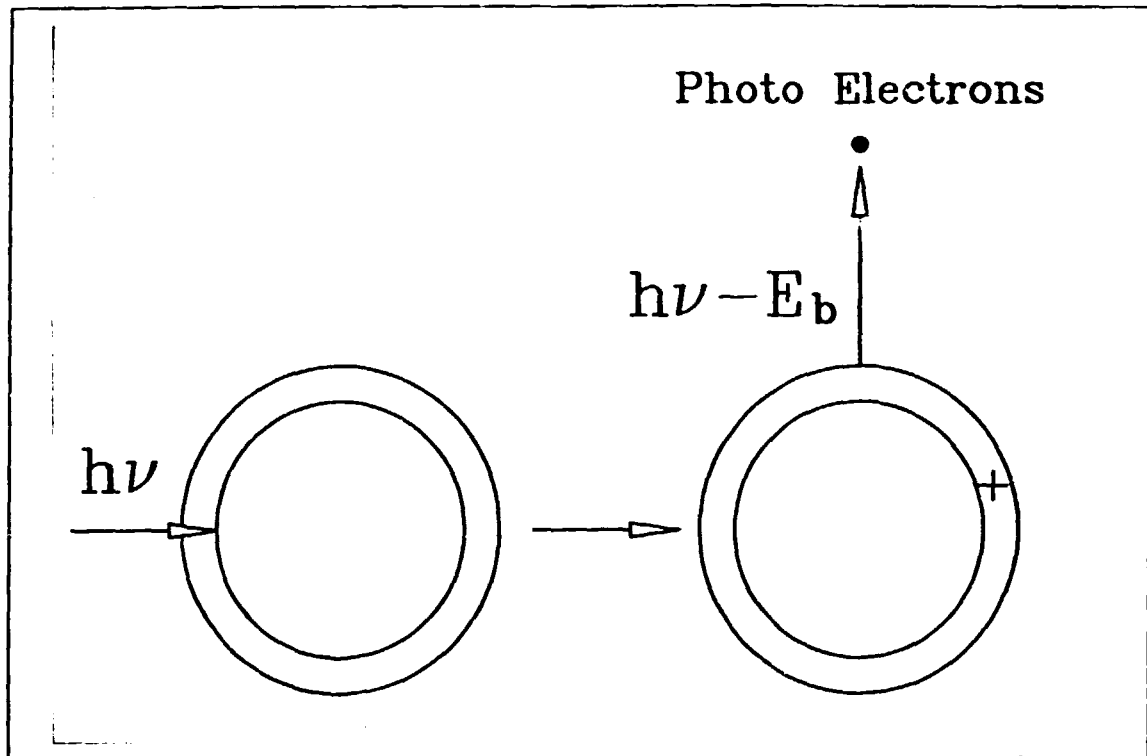
**Figure 3.7-5**
**The physical bases of ESCA, XPS**

The intensity of the signal observed is a function of the amount
of material present. Thus observation of signal intensities in
ESCA spectra can provide semi-quantitative and qualitative
analysis of surface material. In addition to the concentration of
the element producing the signal, ESCA intensities depend upon
the MFP (mean free path) of the electrons and the efficiency of
absorption of the exciting X-rays at the sample material.

The bulk of the published ESCA research has been directed toward
understanding the systematic shift in peak positions resulting
from changes in the chemical structure and oxidation state of
chemical compounds. A chemical shift to higher binding energy
will be observed for most metals when oxidized. The shift is
frequently of the order of 1 eV. Line energies of great many
aluminium and silicon compounds were measured with a high
accuracy by utilizing the possibility that in the conventional
ESCA instruments also the KLL Auger lines could be generated.
Arranging the photoelectron and Auger energies on a two
dimensional "chemical state plot" permits more accurate
delineation of the characteristics of a chemical state. Some
results shown in [4] are given in Table 3.7-3.

Table 3.7-3

Line energies of aluminium compounds. Photoelectron binding energies, Auger kinetic energies, and Auger parameters (Auger kinetic energy + photoelectron binding energy)

| Compound | Al 2p | Al KLL | Al α |
|---|---|---|---|
| Al | 72.72 | 1393.41 | 1466.13 |
| Al | | 1466.2 | |
| AlN | 73.8 | 1389.1 | 1462.9 |
| $Al_2O_3$ sapphire | 73.90 | 1388.07 | 1461.97 |
| $Al_2O_3$ sapphire, heated 450 °C | 74.12 | 13.7888 | 1462.00 |
| $\alpha$-$Al_2O_3$ | 73.65 | 1388.44 | 1462.09 |
| -$Al_2O_3$ | 73.52 | 1388.03 | 1461.55 |
| $Al_{ox}$ a) | 73.95 | 1387.68 | 1461.63 |
| $Al_{ox}$ a), with election flooding | 74.21 | 1387.47 | 1461.68 |
| AlOOH (boehmite) | 74.02 | 1387.80 | 1461.82 |
| $Al(OH)_3$ (gibbsite) | 73.80 | 1387.63 | 1461.43 |
| $Al(OH)_3$ (bayerite) | 74.19 | 1389.55 | 1462.04 |

The most important processes of **XPS** are shown in Figure 3.7-6. This method was often used to investigate the mechanism of adsorption of silicates and phosphates on the surface of synthetic gibbsite. The results have shown the importance of the presence of Ca in the adsorption process. Atomic concentration ratio estimates calculated from peak intensities, kinetic energies, and photoelectron cross-sections, showed that Ca/Si exceeds Ca/P on the alumina surface [5].

XPS could show the differences in organic surface contaminates adsorbed at alumina surface causing differences in its colour [6].

XPS was successfully used to investigate the nature of the surface adsorption of HF on alumina [7, 8]. XPS is particularly well suited to the study of the gas adsorption process. It was stated that when moisture was present (conventional conditions) no $AlF_3$ formation was observed, the absorption of HF involves a weak interaction, probably hydrogen bonding with intermediate layers of water. The measurements was based partly on the comparison with the data of pure compounds being in question (see Table 3.7-4).
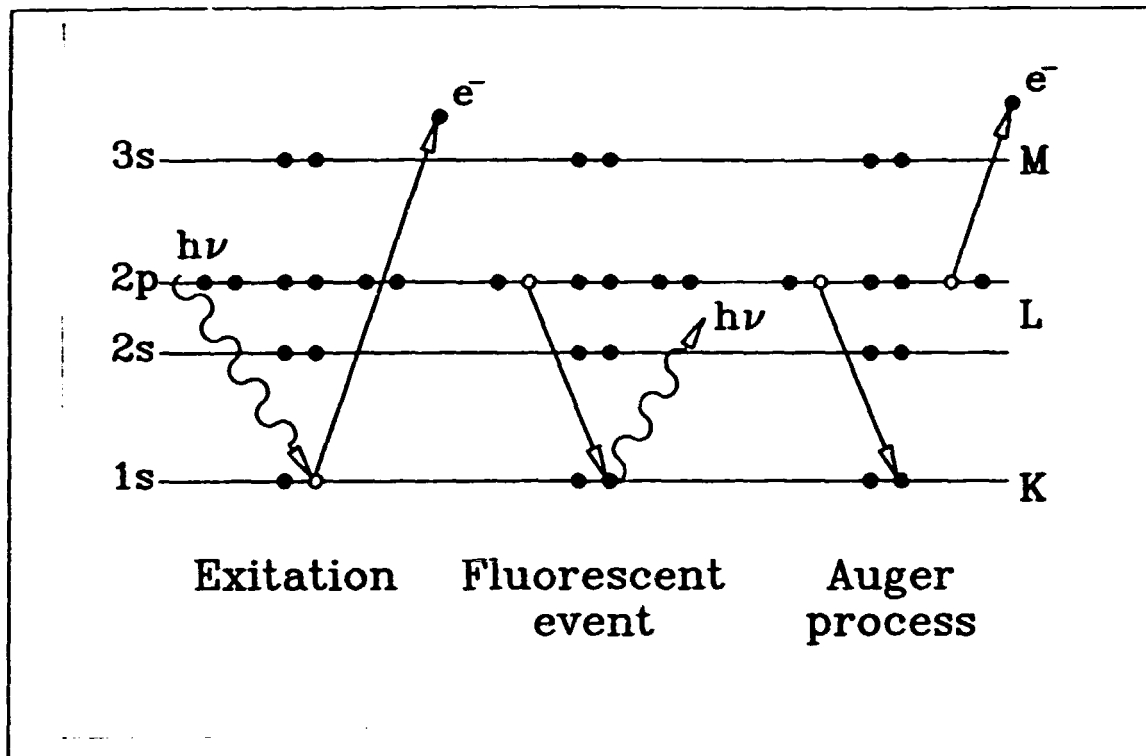
**Figure 3.7-6**
**The most prominent process going on in XPS**

**Table 3.7-4**
**Binding Energies of Aluminium, Oxygen, Sodium and Fluorine [8]**

| Sample | Binding Energies (eV) | | | |
|---|---|---|---|---|
| | $Al_{2p}$ | $O_{1z}$ | $Na_{a'}$ | $F_{a'}$ |
| $Al_2O_3$ | 74.3 | 531.5 | 2062.4 | 1340.5 |
| $AlF_3$ | 77.0 | 533.0 | - | 1339.9 |
| $Na_3AlF_6$ | 76.0 | 531.8 | 2060.3 | 1339.7 |
| NaF | - | - | 2061.0 | 1339.8 |

### 3.7.4 Ion beam induced method: Secondary Ion Mass Spectrometry (SIMS)

The interaction of energetic ions with a solid results in the
ejection of substrate atoms and molecules in both neutral and
charged states. This moderately efficient production of charged
particles (secondary ions) coupled with high sensitivity mass
spectrometric techniques forms the basis of the SIMS method. The
popularity of SIMS as a surface analysis tool can be attributed
to its ability to detect and analyze the full range of elements
and isotopes, from hydrogen to uranium, in the ppm and ppb atomic
range. In practice, SIMS uses focused ion beams to erode atoms
from a selected sample surface, resulting in the emission of
positive and negative secondary ions which are subsequently mass

---

analyzed. The resulting spectrum is used to measure trace elements or analyze any elements as a function of depth.

There are three modes of SIMS: Dynamic, Static and Imaging. **In dynamic SIMS**, an ion beam with high primary current sputters material from the sample, surface, there by permitting the measurement of elemental concentration changes relative to depth (i.e. depth profiling). **Static SIMS** uses an ion beam with extremely low beam current in order to maintain the chemical integrity of the material. Analogous to Scanning Electron Microscopy (SEM), **Imaging SIMS** IMMA records a chemical image of a sample by detecting secondary ions as a function of x-y position on the sample. This results in element-specific images or maps.

Acquiring SIMS data from insulators (e.g. oxides) can be complicated by sample charging. By electron bombardment the positive charge build-up on the sample surface when analyzing can be compensated. By this way positive and negative secondary ions are detected with equal ease and without the need for deposited conductive coating (PHI 6600 Dynamic SIMS). SIMS provides information from the uppermost surface layer (0.3 - 1 nm), the limit of detection is about 0.1 ppm and in good instruments the lateral resolution may be 0.1 - 1 $\mu$m.

### 3.7.5 Study of the morphological features of special products

The various microscopic techniques (see Chapter 3.1) are very useful tools to study the morphological features like *size, shape, surface roughness, homogeneity, state of aggregation and/or sintering* of different powder materials. Here below, the application possibilities of these techniques will be discussed by means of some examples.

### 3.7.5.1 Study of the morphological features of ground aluminium trihydroxide

The morphology of the aluminium trihydroxide (ATH) of technical grade is well known, several publications [9-14] were dealing with the crystallization and agglomeration processes of ATH. ATH has a polycrystalline nature: aggregates and agglomerates consisting of individual crystallites of gibbsite with pseudo-hexagonal structure are characteristic to this material. The size of individual crystallites may vary from about 1 $\mu$m up to several tens of $\mu$m. Typical polycrystals of ATH can be seen in Figure 3.7-7a, while Figures 3.7-7b - d are showing the morphology of some ground products made in ALUTERV - FKI Ltd. These figures demonstrate the effect of grinding on the shape of ATH . Flaky crystallites, sharp edges can frequently be seen in case of normal grinding process. For applications as filler in various resins besides the size the width of the grain size distribution curve is of primary importance. Secondary electron images (SEI)

with  small  or  medium  magnifications  show  the  degree  of
homogeneity of the size distribution of ATH grains.
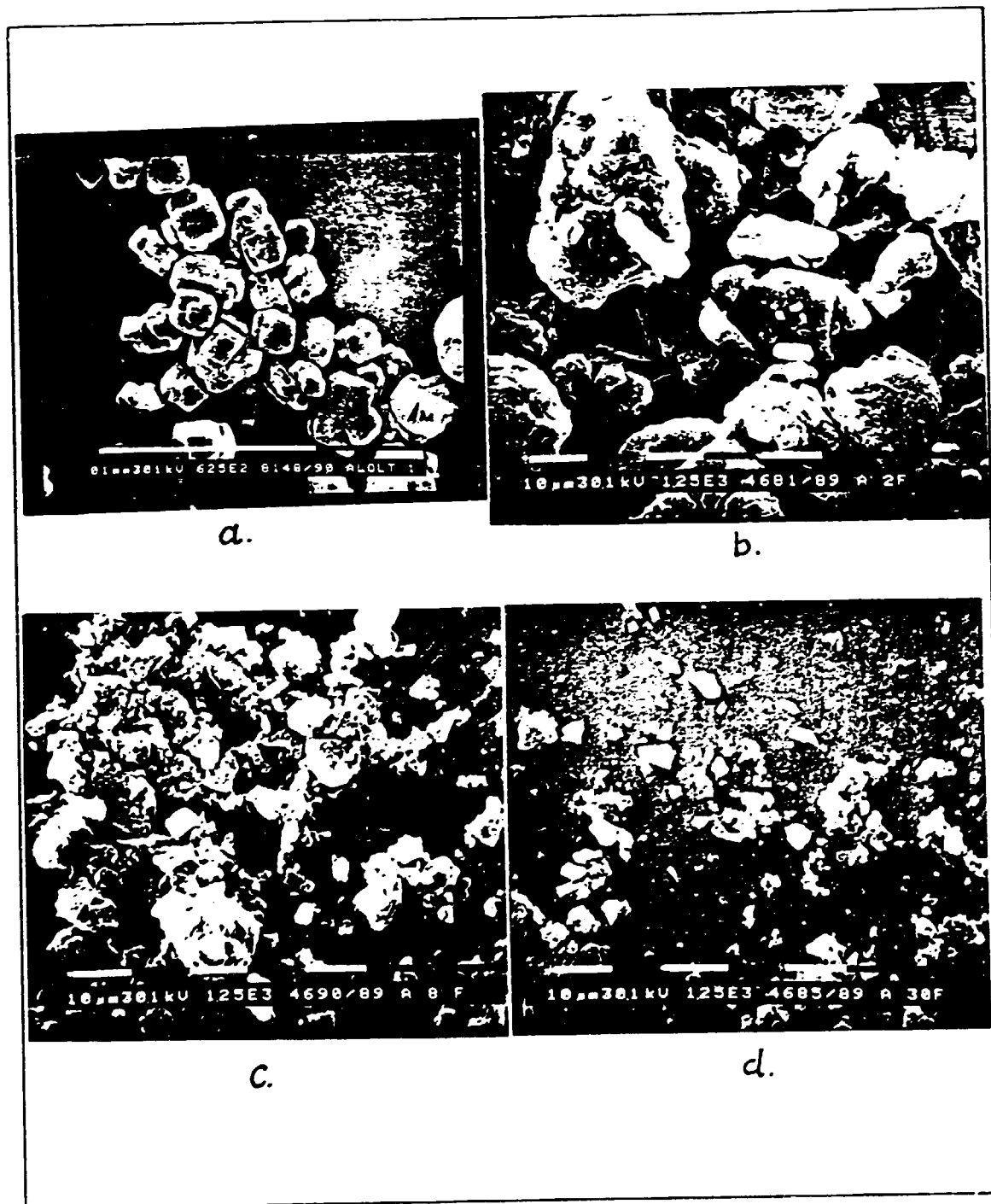


Figure 3.7-7
Scanning electron micrographs of: a) normal ATH produced by Bayer process; b -
d): ground aluminium trihydroxides made by ALUTERV - FKI Ltd.

In  case  of  special  grinding  process  ATH  crystallites  with
spherical  forms  and  rounded  edges  can  be  produced,  so  we  can

follow the grinding process by studying the size and shape of ATH crystals.

### 3.7.5.2 Studying of the transition process of ATH by the effect of heat treatment

Transition aluminas are important materials for a lot of applications like catalysts, ceramics etc. Scanning and transmission electron microscopies can give us valuable information on the fine structure of these powders. It was found by Lippens [15] and Wefers [16] that sponge-like structure develops within a coherent solid while the skeleton of the crystallites remain unchanged. High resolution electron microscopy can reveal the pore structure of various transition aluminas and that of the corundum, too. Figures 3.7-8a and b show the pore structures in particles of chi and eta aluminas. Parallel pores located in the cleavage plane (001) separate the solid into lamellae with 2-3 nm thickness, which is about twice the average pore width. A network of irregularly shaped slits, about 1 nm wide, extends perpendicularly to, and is connected with, the pores parallel to (001). The intersecting pore systems divide the lamellae into interconnected, irregularly shaped domains of solid. The longest dimension of these domains is about 10 nm, equivalent to the length of about 10-15 $AlO_6$ octahedra. It is obvious from the electron micrographs that the surfaces of the domains are "rough" on an atomic scale and do not represent refined crystal faces. At temperatures exceeding approximately 1000K, reordering is no longer confined to short-range consolidation within the layer skeleton of the decomposed ATH. The layer structure of the precursor is still obvious, lamellae with 20-40 nm have formed . These phenomena occur simultaneously with the formation of kappa alumina (see Figure 3.7-8c). They are embedded in a network consisting of interconnected crystallites and pores, each has a size of 10-30 nm, equivalent to a surface area of 30-50 $m^2$/g. This estimation is in good agreement with BET surface areas determined for this transition alumina. This type of morphological pattern persists beyond the formation of $\alpha$ - $Al_2O_3$ at temperatures above 1450K. Lamellae continue to increase in thickness by fusion (see Figure 3.7-8d). The gaps between lamellae also grow with increasing densification, because the habit and parallel texture of the original ATH crystal are retained.
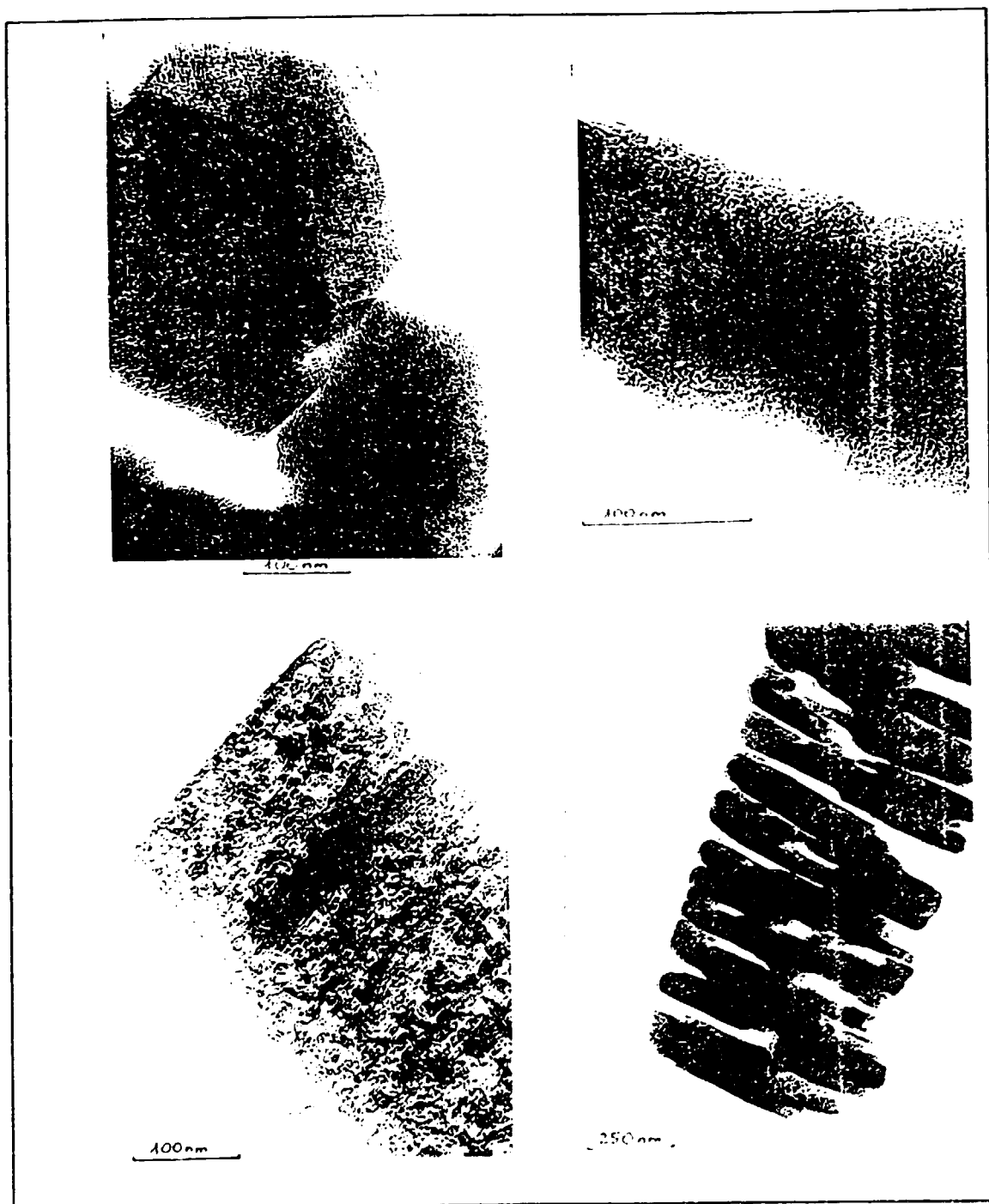
Figure 3.7-8
High resolution electron micrographs of chi (a), eta (b), kappa (c) and alpha
(d) aluminas (see Ref. 8)

### 3.7.6 Studying the size and state of aggregation in case of fine-sized powder materials

Scanning and transmission electron microscopies are routine techniques to study the size and shape of the crystallites of fine sized ceramic materials. In Figures 3.7-9a - d typical SE images of special aluminas made by different technologies can be seen. Figure 3.7-9a shows a super-ground alumina with about 0.5 $\mu$m average size, sharp edges and some irregular forms are the "marks" of the grinding process. Figure 3.7-9b shows particles which are very different in shape and also in phase composition (this powder has a significant amount of kappa alumina) from that of the Figure 3.7-9a. Angular crystallites with a few tenth of $\mu$m are characteristic to this kappa alumina. Both materials are products of Alcoa Aluminium Corporation. Figure 3.7-9c shows rounded particles (average crystallite size is about 0.1 $\mu$m) of a high purity alumina for ceramic applications calcined from a complex aluminium salt (manufactured by Baikowski Chimie). The specific surface area of this powder is about 15 $m_2/g$. Figure 3.7-9d represent also a high purity alumina produced by Showa Aluminium Industry. Worm-like shapes can be seen which are typical for a lot of ceramic powders.

Transmission electron microscopy is a useful technique to reveal the surface structure and the state of aggregation in case of ceramic powders [17-18]. Transmission electron micrographs made by a conventional TEM can show us how the grains of a ceramic powder are building up, whether they are consisting of well-developed facets with sharp edges or they are formed by agglomeration of roughly spherical particles. Differences in the specific surface area measured by BET can be understood by taking TEM images from such materials. Also high resolution electron micrographs of zirconia can reveal the surface structure on an atomic scale. The fine structure and the pore structure of a ceramic material made by sintering can be studied by TEM using ion-thinned preparates.
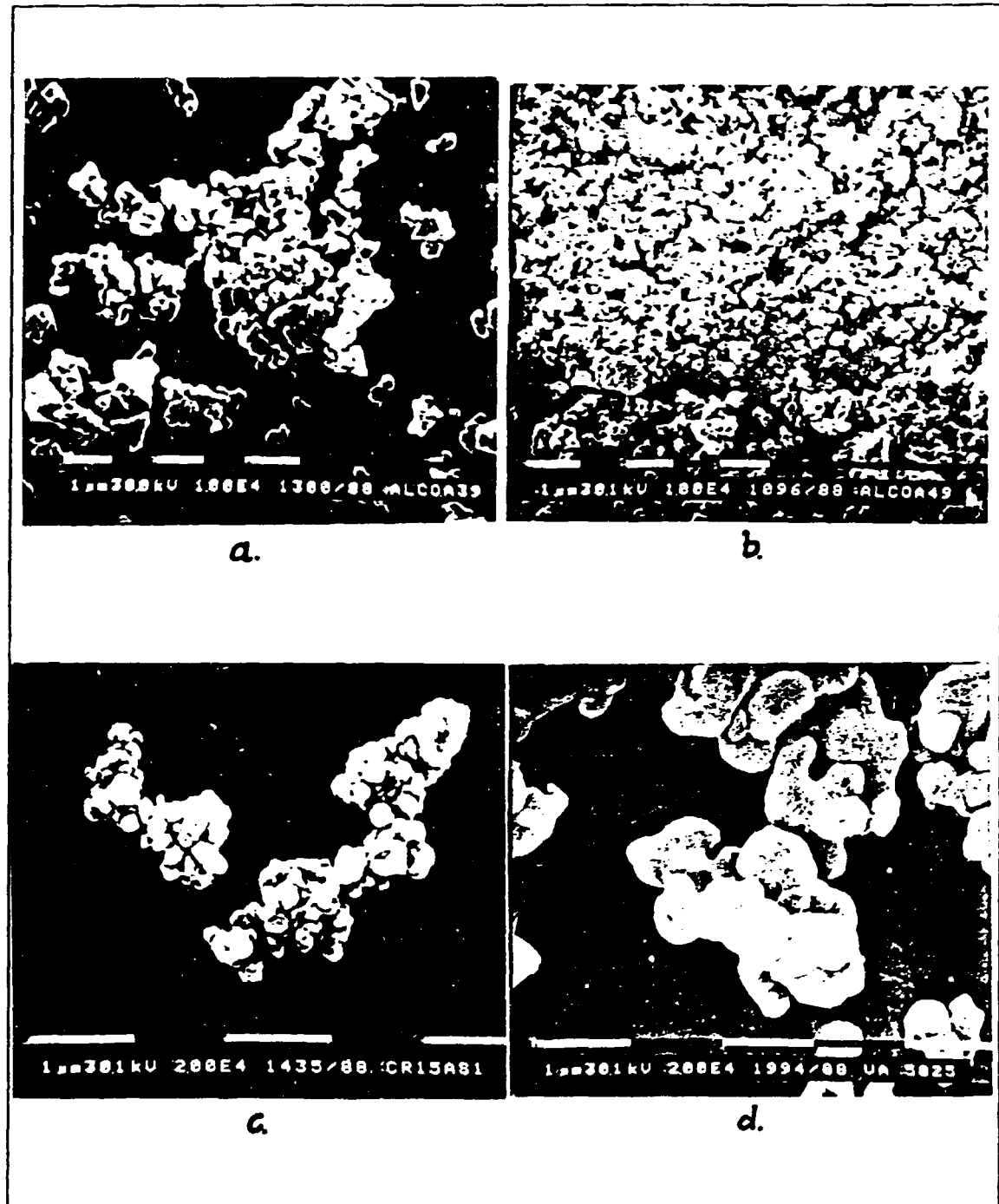
Figure 3.7-9
Scanning electron micrographs of aluminas of ceramic grade
a.) Super ground product of Alcoa b.) Super ground, high purity product of
Alcoa , c.) Fine sized, high purity alumina produced by Baikowski Chimie, d.)
Fine sized, high purity alumina manufactured by Showa Aluminium

### 3.7.7 Quantitative microstructural studies of ceramic materials

By means of image analytical possibilities of the modern SEM-s
quantitative data on the size and shape of pores and crystallites
of ceramic materials can be given. It is possible to take
backscattered electron images of well prepared (carefully ground
and polished) surface of sintered ceramic samples detecting the
pores as areas with black contrast. Also the microstructure, the
boundaries of individual crystallites building up the sintered
ceramic material can be revealed by chemical or thermal etching
of the surfaces. The International Standard ISO DIS 6744 [19]
refers to the determination of the average grain size of metals
(ASTM E 112, [10]) . It says that the surface of the ceramic
probes must be carefully polished, then thermally etched in the
following way:

- etching temperature: 1450 - 1500 °C,
- etching time:          2 - 4 hours.

As average diameter of a grain is usually the equivalent circular
diameter taken i.e. the diameter of a circle having the same area
as the grain has. In Figure 3.7-10 SE micrographs of two fine
sized alumina powders are presented together with typical BE
images showing the fine microstructure of the ceramic materials
produced by sintering of both powders at 1750 °C. It can be seen
that the size of the grains in both sintered product are mostly
below or equal to 3 $\mu$m (see Figure 3.7-10e). To characterize the
shape of the grains the ratio of the maximum and minimum Feret
diameters was chosen [21, 22]. It is obvious from the histogram
of Figure 3.7-10f. that there is a slight difference between the
two ceramics: the shape of the grains made of the Reynolds powder
is more rounded than that of the one produced from the Alcoa
product.
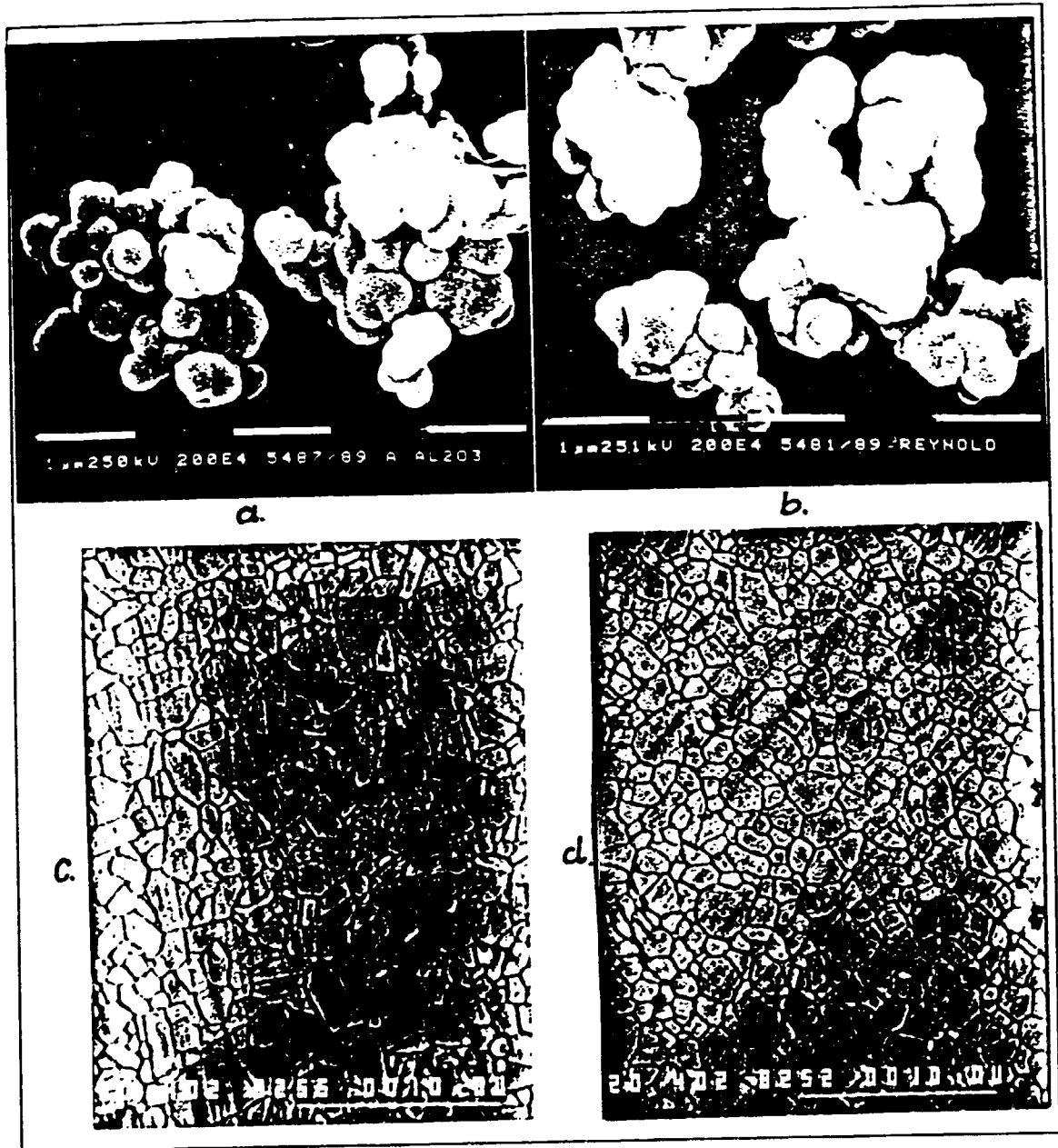
Figure 3.7-10
Scanning electron micrographs showing fine sized aluminas
a.) and b.) starting powders, c.) and d.) the microstructure of the ceramic
products made of them by sintering
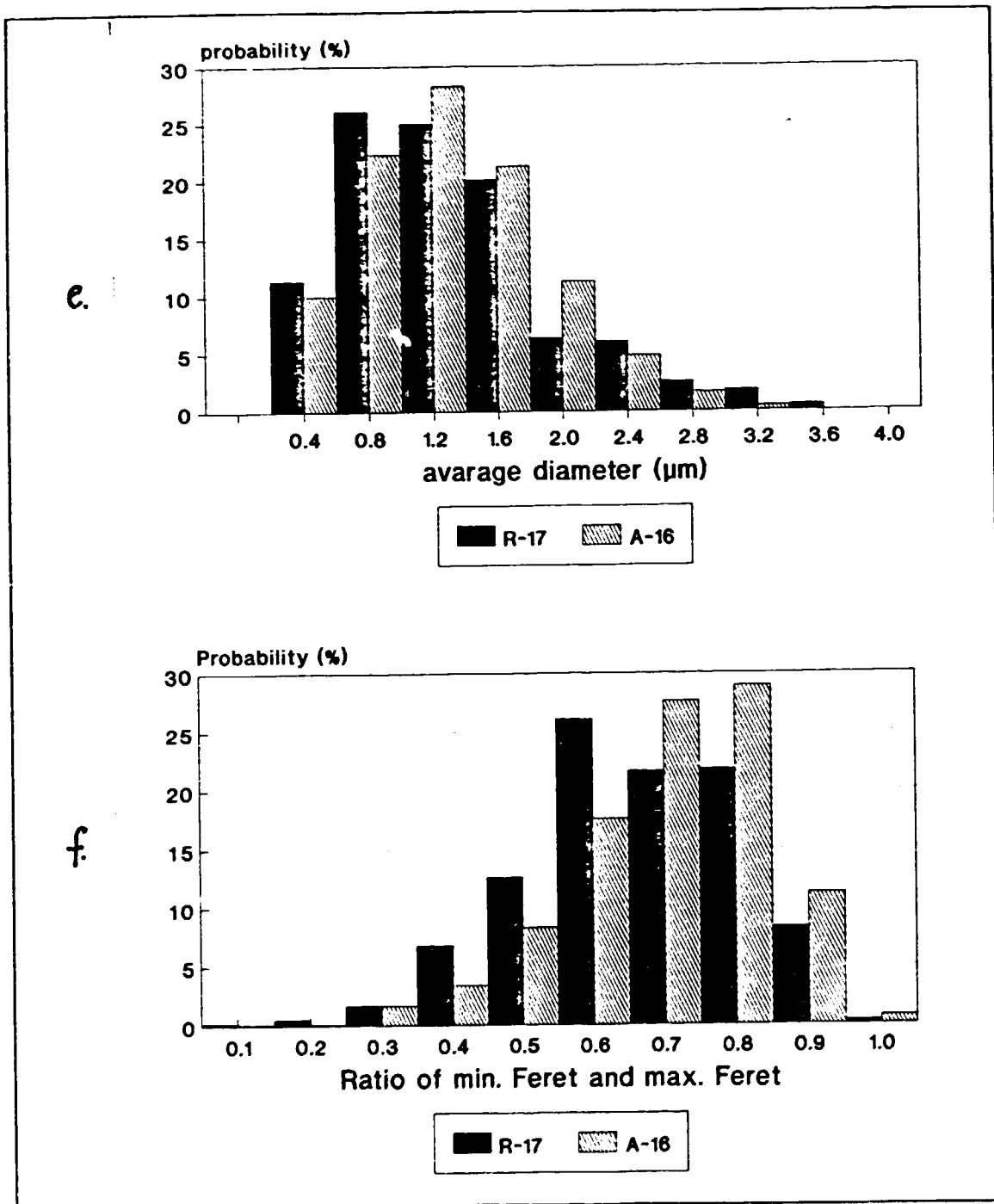
**Figure 3.7-10e-f**
**Fine sized aluminas**
**histograms of the average grain size and that of the shape factor**

Taking into account, that the initial particles of the ceramic powders are very often worm-like, J. Besson and M. Abouaf [23] defined a so called geodesic diameter $D_g$ to characterize the particle shape:

$$F_g = \frac{\pi}{4} * \frac{D_g^2}{S} \qquad \{3\}$$

where $S$ is the area of the particle, $F_g$ is a shape factor equal to one for a circle. The geodesic diameter is defined as:

$$D_g = Max/Min_{A,B \epsilon P} \ d_*(A,B), \qquad \{4\}$$

where $d^*(A,B)$ denotes the distance between the two points $A$ and $B$ along a path included in the particle, represented by the set $P$. An illustration of the concept of geodesic diameter is given in Figure 3.7-11, while variations of the mean shape factor during sintering are shown in Figure 3.7-12 [23]. The data of the Figure 3.7-11 can be explained as follows: initial particles have worm-like shape; they become rounded during densification. For sufficient annealing times, grain growth along specific crystallographic directions can occur resulting in more elongated grains. For characterization of the grain size distribution of ceramic materials the so called median $D_{50}$ value is useful: the grain size for which 50 % of the grains are smaller than this value in $\mu m$ (see Figure 3.7-8 in [23]. Similarly, $D_{10}$ and $D_{90}$ can be defined: $D_{10}$ can represent the size of the smaller fraction of the grains and $D_{90}$ the coarser fraction. It was found by C. Brodhag et al [24], that for normal grain growth during sintering the whole microstructure increases similarly, i.e. $D_{10}/D_{50}$ and $D_{90}/D_{50}$ are almost constant for one type of product.
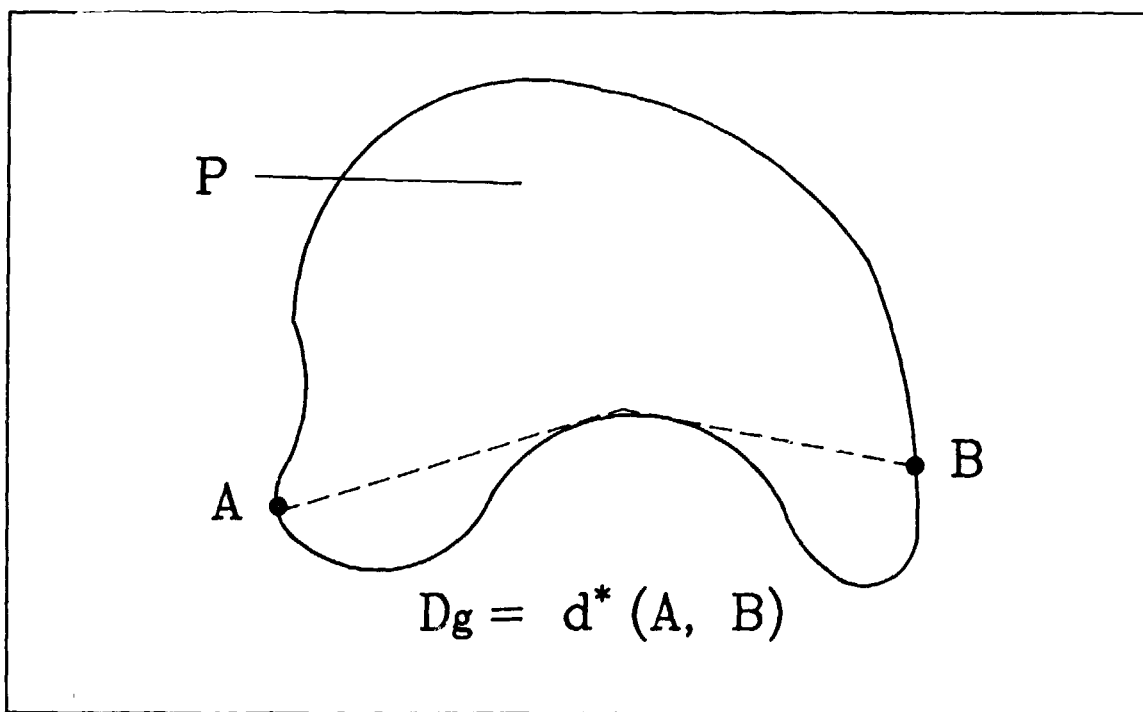


**Figure 3.7-11**
**Illustration of the geodesic diameter D**
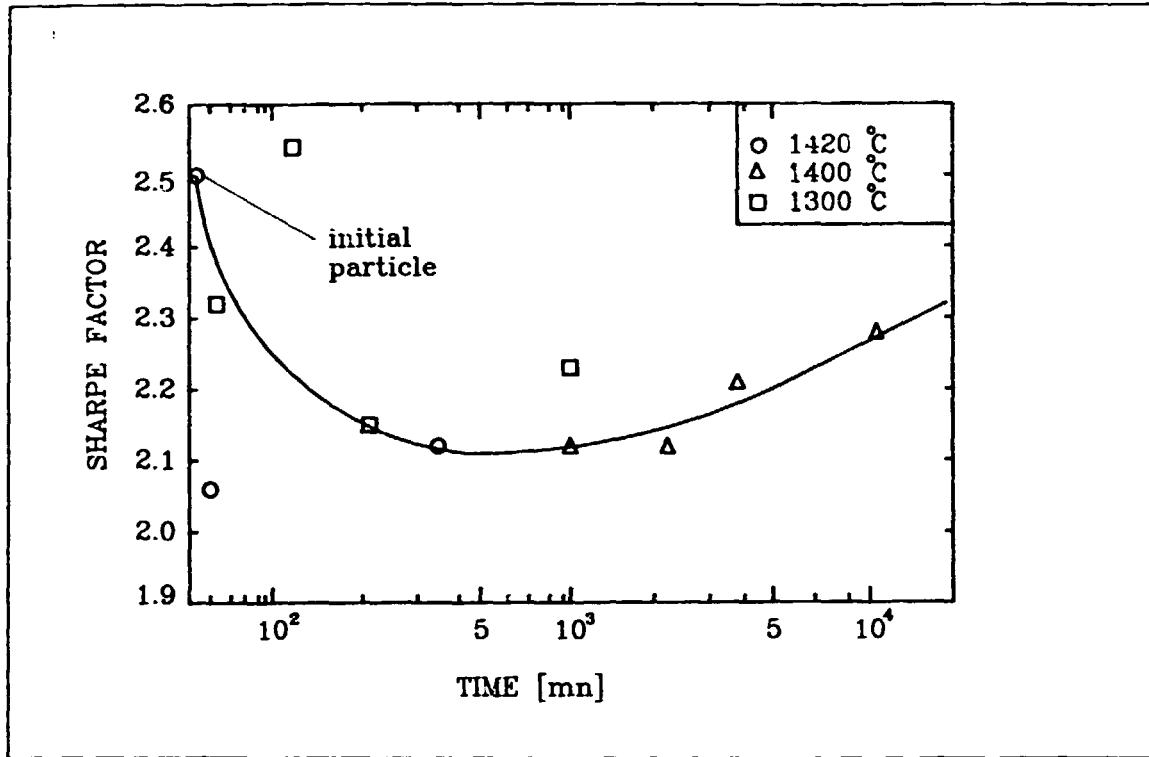
**Figure 3.7-12**
**Mean shape factor during sintering as a function of time**

In case of multiphase ceramics like zirconia-toughened alumina
the average grain size of both zirconia and alumina can be
determined. Besides the state of agglomeration can be established
by using a topological function, where an inspection distance is
defined; if the distance between two particles is less than this
inspection distance they are considered to be agglomerated. The
size of the agglomerates and the number of particles per
agglomerate increase as the inspection distance increases. The so
called topological function is the ratio of the agglomerate size
to the inspection distance. At the final maximum all particles
are considered to be agglomerated. If the maximum occurs before
this, it shows the occurrence of agglomeration, i.e. poor quality
of the dispersion. By means of topological function taken for
ceramic materials made of various types of starting powders
information can be gained on the microstructure of such ceramic
materials. Also it has to be mentioned that the other types of
grain size measuring methods can not be applied for sintered
ceramic materials only microscopic and image analytical
techniques are available.

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# 3.8 SURFACE AREA, PORE- AND GRAIN-SIZE OF BAYER ALUMINA CO- AND BY-PRODUCTS

A. Imre, J. Fekete

The measurement of the special nature of the new products made new classification methods imperative. Three of these new methods are written in the next three paragraphs. These are:

- surface area,
- pore-size distribution and
- grain-size distribution.

## 3.8.1 Specific surface area

The specific surface area is the size of the surface of a solid powder by unit weight or unit volume. Its value can differ by orders of magnitude, in case of porous and nonporous materials, respectively.

In case of nonporous powders the specific surface area is the sum of the "external" surface area of the grains, whereas in case of porous materials it is given by the sum of the grains "external" and the pores "internal" surface area. Comparing the two, the internal surface area by the material which have greater grains than 10 $\mu$m, is greater by orders of magnitude and consequently, the external surface area is almost negligible. As a consequence of the above mentioned the specific surface area ($S_m$) of the porous materials is a function of the pores' size:

$$S_m = \int_{r_0}^{\infty} f/r/ \cdot dr \qquad \{1\}$$

where: $r$ = radius of the pore,
$r_0$ = lower limit of the radius of the pore.

Methods for determining the specific surface area of the dust particles are enlisted in Table 3.8-1.

As it can be seen in the Table 3.8-1 the measuring methods can be classified into three main groups. Owing to their accuracy, realiability, easy automation possibility and relatively simple techniques, the measuring methods of the first group are the extensively used ones. ALUTERV-FKI, too, performs the specific surface area measurements by gas-adsorption methods recognized as

international standards [25, 53, 54], therefore, and because of
their significance and widespread usage, they will be discussed
in details. The study will be started by the discussion of the
theory.

**Table 3.8-1**
**Methods for the determination of the specific surface area**

| Methods | Reference |
|---------|-----------|
| **1. Gas (vapour) adsorption methods** | |
| a./ on the basis of weight | |
| static | 1, 2, 3, 4 |
| dynamic | 5, 6, 7 |
| b./ volumetric | |
| static | 8, 9, 10, 11 |
| dynamic | 12, 13, 14, 15 |
| **2. Solution adsorption methods** | |
| a./ fluid adsorption | 16, 17, 18, 19 |
| b./ paint adsorption | 20, 21, 22, 23 |
| c./ radioactive indication | 24, 25, 26, 27, 77 |
| **3. Different physical methods** | |
| a./ emanation method | 28, 29, 30 |
| b./ porosimetry | 2, 31, 32 |
| c./ X-ray diffusion | 33, 34, 35, 36 |
| d./ gas permeability | 37, 38, 39, 40 |
| e./ microcalorimetry | 41, 42, 43, 44, 78 |
| f./ capillar condensation | 45, 46, 47, 48 |
| g./ electric potential | 25, 49, 50, 51 |
| h./ conductivity | 25, 52 |

**The Brunauer-Emmett-Teller (BET) theory**

The BET theory, is the most commonly used system for this purpose
[8]. When deducing their equation, the authors assumed that first
a layer of a single molecule's width will develop with continuous
growth during the adsorption, followed by a multilayer covered
stage and then by gas condensation (Figure 3.8-1).
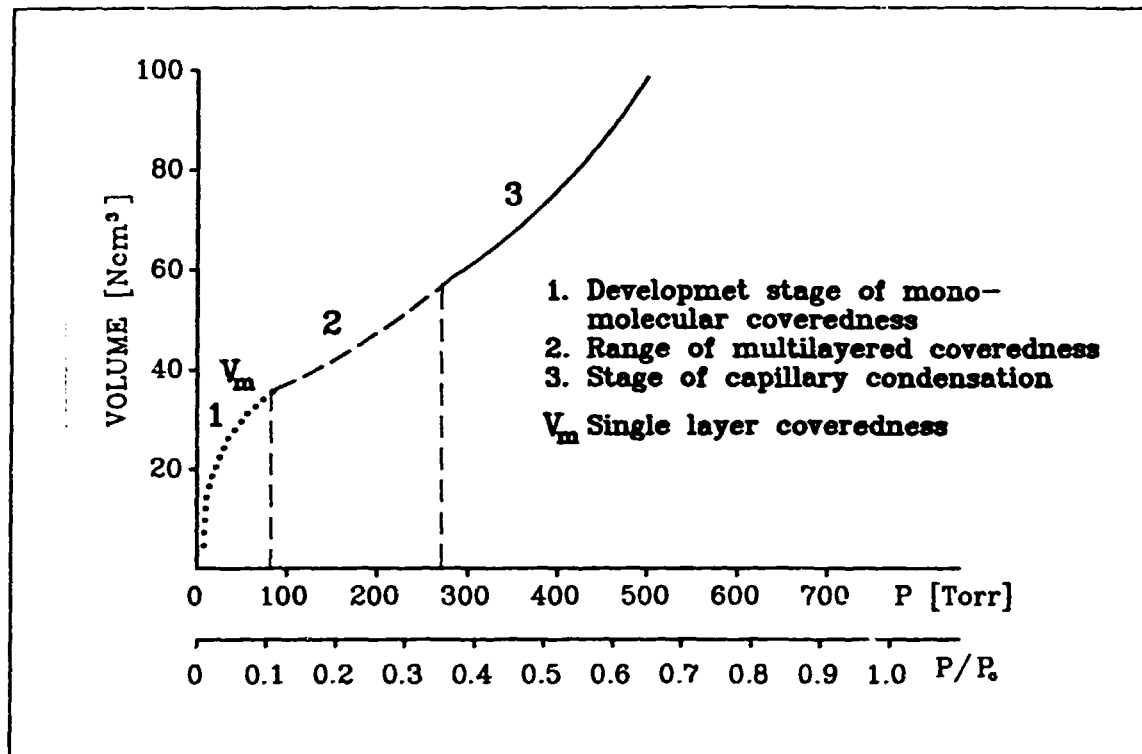
Figure 3.8-1
Nitrogen adsorption isotherm of $Al_2O_3$

In the practice, only the short form of their equation - suitable
for the description of the total adsorption isotherm - is used
for the surface area determination:

$$\frac{P}{V(P_O - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \cdot \frac{P}{P_O} \qquad \{2\}$$

where: $V_m$ = amount of gas required for monomolecular layer
            formation,
       $V$ = adsorbed gas-volume (normal condition),
       $P$ = equilibrium pressure of the adsorbed gas-layer,
       $P_O$ = saturated gas-pressure of the adsorbed gas,
            belonging to the given temperature,
       $C$ = constant.

Specific surface area is determined on the basis of $V_m$. For the
determination of its value, $V_m$ can be expressed from the equation
{2} or it can be graphically determined by using the above linear
form. In this case several P-V values will be plotted in the

$$\frac{P}{P_O} = \frac{P}{V(P_O-P)} \qquad \{3\}$$

co-ordinate system and the value of $V_m$ is determined from the
axial section and slope of the resulting straight line.

In equation {2} the constant C is a number without dimension: in the first approach its value can be calculated by means of the following relationship [9]:

$$C = exp. \frac{E_I - E_L}{R_O T} \qquad \{4\}$$

where: $E_I$ = adsorption energy of the single layer,
$E_L$ = condensation energy of the adsorbed gas or vapour,
$R_O$ = universal gas constant.

In case of the most frequently used nitrogen-adsorption calculations, the value of $C = 240$ is resulted [10, 11].

The specific surface area $(S_m)$ is given from the value of $V_m$ by the following relationship [9]:

$$S_m = \frac{S_O V_m}{W} \qquad \{5\}$$

where: $W$ = weight of the adsorbent (g),
$S_O$ = is a constant, it represents the surface requirement of 1 $cm^3$ normal condition gas, in case of monomolecular adsorption. Its dimension is $m_2/m^3$. Its value can be calculated from surface area requirement of the adsorbed molecules by using the following formula [9, 10, 11]:

$$S_{o1} = S_1 \cdot n \qquad \{6\}$$

where: $n$ = the Loschmidt number,
$S_1$ = surface area requirement of the gas molecule, calculated on the basis of the liquid state density,
$S_{o1}$ = surface area requirement of 1 $cm^3$ of normal condition gas, calculated on the basis of the liquid state density.

Surface area requirement of the gas molecule $(S_1)$ according to Brunauer, can be calculated as follows [55]:

$$S_1 = 4 \cdot 0.866 \left[ \frac{M}{4\sqrt{2}N \cdot 1} \right]^{2/3} \quad cm^2 \qquad \{7\}$$

where: $M$ = molar weight of the gas (or vapour),
$1$ = density of liquid state adsorbate,
$N$ = Avogadro number.

Equation {2} can be used for the majority of adsorbents in the:

$$\frac{P}{P_O} = 0.05 - 0.35 \qquad \{8\}$$

or sometimes in the:

$$\frac{P}{P_O} = 0.05 - 0.50 \qquad \{9\}$$

relative pressure range, which preceds and follows the shaping of the single molecule layer.

The most accurate determination of the specific surface area by the BET method can be done using the values measured on 4-5 points of the isotherm. The result of the three-point determination deviates from this value only slightly [56]. In case of large series measurements the one-point method can also be used [2].

Measuring units of the specific surface area were first used in the alumina industry when production of special aluminas was started. Since that time it is an important qualification parameter of $Al_2O_3$ adsorbents, catalyst carriers, synthetic industry fillers and abrasives [57].

During the 20-30 years that have passed since the introduction of surface measurements in the alumina industry, it proved to be evident that the information gained by these measurements can variously be utilized in the industrial technology, and that they also provide significant data for the technological development. To demonstrate these, the surface area of some special products are collected in Table 3.8-2.

Table 3.8-2
Surface area of some special products of the alumina industry

| Products | Surface area $m^2/g$ |
|---|---|
| **Special alumina BAIKALOX** | |
| CR 30 | 30,1 |
| CR 15 | 15 |
| CR 10 | 10 |
| CR  6 | 6 |
| A  85 | 85 |
| CR 85 | 85 |
| A 125 | 105 |
| CR125 | 125 |
| **Special alumina REYNOLDS** | |
| RC-HP | 3-6 |
| RC-HP DBM | 6-9 |
| **Special alumina ALCOA** | |
| AL-150 SG | 5 |
| AL-160 SG1 | 8 |
| AL-170 | 2,5 |
| A-50 N | 15 |
| **High purity alumina Vereinigte Al-werke** | 415 |
| **Special alumina SHOWA ALUMINIUM** | |
| AL-150 SG | 5 |
| A-171 | 1,5 |

## 3.8.2 Porosity and distribution of pore volume

The relation between the pore volume ($V_{pore}$) and the total volume ($V_{total}$) of the porous material is called porosity ($\mathcal{E}$).

$$\mathcal{E} = \frac{V_{pore}}{V_{total}} \qquad \{10\}$$

The porosity can be calculated with best accuracy using volumes measured in helium and mercury. In this case $V_{total}$ represents the volume measured in mercury and $V_{pore}$ is the difference of the

volumes measured in mercury and helium.

The measuring unit of porosity gives information only for the total volume of pores in a unit volume material. In case the dimensions and size distribution of the pores are also required, the pore-size distribution function must also be determined (Figure 3.8-2). The function provides information about the pore-sizes and the frequency of the different size pores. These data serve as information for the accessibility of the so-called internal surface (surface area of the pores), i.e. they will indicate the size of molecules able to penetrate into the pores.
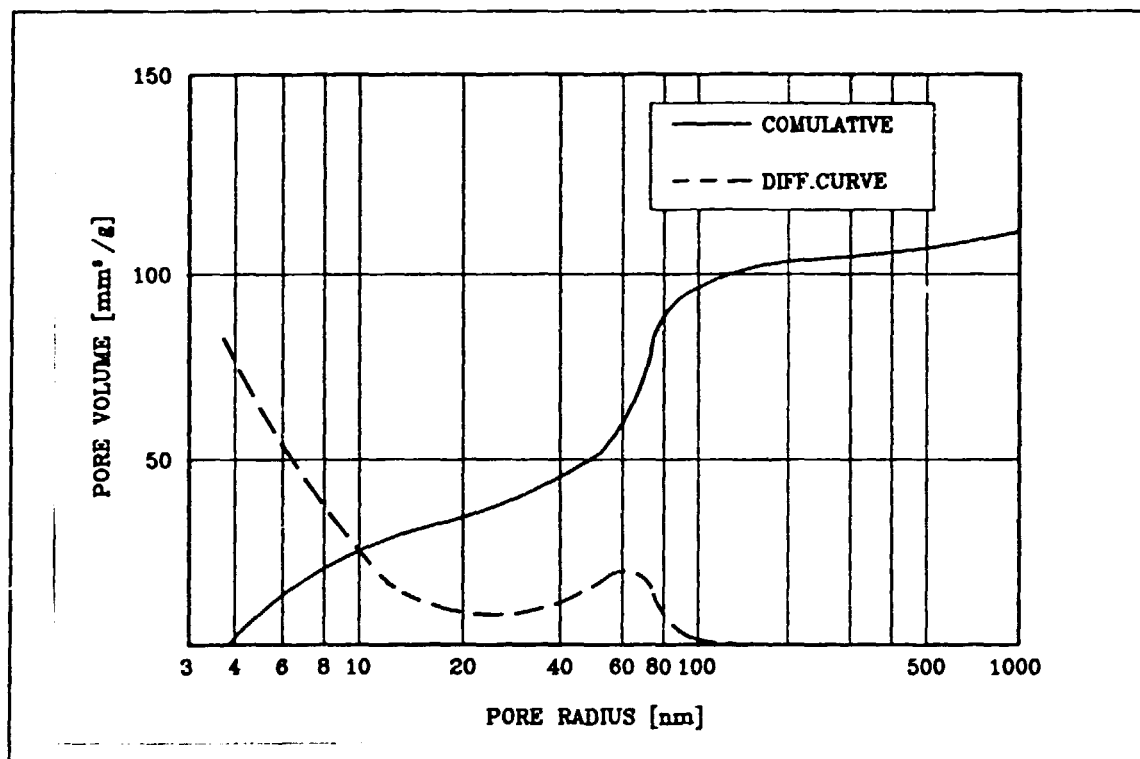


**Figure 3.8-2**
**Pore-size distribution function**

Apart from this, the size of the pores and their size distribution is in relationship with the solidity, contraction, compressibility [58], moreover, in case of fillers, with the grain-bounding characteristics of the binding material, too.

## 3.8.2.1 Determination methods of pore-size distribution

Several measuring methods have been developed for the determination of the size distribution curve [58]. The most important measuring processes and the related literature are enlisted in Table 3.8-3.

Table 3.8-3
Most important methods of determination of porosity- and pore distribution

| Designation of the measuring method | Reference | Remarks |
|---|---|---|
| Density tests in Hg and helium | 59, 60 | Provides only the total pore volume or porosity, resp. |
| Optical microscopy | - | Measuring limit: 0.5 $\mu$m. Provides the pore diameter and pore shape, but not the pore volume |
| Electron microscopy | 61 | Gives the pore diameter and pore shape |
| Gas-adsorption method with the help of adsorption and desorption isotherms | 62, 63 | Determination of pore volume and pore size distribution in the pore-range of r=1.4-30 nm |
| Mercury porosimetry | 64, 65 | Range of measuring: $r = 3 - 10^5$ nm |
| Small angle X-ray dispersion | 66 | Suitable to measure the pore distribution of materials containing pores of relatively homogeneous size distribution and of small diameter (20 nm) |
| Measurement of gas/vapour sucking over velocity | 67 | Difficult to reproduce |
| Luminescence method | 79, 80 | Pore diameter average only |

As it can be seen, density test provides only the pore volume. The optical microscopy does not give the pore volume since either its measuring range is not sufficient, or it is not proper for the determination of the total distribution. The X-ray dispersion method is applicable only in case of certain materials. The measuring method of the sucking over velocity can be used for comparative measurements of materials of the same type, and the luminescence method gives only pore diameter average. As a result of the above, the gas-adsorption and mercury methods became widespread in the practice. The data of the two methods satisfactorily correspond to each other in the range of greater pore-sizes. In the size range of pores with radiants <10 nm,

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there can be a considerable deviation between the data gained by
the two methods. Among others, the deformation effect of the high
pressure mercury is mentioned as the reason of this deviation
and, therefore, in the size range of <10 nm, data of the gas-
adsorption method are considered to be more reliable. Owing to
the above, the two measuring techniques practically complete each
other.


### 3.8.2.2 Determination of pore-size distribution by gas-adsorption

In case the gas/vapour isotherm on an adsorbent is determined by
means of increasing and then decreasing series of pressures, the
adsorption- and desorption-isotherms of the given material will
be obtained as a result Figure 3.8-3.
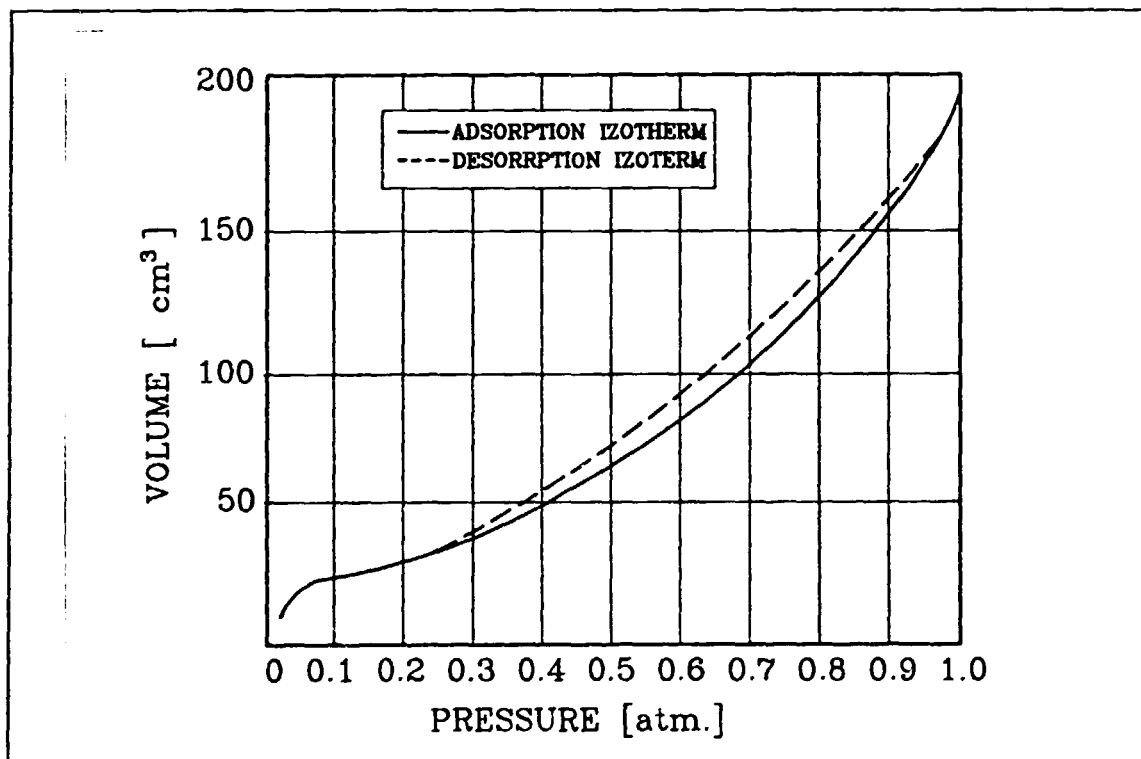


**Figure 3.8-3**
**Nitrogen adsorption and desorption isoterm**

The relationship between the pore radii  of the adsorbent and the
equilibrium saturation vapour pressure of the isotherms is
described by the Kelvin equation [57]:

$$\lg \frac{P}{P_O} = - \frac{2\Gamma V}{rRT} \cdot \cos Q \qquad \{11\}$$

where: $P$ = pressure of the adsorbate (gas/vapour),
       $P_O$ = equilibrium vapour pressure of the adsorbate at
            its boiling point temperature,

--------------------------------------------------------------------------

$\Gamma$ = surface tension of the adsorbate, in liquid
     state,

V = molar volume of the adsorbate = $\frac{M}{\rho}$,

M = molar weight of the adsorbate,
$\rho$ = density of the adsorbate, in liquid state,
r = pore-radius,
R = universal gas constant,
T = temperature (K),
Q = wetting contact angle.

After expressing the value of "r" from the Kelvin equation, the
pore-radius sizes belonging to the individual p-values of the
isotherm can be calculated. With the help of these values and of
the total pore spaces, the pore distribution function can be
determined (Figure 3.8-4).
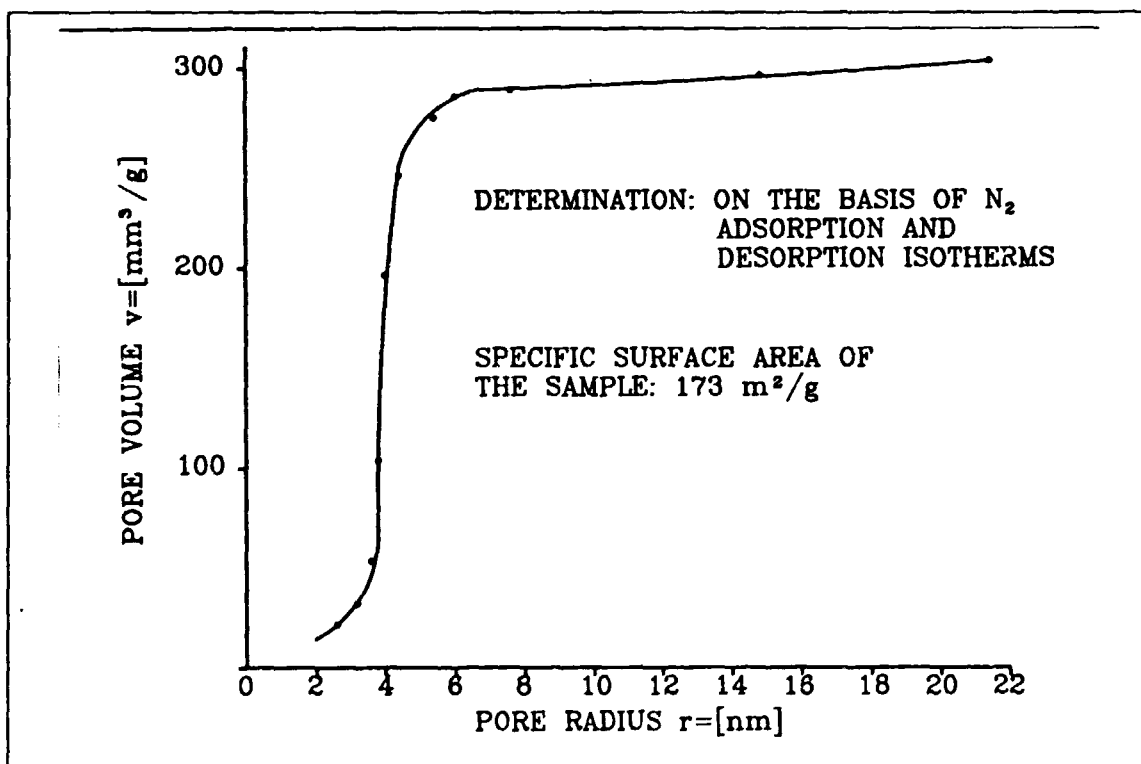


**Figure 3.8-4**
**Cumulative por distribution curve of Bayer alumina**

### 3.8.2.3 Determination of pore distribution by mercury porosimetry

Tests of gas-adsorption pore-size determination are mostly
performed with nitrogen gas. The distribution function of the 1.5
- 30 nm pore-radius range can be determined with nitrogen (65-
68). Within the range of pores above this size, the tests are
generally performed by mercury porosimeters [58, 65, 68, 69, 70].

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Mercury porosimetry is based on the realization that liquids having a wetting contact angle (Q) on the given material greater than 90°, can only intrude into the pores in case pressure is applied on them. The restrictive factor which must be suppressed by pressure is the surface tension of the liquid. Quantitative relationship between the radius (r) and the pressure (P) necessary to fill the capillary of the given dimension is described by the Washburn or Young-Laplace formula [58, 68, 69]:

$$Pr = 2 \Gamma \cos Q \qquad \{12\}$$

where:  $\Gamma$  =  surface tension of the liquid,
        Q  =  wetting contact angle of the liquid on the  surface of the capillary.

The pore distribution can be determined by the help of the formula, in case the amount of liquid intruding into the pores is determined in function of the pressure (P).

Distribution measurements are generally performed with mercury and in most of the tests, the value of the peripheral angle is accepted to be 140 °.

As for the accuracy of tests, the purity of the mercury is  high importance, as its contaminants considerably change the surface tension ($\Gamma$). Surface tension of the pure mercury is 480 din/cm (0.048 N/nm) [69]. Calculating with Q = 140 ° and  $\Gamma$ = 480 din/cm, and assuming that the pores are of cylindric shape, the relationship [8] can be simplified to the following form [69]:

$$r = \frac{7500}{P} \ nm \qquad \{13\}$$

With the help of the formula, the size of radius belonging to the individual pressure values can quickly be calculated, and the cumulative and frequency curves, respectively, can be constructed by the method described at the gas-adsorption system (Figure 3.8-2 and 3.8-5).
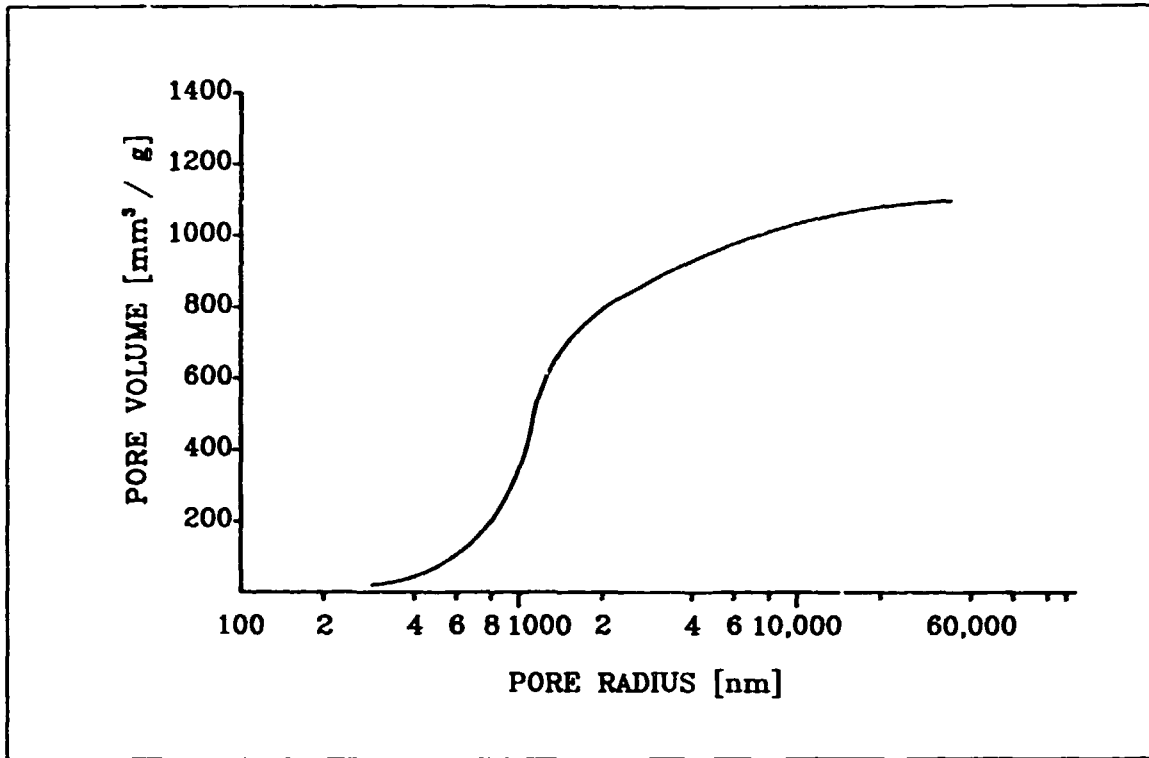
**Figure 3.8-5**
**Cumulative pore distribution curve of plant alumina**

## 3.8.3 Grain-size distribution

Several methods were elaborated to determine the grain-size. The
different methods are collected in Table 3.8-4. Owing to their
accuracy   and   reliability   the   methods   of   sedimentation   are
extensively used for measurement of  Bayer alumina co- and by-
products. Therefore, and because of their significance, they will
be discussed in details. References on the other methods are
given  in  Table 3.8-4.

Table 3.8-4
Methods for determination of the grain-size

| Methods | Measuring range μm | References |
|---------|--------------------|-----------|
| Screening | >10000 | - |
| Sieve | 25-10000 | 73, 74 |
| Sieve with micro mesh sieves | 5-150 | 75, 76 |
| Hindered sedimentation | 4-3000 | 74 |
| Spiral air-elutriator | 5-60 | 75, 76 |
| Sedimentation | 0.5-200 | 75, 81 |
| Sedimentation in gas | 2-200 | 74, 75 |
| Measuring of electric conduction | 2-200 | 74 |
| Optical microscopy | 0.5-300 | 81,82,83 |
| Flow-percussion | 0.2-100 | 74 |
| Absorption of radiation | 0.2-50 | 84, 85 |
| Measuring of light dispersion | 0.1-30 | 75, 81 |
| Gotz-aerosol spectrometer | 0.03-5 | 75, 76 |
| X-ray method | 0.01-0.1 | 74, 81 |
| Centrifugal sedimentation | 0.001-20 | 76, 86 |
| Electron microscopy | 0.001-10 | 74, 75 |
| Measurement with pulverisation | - | 81 |
| Classifying by gassteam | only grain size average | 81, 87 |
| Calculated from specific surface area | only grain size average | 81 |

### 3.8.3.1 Sedimentation methods for determination of grain-size distribution

Several methods and measuring units are known in this field, however, evaluation is always based on the Stokes' equation:

$$V = \frac{1}{18} \; (\mathcal{P}_s - \mathcal{P}_1) \cdot a \cdot d^2 \qquad \{14\}$$

where:  $V$  =  final velocity,
        $d$  =  diameter of the equivalent sphere,
        $\mathcal{P}_s$ =  density of the solid sample,
        $\mathcal{P}_1$ =  density of the measuring medium (liquid or
               gas),
        $\eta$  =  dynamic viscosity of the measuring unit,
        $a$  =  acceleration of the field/gravitional (g), or
centrifugal $(r \cdot \omega^2)$.

But $V = \dfrac{h}{t}$ , therefore can be written:

$$d = \frac{18\,\eta}{(\mathcal{P}_s - \mathcal{P}_1)a} \cdot \frac{h}{t} \qquad \{15\}$$

where:  $h$  =  height of the liquid (gas) column,
        $t$  =  time.

On the basis of determining the quantity of the settled solid as function of the time, can be calculated the grain-size distribution (Figure 3.8-6).
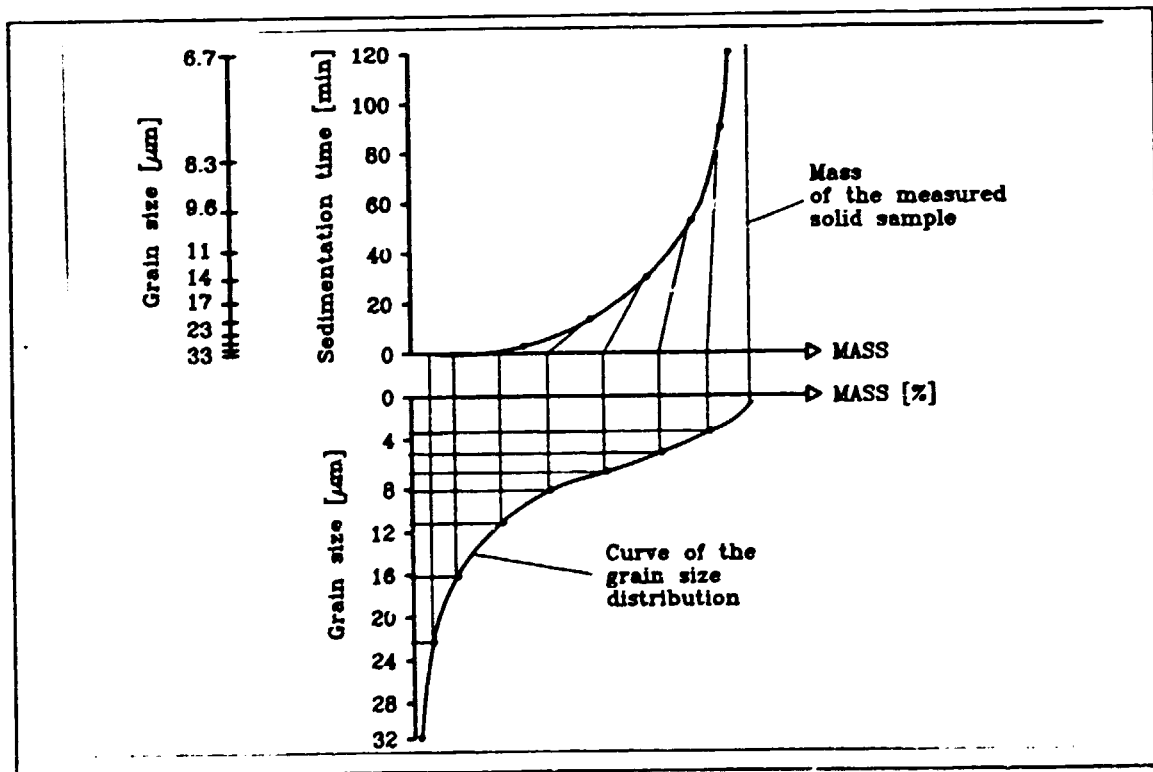


Figure 3.8-6
Determination of the grain-size distribution

Sedimentation in liquids is generally more accurate than in gas, therefore, the former method is more widespread. The equipment of the traditional, old methods are very simple, but the up-to-date methods are significantly quicker and generally of automatic evaluation.

These up-to-date instruments determine the quantity of a given time settled, solid sample with:

- measure of the absorption of light,
- measure of the absorption of radioactive Γ-radiation,
- measure of the absorption of X-ray,
- measure of the absorption of laser-ray.

There are instruments in which the gaseous or liquid medium flow upwards and other ones which work in centrifugal field [88, 89, 90].

These modern instruments give not only the mass grain-size distribution, but the number and area distribution, too. In Figure 3.8-7 grain-size distribution curve of special alumina determined with such instruments is given.
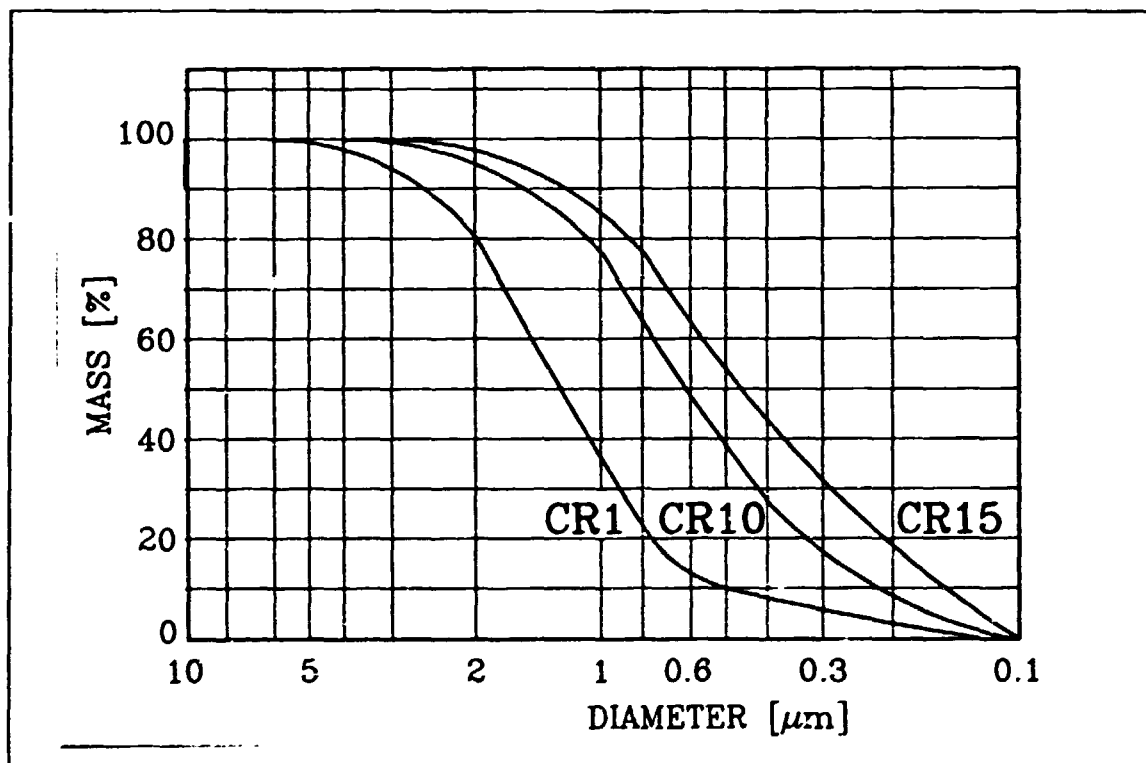


Figure 3.8-7
Grain-size distribution of high purity ceramic aluminas

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# 3.9 PRECISION OF TEST METHODS - DETERMINATION OF REPEATABILITY AND REPRODUCIBILITY OF TESTS

J. Sasvári

Determination of repeatability (r) and reproducibility (R) may be applied in a variety of ways. They can serve:

- to verify that the experimental technique of a laboratory is up to standard;
- to test the results of standardization experiments;
- to compare tests performed on a sample from a batch of material witht a specification;
- to compare test results obtained by a supplier and a consumer on the same batch of material, etc.

## 3.9.1 Definitions

The **repeatability** r is the value below which the absolute difference between two single test results obtained with the same method on identical test material, under the same conditions (same operator, same apparatus, same laboratory, and a short interval of time), may be expected to lie with a specified probability; in the absence of other indications, the probability is 95%.

The **reproducibility** R is the value below which the absolute difference between two single test results obtained with the same method on identical test material, under different conditions (different operators, different apparatus, different laboratories and/or different time), may be expected to lie with a specified probability; in the absence of other indications, the probability is 95%.

## 3.9.2 Practical implications of the definition

That standard must be applied in all the tests forming part of a precision experiment. The values of r and R derived from such an experiment should always be quoted as valid only for tests carried out according to that standard.

## 3.9.3 Statistical model

For estimating the precision of a test method, it is useful to assume that every single test result y is the sum of the three components:

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$$y = m + B + e \qquad\qquad \{1\}$$

where, for the particular material tested, m is the average, B is
a term representing the deviation of the laboratories from m and
e is a random error occurring in every test. It is considered
that equation {1} will cover the majority of practical cases.

The average m of the material tested will be called the **level of
the test property**; different materials (for example different
compositions of alumina) will correspond to different levels.

The term B is considered to be constant during any series of
tests performed under repeatability conditions, but to behave as
a random variable in a series of tests performed under
reproducibility conditions. Its variance will be denoted by
**var(B)** = $\sigma_L^2$ and called the laboratory variance. $\sigma_L^2$ includes the
between-operator and between-equipment variabilities. The error
term e in the model represents a random error occuring in every
single test result. Within a single laboratory, its variance
**var(e)** = $\sigma_W^2$ is called the within-laboratory variance.

It may be expected that s will vary between laboratories due to
differences in the skills of the operators or in the quality of
the equipment used.

This common value, which is an average of the variances taken
over the laboratories participating in the precision experiment,
will be called the repeatability variance and be designated by
**var(e)** = $\sigma^{r2}$.

When the model characterized above is adopted, the repeatability
r and the reproducibility R are given by

$$r = f \sqrt{2} \, s \qquad\qquad \{2\}$$

$$R = f \sqrt{2} \sqrt{\sigma_L^2 + \sigma_r^2} = f \sqrt{2} \, \sigma_R^2 \qquad\qquad \{3\}$$

The coefficient 2 is derived from the fact that r and R refer to
difference between two single test results.

The factor f will generally not differ much from the value 2 and
the use of this value is therefore recommended in this
International Standard. Hence:

$$r = 2.83 \, \sigma_r^2 \qquad\qquad and \qquad\qquad R = 2.83 \, \sigma_R^2$$

### 3.9.4 Design of a precision experiment

One layout is as follows: samples from q batches of material,
representing q different levels of the test property, are sent to
p different laboratories, which are instructed to perform n tests

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under repeatability conditions at each level. These n tests are
thus made on identical material and this type of experiment will
be called a **uniform-level experiment**.

An alternative, preferred in certain cases is the **split-level
experiment**; each level is split into two sub-levels **A** and **B**,
which are slightly different only. Each laboratory receives one
sample from each of these sub-levels for testing. Analysis of the
data The analysis of the data produced by a precision experiment
must be considered as a statistical problem.

## 3.9.5 Analysis of the data

The analysis of the data produced by a precision experiment must
be considered as a statisitcal problem.

Three successive stages can be recognized, namely

a)   a critical examination of the data in order to identify and
     treat outliers or other irregularities, and contingently to
     test the suitability of the model;

b)   computation of preliminary values of r and R for each level
     separately;

c)   establishment of final values of r and R including the
     establishment of a relation between r, R and m when the
     analysis indicates that they depend on the level m. If r
     and/or R are judged to be independent of m, the final values
     taken are the simple average over the levels. The analysis of
     a precision experiment recommended in this International
     Standard first computes for each level estimates, $s_r^2$ and
     $s_R^2$, of the repeatability variance and the between-laboratory
     variance, and from these derives the values of the
     repeatability r and the reproducibility R.

## 3.9.6 Statistical analysis of results of an inter-laboratory experiment

Each combination of a laboratory and a level will be called a
cell of the precision experiment. In the ideal case, the results
of an experiment with **p** laboratories and **q** levels will consist of
a table with **pq** cells each containing n replicate results, that
can **all** be used for computing the repeatability r and the
reproducibility R. This ideal situation is not, however, always
attained in practice. Departures occur due to redundant data,
missing data, and outliers.

## 3.9.7 Recommended practice for investigating outliers

For this purpose, this International Standard recommends the use
cf Cochran's maximum variance test and Dixon's outlier test in

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combination with the following procedure.

If the Cochran's or Dixon's test statistic (P) is **less than** its
5% critical value: the item tested is accepted as correct; the
test is said to be statistically insignificant.

If the test statistic lies between its 5% and 1% critical values:
the item tested is called a **straggler** and marked with a single
asterisk; the test is said to be statistically significant.

If the test statistic is **greater than** its 1% critical value: the
item is called a **statistical outliers** and is marked with a double
asterisk; the test is said to be statistically highly
significant.

**P** is the probability of the observed value of the test statistic.
The 5% and 1% critical values for Cochran's and Dixon's tests are
given in [1].

### 3.9.8 Notation, definitions and basic formulas

The ideal case is p laboratories $L_i$ (i=1,2,..,p) q levels $M_j$
(j=1,2,..,q) and n replicates per $L_iM_j$ combination, with a total
**npq** results of the test. This ideal situation is not always
attained because of the existence of redundant, missing or
outlying results, or outlying laboratories.

#### 3.9.8.1 Original test results

Case of a uniform-level experiment $n_{ij}$ is the number of results
in cell $L_iM_j$ , $y_{ijk}$ is any one of these results (k=1,2,..,n).
When all the results from one or more laboratories are eliminated
at a level j, the number of the laboratories for this level is
designated by $p_j$.

Case of a split-level experiment $y_{ijA}$ and $y_{ijB}$ are the results
obtained, respectively at sub-levels A and B, level j, lab. i.
The notation **p** is also applicable to this case.

#### 3.9.8.2 Measures of cell spread

Case of a uniform-level experiment, for the general case, use the
intra-cell standard deviations $s_{ij}$, given by equation {4}

$$s_{ij} = \sqrt{\frac{1}{n_{ij}-1} \sum_{k=1}^{n_{ij}} (y_{ijk} - \bar{y}_{ij})^2}$$

{4}

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For particular case where all $n_{ij}=n=2$, use the cell range without

$$w_{ij} = |\ y_{ij1} - y_{ij2}\ | = s \cdot \sqrt{2}$$

regard for sign.

Case of split-level experiment, the cell difference is given

$$d_{ij} = y_{ijA} - y_{ijB}$$

taking the sign account.


### 3.9.8.3 Cell averages for uniform split-level experiment

$$\bar{y}_{ij} = \frac{1}{n_{ij}} \sum_{k=1}^{n_{ij}} y_{ijk}$$

The cell averages should be given with one more significant
figure than the test results.


### 3.9.8.4 Repeatability variance $s_r^2$ and between-laboratory variance $s_L^2$

For a given level j, the values of $s_r^2$ and $s_L^2$ are given by the
following equations where, for convenience, the index j has been
dropped.

Case of a uniform-level experiment

$$s_r^2 = \frac{\sum_{i=1}^{p} (n_i - 1) s_i^2}{\left(\sum_{i=1}^{p} n_i\right) - p} \qquad\qquad s_L^2 = \frac{\frac{1}{p-1}\sum_{i=1}^{p} n_i (\bar{y}_i - \bar{y})^2 - s_r^2}{\bar{n}}$$

$$\text{and } \bar{n} = \frac{1}{p-1}\left[\sum_{i=1}^{p} n_i - \frac{\sum_{i=1}^{p} n_i^2}{\sum_{i=1}^{p} n_i}\right] \qquad \text{with } \bar{y} = \frac{\sum_{i=1}^{p} n_i \bar{y}_i}{\sum_{i=1}^{p} n_i}$$

Case of split level experiment

$$s_L^2 = \frac{1}{p-1} \sum_{i=1}^{p} (\bar{y}_i - \bar{y})^2 - \frac{s_r^2}{2} \qquad\qquad s_r^2 = \frac{1}{2} \cdot \frac{1}{p-1} \sum_{i=1}^{p} (d_i - \bar{d})^2$$

$$\text{with } \bar{y} = \frac{1}{p} \sum_{i=1}^{p} \bar{y}_i \qquad\qquad \text{with } \bar{d} = \frac{1}{p} \sum_{i=1}^{p} d_i$$

### 3.9.9 Maximum variance test of Cochran

Cochran's test applies only to uniform level experiments as it is of homogeneity of variance. Cochran's criterion investigates only the highest value in a set of standard deviations or ranges and therefore it is considered as a one-sided outlier test.

Given a set of p standard deviations s , all computed from the same number n of replica test results, Cochran's criterion C is given by

in the case of **n** replicates                          in the case of 2 replicates

$$C = \frac{s_{max}^2}{\sum_{i=1}^{p} s_i^2} \qquad\qquad C = \frac{w_{max}^2}{\sum_{i=1}^{p} w_i^2}$$

In these expressions, $s_{max}$ and $w_{max}$ stand for the highest values in the set. If the test is significant, $s_{max}$ (or $w_{max}$) is classified as straggler or statistical outlier. Critical values for Cochran's criterion at 5% and 1% levels for h=3 to 40 are given in [1].

## 3.9.10 Outlier test of Dixon

Given a set of data $z(h)$, $h=1,2,3,..,H$, arranged in order of magnitude, then Dixon's test uses the following test statistics:

| H | Test statistic |
|---|---|
| 3 to 7 | $Q_{10}$ = the larger of $\dfrac{z(2) - z(1)}{z(H) - z(1)}$ and $\dfrac{z(H) - z(H-1)}{z(H) - z(1)}$ |
| 8 to 12 | $Q_{11}$ = the larger of $\dfrac{z(2) - z(1)}{z(H-1) - z(1)}$ and $\dfrac{z(H) - z(H-1)}{z(H) - z(2)}$ |
| 13 or more | $Q_{22}$ = the larger of $\dfrac{z(3) - z(1)}{z(H-2) - z(1)}$ and $\dfrac{z(H) - z(H-2)}{z(H) - z(3)}$ |

Critical values of these test statistics at the 5% and 1% level and for $H=3$ to 40 are reproduced in [1].

In analysing a precision experiment, Dixon's test can be applied

a)  to the test results within a cell when $n_{ij} >=3$, but this procedure should only be used where Cochran's test has suggested an outlier or straggler, in order to see whether this was due solely to one observation; in that case $h=k$, $H=n_{ij}$, and $z(h)=y_{ijk}$, $i$ and $j$ both being fixed;

b)  to the cell averages for a given level $j$ in table C, when in that case $h=i$, $H=p_j$, and $z(h)=\text{average}(y_{ij})$, $j$ being fixed;

c)  to the cell differences, $d_{ij}=y_{ijA} -y_{ijB}$, for a given level of a split-level experiment, when in that case, $h=i$, $H=p_j$, and $z(h)=d_{ij}$, $j$ being fixed.

In split-level experiment, Dixon's outlier test must be applied
to the cell differences $d_i$.

### 3.9.13 Establishing a functional relation between r (or R) and m

It cannot always be taken for granted that there exists a regular
functional relation between r (or R) and m. The reasoning and
computational procedures presented below apply to both r and R;
they are presented for r only. Only two types of relationship
will be considered:

a linear relation:              $r = u + v\,m$
a logarithmic relation:   $\log r = \log C + d\,\log m$

This should be a weighted regression because, statistically, the
standard error of r is proportional to the value of r. The
weights W must be proportional to $r^{-2}$,

### References

[1] International Standard ISO 5725

# CHAPTER 4

# ESTABLISHMENT OF NEW CAPACITIES

# 4.1 SOME ASPECTS OF ENGINEERING IN A DEVELOPMENT PROJECT: A CASE STUDY

Gy. Bánvölgyi, E. Molnár, Zs. Porkoláb, E. Szabados

Someone said, "The scientist makes things known, the engineer makes things work." [1]. This statement is not an exact definition, nevertheless it shows the core of engineering.

Engineering is a highly complex service which is necessary to carry out a task of a technical nature from the origination of the idea until the smooth operation.

There are lots of investments, such as roads, railways, water supply systems, hospitals, universities, etc., where the indirect, sometimes long-term effects prove the benefits of the implementation.

A project may last from some weeks to several years. Its value can vary from some ten thousands of USD up to several billions if the implementation is included. In spite of the great variety of complexities of such projects, a number of common aspects can also be found.

## 4.1.1 Preliminary considerations

Thinking a project idea (for example, setting up a new aluminium-sulphate plant) over thoroughly, several questions arise:

Which processes known for manufacturing aluminium-sulphate are used in industrial scale?
What kind of materials and energy are needed?
What quality of the product can be maintained by the processes?
What capacity plant should be set up?
Can our product replace the present supply?
Is the manufacturing process in the public domain or is it protected by patents?
Who will supply the designs, the equipments, the production know how?
Shall we consider a turn-key investment?
Where to locate the plant?
How will the raw materials and energy sources be transported to the site?
Does the plant generate any waste product and/or environmental hazard?
How large an area is needed for the plant?
How many employees are required for the smooth operation, with what qualifications and skills?
How much capital is needed to set up a new plant?

What parts of the plant can be/worth to supply from domestic sources?
What operating costs and production costs can be expected in the plant?
How much time is needed to implement the investment?

Considerable skilled engineering work is needed to figure out the reasonable answers.

## 4.1.2 Stages of a typical development project

I. Pre-investment phase

- Identification of investment opportunities (project ideas)
- Preliminary selection stage (Opportunity Study, Pre-feasibility Study)
- Techno-economic Feasibility Study
- Evaluation and decision

II. Investment phase

- Basic engineering
- Negotiation and contracting
- Project design and detailed engineering design
- Construction
- Training, Start up

III. Operational Phase

The duration and peaks in the activity of investment promotion, implementation planning, and management and capital investment expenditures are shown in Figure 4.1-1.
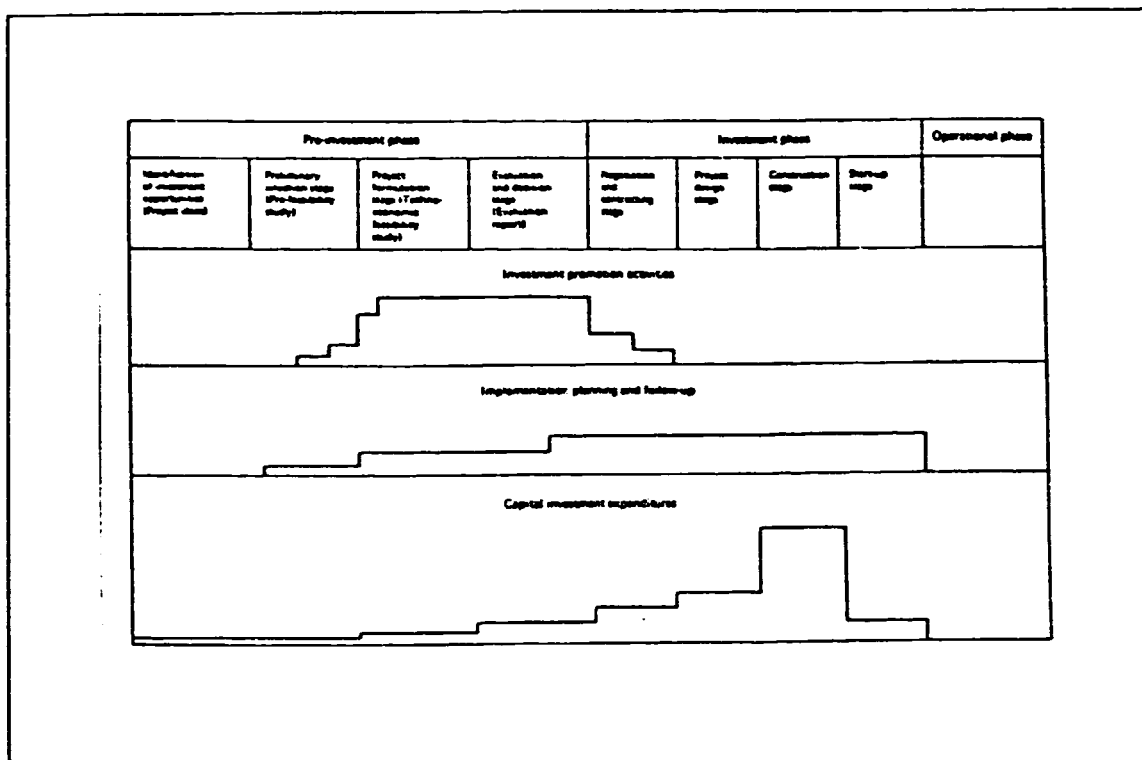
**Figure 4.1-1**
**Phases of investment activity**

## 4.1.3 Project formulation, promotion

It is not too easy to find a partner whose interest is to work
out project ideas, moreover, who has the financial resources to
cover the costs of the pre-investment phase. International
organizations such as UNIDO, UNDP, WHO, FAO, UNESCO, IBRD, IDA,
UNDR, UNEP, etc., international development banks and agencies
play an important and unique role in the developments. The
contribution of governments in formulation and promotion of
development projects should be emphasized.

## 4.1.4. Pre-investment studies

A comprehensive survey of technical, financial, social aspects of
a new development can establish an investment decision. Various
kinds of studies are prepared with this purpose. A short review
of these studies is based on the respective UNIDO Manual [2].

### 4.1.4.1 Opportunity study, Pre-feasibility study

An opportunity study is usually the first, fairly general
approach to formulate the development needs/possibilities of an

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area, a region, a subsector of the economy, etc. The opportunity
study should identify investment opportunities or project ideas
which will be subject to further scrutiny once a proposition has
been proved viable.

A Pre-feasibility study is an intermediate stage between a
project opportunity study and a Feasibility study. The pre-
feasibility and feasibility study usually deal with the following
items:

(a) Market and plant capacity: demand and market study, sales
    and marketing, production programme and plant capacity,
    prices;
(b) Material and energy inputs;
(c) Location and site;
(d) Project engineering: technologies and equipment, and civil
    engineering works;
(e) Overheads: factory, administrative and sales;
(f) Manpower: labour and staff, training;
(g) Project implementation;
(h) Financial analysis: investment costs, project financing,
    production costs, and commercial profitability.

Both opportunity study and pre-feasibility study are rarely
carried out before preparation of a feasibility study.


### 4.1.4.2 Support (functional) studies

- Market studies of the products to be manufactured, including
  demand projections in the market to be served together with
  anticipated market penetration.
- Raw material and input studies, covering present and projected
  availability of raw materials and inputs basic to the project,
  and the present and projected price trends of such inputs.
- Laboratory and pilot plant tests. These tests are carried out
  in cases when raw materials have individual characteristics,
  developments are envisaged, etc.
- Location studies. Particularly for potential projects where
  transport costs would constitute a major factor of costs.
- Economics of scale studies. The task of these studies is to
  evaluate the size/capacity of the plant that would be the most
  economic considering alternative technologies, investment
  costs, production costs, prices.
- Equipment selection studies. Large investments, especially,
  need special support studies of this kind.
- Environmental impacts. These studies can be important to
  eliminate the environmental hazards as much as possible; to
  evaluate processing and/or disposal of wastes.

These support studies can be parts of the pre-investment studies,
however, they can also be elaborated separately, parallel to, or
prior to the particular study.

### 4.1.4.3 Feasibility Study

The Feasibility Study must provide a base - technical, economic and commercial - for an investment decision on an investment project. It should define and analyze the critical elements that relate to the production of a given product together with alternative approaches to such production. Such a study should provide a project of a defined production capacity at a selected location, using a particular technology in relation to defined materials and inputs, at identified investment and production costs, and sales revenues yielding a defined profitability of investment.

The scope of the feasibility study must be well clarified. The study should include all activities scheduled at the plant site; the auxiliary operations related to the production, extraction, off-site transport and storage of inputs, as well as that of outputs (final products, by-products, wastes and emissions) and such off-site ancillary activities as housing schemes and educational, training and recreational facilities.

The feasibility study is not an end in itself, it is a means to arrive at an investment decision that need not agree with the conclusions of the study.

The project planner should divide the entire project into easily calculable or computable components.

## 4.1.5 Alternatives, optimization

When a project idea is formulated, several variations occur, such as:

Raw material, energy sources
Process alternatives
Product quality
Capacity
Site location

Some of these variants can be studied and optimized within the battery limits, others in accordance with location of the plant.

Several assumptions are made when a project is carried out, especially in the early stages of the project (the costs of various equipment, expected unit prices, transportation costs, etc.). As the pre-investment phase progresses the number of variations decreases. Assumptions are replaced by offers, the time and cost estimations become more and more accurate as a result of calculations, discussions, and considerations.

The investment expenditures should occur within the least reasonable period, while the production costs occur continuously throughout the entire duration of operation. It is an art of the

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design to minimize the sum of the investment and the production costs. In many cases operating costs can be reduced by increasing the investment cost (counter-current heat recovery systems, etc.). Optimization is the tool for maximization of the profit. Using computers for this purpose is the general practice.

## 4.1.6 Accuracy of cost estimates

The approximate accuracy of estimates of investment and production costs [2]:

|                          | Percentage |
|--------------------------|------------|
| An opportunity study     | - 30 %     |
| A pre-feasibility study  | - 20 %     |
| A feasibility study      | - 10 %     |

These figures differ from project to project and according to applied cost estimation method. The investment cost estimations can be based on

(a) Calling for tenders based on specifications and bills of quantities. This is the most accurate but also most expensive and time consuming method.
(b) Using the unit cost parameters from comparable operational projects.
(c) Estimating the totals for groups of equipment or functional project parts based on the costs of a comparable existing process.

The degree of accuracy decreases with the increase of coverage of the lump sums.

The material and energy demands can be calculated usually rather accurately for operating cost estimation than e.g. to make a forecast about the unit prices. The material and energy consumption can usually be calculated using laws of nature such as conservation of material and energy and reaction kinetic laws. Unit prices depend on highly unpredictable factors, such as shortages and surpluses, and sometimes economical and political crises.

## 4.1.7 Costs of the engineering

The costs of the pre-investment studies are approximately relative to the total implementation costs:

| An opportunity study     | 0.2  - 1.0 % |
|--------------------------|--------------|
| A pre-feasibility study  | 0.25 - 1.5 % |
| A feasibility Study      | 1.0  - 3.0 % for small industries, |
|                          | 0.2  - 1.0 % for large industries with sophisticated technology. |

The complexity of the engineering work to be done is highly

unrelated to the capacity of the particular plant. Consequently, the relative cost of the engineering work is higher for a small capacity plant than for a large one.

Typically, the costs of engineering in the pre-investment phase are marginal compared to the further investment expenditures.

## 4.1.8. The project team

The team which elaborates the pre-investment study should normally have members with the following expertise:

- Industrial economist
- Market analyst
- Technologist (process engineer) having skill in the particular industry
- Mechanical engineer
- Civil engineer
- Electrical engineer
- Process control engineer
- Industrial management/accounting expert

The team leader's responsibility, besides his role as a specialist, is to plan, organize, direct, and supervise all activities of the team until the study is finalized.

A project team may include departments of an engineering company or even outside consultants, contractor(s) for specific tasks (such as logistics, financing, legal and patent right issues).

## 4.1.9. The professionals and their role in the design process

Preparation of a Techno-economical Feasibility Study is focused on. All participants in the engineering have certain tasks and responsibilities, the extent of their activity is different from the basic engineering and detailed design. The design process and the role of the participants is presented in this chapter.

### 4.1.9.1. Process engineer

His task is the preparation of the process flow-sheet, elaboration of material and heat balances, and description of the process technology. These make a foundation for the following steps of the process and plant design. Determination of the process parameters (e.g.. concentrations, temperatures, reaction times, etc.) and certain main sizes of the equipment (such as reaction time) is the responsibility of the process engineer, however the mechanical engineer is to be involved in these decisions.

The process engineer and process control engineer should be in

very close cooperation when the concept of process control is elaborated, however sometimes the mechanical engineer should also be involved.

The material and energy demands and outputs of the processing plant are also results of the material and heat balances. The quality of the product and its control is determined first of all by the process engineer.

### 4.1.9.2. Mechanical engineer

Sizing of the equipment (such as pumps, conveyors, mixing tanks. etc.) and the decision about its placement is the responsibility of the mechanical engineer. The mechanical engineer should be in close cooperation with process and civil engineers and also with the suppliers of equipment.

The mechanical engineer makes equipment lists showing the main features of the specifications, weight, and number of operating items. Certain auxiliary services, such as repair shops, are determined by the mechanical engineer.

The mechanical engineer and the civil engineer usually have great impact when the investments costs are determined.

### 4.1.9.3. Civil engineer

The feasibility study has to define the location and site suitable for the industrial project under consideration. The choice of location should be made from a fairly wide geographical area within which several alternative sites may have to be considered. The impact on the environment, of erecting and operating the industrial plant has to be studied during the site selection.

The data for the climate, sites and terrain, transport facilities, supply of input materials and energy (including power), waste disposal, and living conditions should be considered when the location is chosen. The transportation costs and costs of the site can have an important impact on the selection.

The mechanical engineer and civil engineer plan the plant lay-out. The climate, the properties of soil, etc. should be taken into consideration. Conceptual designs of the steel, concrete, reinforced concrete structures, and buildings are made during the feasibility study. The water supply, sewage system, and the power supply within the plant are also designed. The storage capacities, maintenance facilities, buildings for laboratory, management, canteen, and waste disposal are shown on the plant lay-out and they are also designed and described. An estimation of the required quantity of steel, concrete, bricks, etc. and the work force for the construction are also tasks of the civil engineer.

### 4.1.9.4. Electrical engineer

When the lay-out of the equipment is determined sizing the transformers according to the power consumption data is performed by the electrical engineer. The power demand of auxiliary services, and lighting should be taken into consideration.

### 4.1.9.5. Process control engineer

The process control engineer is deeply involved in the preparation of the concept of process control with the process engineer. The process control engineer implements the tasks of measurements, data logging, regulations etc. specified by the partners.

All kinds of professionals make investment cost estimations for those equipment and systems of the project which have been designed by the individual professional.

### 4.1.9.6. Economist

The economist calculates the components of the total investments cost (fixed assets, working capital, financial costs), sources of finance (equity and loans), and repayment period taking into consideration the grace-period and interest rate. It is also his task to calculate the production costs as a total of direct and indirect costs. The cash flow is a kind of balance of the sales revenue and expenditures. The internal rate of return and the break even point are also important results of the calculations made by the economist.

As it was previously mentioned, several assumptions are involved in the studies during the pre-investment phases. A sensitivity analysis shows the impact of the change of investment costs, time of implementation, financing conditions, unit prices, etc. on the production costs, return of investment, and other factors concerning the viability of the investment.

## 4.1.10. Organizational aspects

There are several organizational schemes which may be applied to the relationships among the Owners, contractors, consultants, sub-contractors, etc.

Participation of expert(s) as consultant partner(s) of the Owner can be useful especially when a project idea is formulated.

Opportunity and/or pre-feasibility studies, and feasibility studies are often prepared by engineering companies acting as contractor. It is more and more common that location of the company making these studies is far from the site of the intended

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investment. Regular talks in the country of the planned new plant
and in the country where the engineering company is located can
be useful, especially when a complex project is prepared. The
presence of experts at the company headquarters for an extended
time may be necessary to facilitate cooperation. The goal is the
open, continuous and thorough communication among the partners.

Consultants for specific tasks (such as logistics, financing,
legal and patent right aspects) can extend the abilities of the
project team.

The experts of the engineering company and local professionals
may belong to a common team. In these case cost plus fixed fee is
commonly selected for the compensation.

The time schedule is a useful tool for timing the various
activities. A typical schedule for the implementation phase of an
alumina plant is shown in Figure 4.1-2. Similar charts are
prepared for most engineering works.
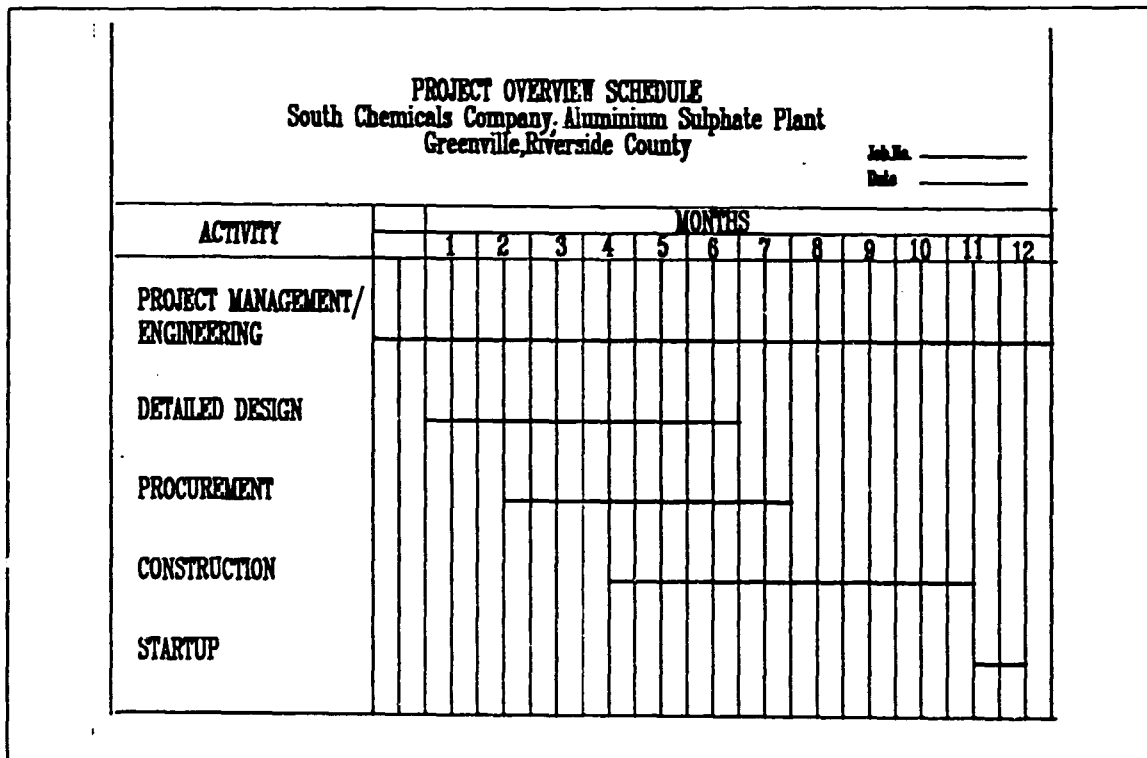


Figure 4.1-2
Project time schedule

## 4.1.11 The engineering company

The following activities belong to the scope of an engineering
company: design, making specifications, bid analysis, vendor data
review, assistance with construction, training and start up. The

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role of the engineering company in the investment phase can be
different from its participation in the Feasibility Study stage.
For example, the engineering company can be a contracting partner
for the design work, and can supervise the construction and
provide training; however, the contractor for the whole
implementation may be a special organization.

The engineering company is responsible for the proper design
(process and equipment), equipment selection, estimation of the
investment, and production costs. The engineering company cannot
control the investment budget unless its task is a turn-key
project. The engineering company can also play a consultant's
role (e.g.. it can provide laboratory tests for the Owner). The
marketing of the product is usually beyond the scope of an
engineering company; however, it can provide assistance in
marketing.

The engineering company is a relatively stable organization,
consisting of departments of process engineering, mechanical
engineering, civil engineering, electrical engineering, process
control engineering, economic analysis, procurement, and project
management. These departments accumulate the experience of
engineering gained through a number of projects. They delegate
members to the team whose task is the preparation of the
particular engineering activity.

## 4.1.12 A case study: Setting up of an aluminium sulphate plant

Some aspects of engineering in the pre-investment phase is
demonstrated by a case study of setting up a new aluminium-
sulphate plant.

### 4.1.12.1 Project background

Let us suppose that there is a developing country where the
single water supply plant in the capital provides only 20 % of
the population of the city with good-quality potable water. Some
5 % of the sewage water generated in the capital goes into a
sewage treatment plant where purification takes place before
disposal. An investment project has been started to develop the
water supply and sewage treatment system. The investment is under
way with the help of a development bank. After completion of the
first stage, some 60 % of the population will be provided with
good quality potable water and the sewage treatment plant will
handle 60 % of the sewage water generated in the capital.
Aluminium-sulphate is used for water and sewage purification
systems as the settling aid. Aluminium-sulphate has been used in
the country for a long time. Traditionally it has been imported
by a trading company.

The following idea for an investment project arose: Should we set
up a plant for domestic production of aluminium-sulphate?

Let us suppose A, B and C, (all of them engineering, consulting and contracting companies), have skills in the field of alumina production. An inquiry was sent to them about a possible aluminium-sulphate plant, and some information was requested.

From the answers it is known that there are processes available using bauxite or aluminium-hydroxide as raw material. (There are processes to manufacture aluminium-sulphate from clays, however they are not in operation in industrial scale.) There are various product grades at different prices on the world market. The main users of aluminium-sulphate are water and sewage treatment plants and paper mills. The paper mills require the best quality.

There is bauxite mining and export and also alumina production and export in one of the neighbouring countries. Therefore the raw material supply can be provided for a new aluminium-sulphate plant. The sulphuric acid production is located some 1000 km from the capital, near to the site of crude oil mining and processing. Both sea-water and sweet water supply are available in various regions. There is a national high-voltage grid throughout the country.

### 4.1.12.2. Preparation of the study; design part

A decision was made to prepare a pre-feasibility study for a possible new aluminium-sulphate plant. A tender was called for this project and the engineering companies having expertise in this field. One of them was chosen. Common preparatory negotiations were held during the formulation of the scope of the pre-feasibility study.

A local company was sought to carry out the marketing of the product as consultant and also a bank to clarify the benefits granted for the investors and financial aspects of an implementation. The marketing company required assistance from the engineering company during discussions with the potential customers.

In order to obtain basic design data for the study, bauxite samples were required for laboratory tests by the engineering company. The aluminium trihydroxide is a common product with predictable behaviour in the particular process technology, therefore specification of quality is enough for study purposes.

A reference is made on the process technology of aluminium-sulphate production as it is detailed in Chapter 2.4.

The process and plant design work have been carried out as it was previously described. Some results of the design and evaluation stages are shown as examples here.

The quality of the possible raw materials is shown in Table 4.1-1. Table 4.1-2 contains the product quality for the two process alternatives i.e. when bauxite or aluminium trihydroxid is used as raw material.

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Table 4.1.-1
Quality of the raw materials

| BAUXITE | Moisture | : 25 | % |
| | $Al_2O_3$ | : 55 | % |
| | $Fe_2O_3$ | : 8 | % |
| | $SiO_2$ | : 5 | % |
| | | | |
| ALUMINIUM TRIHYDROXIDE | Moisture | : 11-12 | % |
| | $Al_2O_3$ | : 57.5-58.5 | % |
| | Fe max. | : 0.015 | % |
| | Grain size | | |
| | over 100 mm, max.: 8.0 | | % |
| | | | |
| SULPHURIC ACID | $H_2SO_4$ | : 98.0-98.5 | % |
| | Fe max. | : 0.004 | % |

Table 4.1-2
Quality of the product

| | RAW MATERIAL | |
| | BAUXITE | HYDRATE |
| --- | --- | --- |
| $Al_2O_3$ | : 14.7 % | 17-18 % |
| $Fe_2O_3$ | : 1.3 % | - |
| Alkalinity, max.: | - | 0.5 % |
| Free $H_2SO_4$ | : - | 0.0 % |
| Fe max. | : - | 0.02 % |
| Residue max. | : 0.3 % | 0.08 % |

The conceptual process flowcharts for the two process variants
are shown in Figure 4.1-3 and 4.1-4. The material consumptions,
derived from the material and heat balances, when aluminium
tryhydroxide is processed, is shown as an example, in Table 4.1-
3. Table 4.1-4 contains the specific material and energy
consumptions for both process variants. A typical main equipment
list, Table 4.1-5, refers to the variant, when aluminium
trihydroxide is the raw material. (The serial numbers are the
respective ones shown in Figure 4.1-4.) Table 4.1-6 shows the
investment cost estimate, and Table 4.1-7 the manpower for the
two alternative process variants. The auxiliary and service
equipment have been considered.
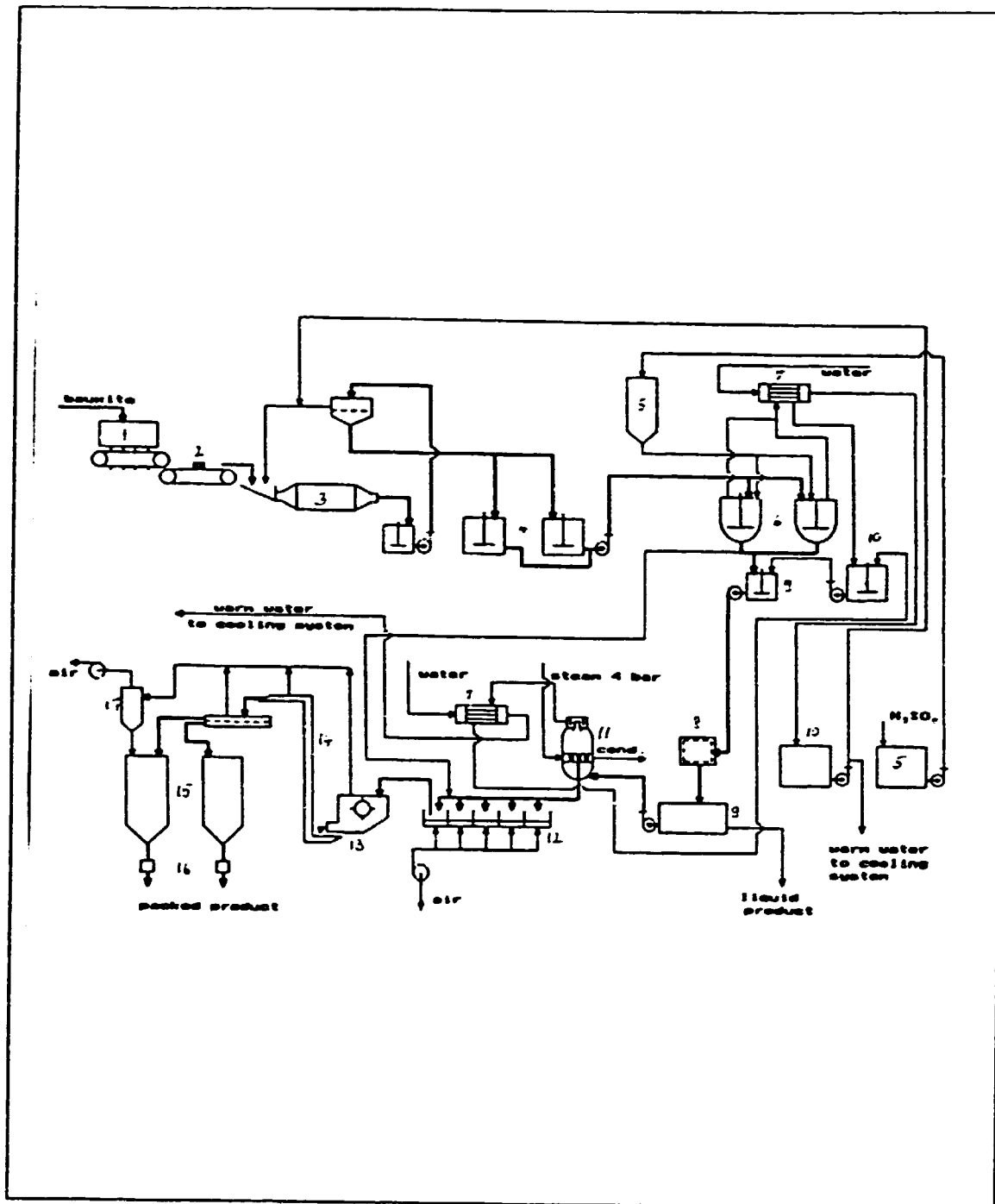
**Figure 4.1-3**
**Conceptual process flow-sheet**
**aluminium sulphate production from bauxite**
1-hopper;  2-weighing belt;  3-roll mills;  4-slurry tanks;  5-sulphuric
acid tanks; 6-acid resistant lined reactors;  7-heat exchanger; 8-aluminium-
sulphate solution filters or centrifuges;  9-aluminium-sulphate solution
tanks;  10-cooling water tanks;  11-evaporator; 12-cooling plates; 13-
crusher; 14-bucket elevator;  15-silos; 16- bag weights; 17-dust filters.
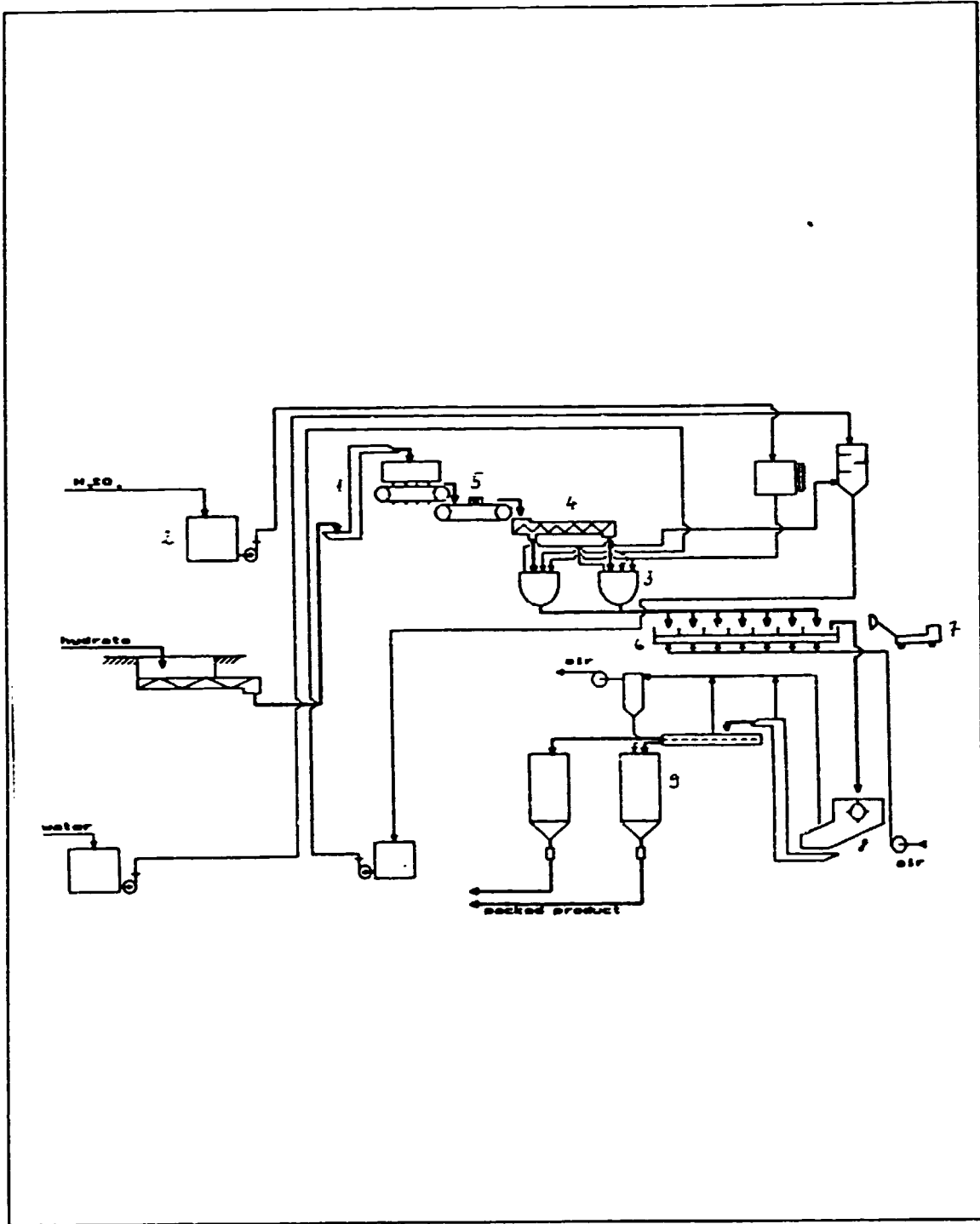
Figure 4.1-4
Conceptual process flow-sheet
aluminium sulphate production from aluminium trihydroxide

**Table 4.1-3**
**Material consumption of the production of aluminium sulphate**
**Production rate: 36,000 t per year**
**Raw material: ATH**

| Constituents | Hydrate (12% moisture) kg | Sulphuric acid (98.5 %) l | Water l | Water (for washing) l | Steam (0.4 MPa) kg | NaClO3 kg |
|---|---|---|---|---|---|---|
| Per dosages | 1,885 | 1,686 | 1,872 | 184 | 16 | 0.6 |
| Flow rate during | | | | | | |
| dosages (1/min) | 100-120 | 160 | 150 | - | - | - |
| Daily consumption | 50,895 | 45,533 | 50,555 | 4,968 | 432 | 17 |

(Production rate: 167.4 t/day, 27 dosages/day, 6.2 t/dosages, 5,160 operating hours/years*)

* 5 days/weeks the maintenance including

**Table 4.1-4**
**Specific consumptions**

| | | RAW MATERIAL | |
|---|---|---|---|
| | | BAUXITE (16 % product) | ATH (17 % product) |
| Alumina hydrate (12 % moisture), | t | - | 0.304 |
| Bauxite (25 % moisture), | t | 0.285 | - |
| Sulphuric acid (98.5 %), | t | 0.470 | 0.501 |
| Water, | m³ | 1.5 | 0.332 |
| Steam (0.4 MPa), | t | 1.2 | 0.003 |
| Power, | kwh | 35.0 | 10.0 |

Table 4.1-5
Main equipment list
Plant: aluminium sulphfate production
Variant: alumina hydrate as raw material

| Ser. No. | Equipment | Technical data | Number Tot Op. | Weight (t) Total | Power (kW) Total |
|---|---|---|---|---|---|
| 1 | Bucket elevator | Q = 12 t/h | 1  1 | 3.2 | 5.5 |
|   |   | H = 17.5 m |   |   |   |
| 2 | Sulphuric acid tank | V = 120 m³ | 2  2 | 10.0 | - |
|   |   | D = 5000 mm |   |   |   |
|   |   | H = 6300 mm |   |   |   |
| 3 | Reactors, lead lined, | V = 7.25 m³ | 4  4 | 32.0 | - |
|   | acid resistant | D = 2880 mm |   |   |   |
|   | brick wall | H = 2218 mm |   |   |   |
| 4 | Screw conveyor | Q = 10 m³/h | 1  1 | 1.3 | 2.2 |
|   |   | L = 14500 mm |   |   |   |
| 5 | Weight belt | Q = 2.4-12 t/h | 1  1 | 0.5 | 2.2 |
|   |   | B = 650 mm |   |   |   |
|   |   | L = 2700 mm |   |   |   |
| 6 | Cooling plate | F = 60 m² | 10  10 | 40.0 | - |
| 7 | Front end loader | Q = 1.5 t | 2  1 | - | - |
|   |   | lifting max 4000 mm |   |   |   |
| 8 | Crusher | Q = 15 t/h | 1  1 | 2.2 | 40.0 |
| 9 | Silos | V = 300 m³ | 4  4 | 100.0 | - |
|   |   | D = 6300 mm |   |   |   |
|   |   | H = 13000 mm |   |   |   |

Table 4.1-6
Investment costs
(1000 USD)

|  | RAW MATERIAL BAUXITE | RAW MATERIAL HYDRATE |
|---|---|---|
| Equipment | 2,970 | 1,486 |
| Civil works, site preparation | 1,880 | 940 |
| Construction | 850 | 470 |
| Design, know-how, organization | 600 | 300 |
| Construction supervision | 240 | 120 |
| Start-up, training | 385 | 195 |
| Contingencies (10 %) | 690 | 355 |
| Total | 7,615 | 3,866 |
| Implementation time | 1 year | 1 year |

Table 4.1-7
Manpower
(persons)

|  | RAW MATERIAL | |
|  | BAUXITE | HYDRATE |
|---|---|---|
| Supervision | 3 | 3 |
| Administration | 1 | 1 |
| Labour | 30 | 20 |
| Total | 34 | 24 |

## 4.1.12.3. Financial and economic evaluation of the study

The capital investment cost is the following for the two process alternatives:

thousand USD

| Item | Raw material | | Difference |
|  | Bauxite | ATH |  |
|---|---|---|---|
| Fixed assets | 7,615 | 3,886 | 3,749 |
| Working capital | 1,050 | 1,400 | - 350 |
| Financing cost | 305 | 155 | 150 |
| Capital investment cost | 8,970 | 5,421 | 3,549 |

As results show, the fixed assets and financing cost for the variant when aluminium trihydroxide is used as raw material, amount to only one half of the respective figures of the case, when bauxite is processed. The financing cost is due to the interest paid during the implementation.

The working capital includes the inventories, and the balance of other assets and liabilities. The difference between the two process variants is mainly due to the deviation in the receivables, cash in hand, and payables.

The capital investment cost for the aluminium trihydroxide processing is only 60 % of the same for the bauxite processing.

### Sources of finance

It was assumed that the fixed assets consist of 20 % equity and 80 % loans. The interest rate for the loan of the fixed assets is 10 % per year as an average, the repayment period is 5 year, after a one year grace period. The working capital is covered by a rolling loan with an annual interest rate of 15 %.

## Production costs and sales revenue

Table 4.1-8 includes the items of direct material costs, wages and salaries and overheads, and the sales revenue as well, for one ton of product aluminium sulphate. As the table shows, the production cost is 144 USD/ton product for bauxite processing and 159 USD/ton for aluminium trihydroxide processing. The bauxite processing gives less material costs, but much more overhead costs.

### Table 4.1-8
### Production cost and profit
### (1991 price level)

| Item | Bauxite Value USD/t | % | Hydrate Value USD/t | % |
|---|---|---|---|---|
| Bauxite or aluminium hydrate | 9 | 6.06 | 50 | 31.69 |
| Sulphuric acid (98.5 %) | 38 | 26.63 | 40 | 25.32 |
| Water | 0 | .22 | 0 | .04 |
| Steam | 18 | 12.75 | 0 | .04 |
| Power | 2 | 1.24 | 1 | .32 |
| Other material costs (10 %) | 7 | 4.68 | 9 | 5.74 |
| DIRECT MATERIAL COST | 74 | 51.57 | 100 | 63.13 |
| Direct wages and salaries | 5 | 3.54 | 3 | 2.11 |
| Social security, etc (50 %) | 3 | 1.77 | 2 | 1.05 |
| DIRECT COST | 82 | 56.88 | 105 | 66.29 |
| Depreciation | 18 | 12.49 | 9 | 5.67 |
| Maintenance and repair | 4 | 2.91 | 2 | 1.30 |
| Utilities | 6 | 3.93 | 6 | 3.51 |
| General and administration expenses | 9 | 6.14 | 13 | 8.21 |
| Contingencies, 10 % | 12 | 8.24 | 13 | 8.49 |
| PRODUCTION COSTS (EXCL. INTEREST) | 131 | 90.60 | 148 | 93.47 |
| Interest:- for investment cost (avarage) | 9 | 6.29 | 5 | 2.84 |
|       - for working capital | 4 | 3.11 | 6 | 3.68 |
| PRODUCTION COSTS (INCL. INTEREST) | 144 | 100.00 | 159 | 100.00 |
| SALES REVENUE | 217 | | 325 | |
| PROFIT - excl. interest | 89 | | 177 | |
|       - incl. interest | 76 | | 167 | |

A much more valuable product can be manufactured by processing aluminium trihydroxide than bauxite as raw material, in spite of that the production costs are higher in that case.

The sales price, based on world market price lists, are 217 USD/ton and 325 USD/ton for the two processing alternatives, respectively.

## Cash flow

The cash flow tables for the first 10 years of the investment are shown in Table 4.1-9 and Table 4.1-10 for the two variants.

**Table 4.1-9**
**Cash flow**
**Variant: aluminium sulfate production from bauxite**
**(1991 price level)**

| Item / years | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sales (kt) | 0 | 36 | 36 | 36 | 36 | 36 | 36 | 36 | 36 | 36 | 324 |
| Capital investment | 8970 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 8970 |
| - Fixed assets | 7615 | | | | | | | | | | 7615 |
| - Working capital | 1050 | | | | | | | | | | 1050 |
| - Financing cost | 305 | | | | | | | | | | 305 |
| Sources of finance | 8970 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 8970 |
| - Equity | 4322 | | | | | | | | | | 4322 |
| - Loans | 4648 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4648 |
| - Others | | | | | | | | | | | 0 |
| Cash-flow | | | | | | | | | | | |
| Sales revenue | 0 | 7812 | 7812 | 7812 | 7812 | 7812 | 7812 | 7812 | 7812 | 7812 | 70308 |
| Production cost (excl.interest) | 0 | 4606 | 4606 | 4606 | 4606 | 4606 | 4606 | 4606 | 4606 | 4606 | 41454 |
| Interest | 0 | 734 | 606 | 478 | 350 | 222 | 158 | 158 | 158 | 158 | 3022 |
| Production cost (incl.interest) | 0 | 5340 | 5212 | 5084 | 4956 | 4828 | 4764 | 4764 | 4764 | 4764 | 44476 |
| Gross profit | 0 | 2472 | 2600 | 2728 | 2856 | 2984 | 3048 | 3048 | 3048 | 3048 | 25832 |
| less: tax | 0 | 742 | 780 | 818 | 857 | 895 | 914 | 914 | 914 | 914 | 7748 |
| Tax - relief | | | | | | | | | | | 0 |
| Profit after tax | 0 | 1730 | 1820 | 1910 | 1999 | 2089 | 2134 | 2134 | 2134 | 2134 | 18084 |
| less: repayment | 0 | 2329 | 2329 | 2329 | 2329 | 2331 | 1050 | 1050 | 1050 | 1050 | 15847 |
| Profit after tax and repayment | 0 | -599 | -509 | -419 | -330 | -242 | 1084 | 1084 | 1084 | 1084 | 2237 |
| Depreciation | 0 | 635 | 635 | 635 | 635 | 635 | 635 | 635 | 635 | 635 | 5715 |
| Cash-flow | 0 | 36 | 126 | 216 | 305 | 393 | 1719 | 1719 | 1719 | 1719 | 7952 |
| Cumulative cash-flow | 0 | 36 | 162 | 378 | 683 | 1076 | 2795 | 4514 | 6233 | 7952 | |

Table 4.1-10
Cash flow
Variant: aluminium sulfate production from hydrate
(1991 price level)

| Item / years | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sales (kt) | 0 | 36 | 36 | 36 | 36 | 36 | 36 | 36 | 36 | 36 | 324 |
| Capital Investment | 5421 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5421 |
| - Fixed Assets | 3866 | | | | | | | | | | 3866 |
| - Working Capital | 1400 | | | | | | | | | | 1400 |
| - Financing Cost | 155 | | | | | | | | | | 155 |
| Sources of Finance | 5421 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5421 |
| - Equity | 773 | | | | | | | | | | 773 |
| - Loans | 4648 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4648 |
| - Others | | | | | | | | | | | 0 |
| Cash-flow | | | | | | | | | | | |
| Sales Revenue | 0 | 11700 | 11700 | 11700 | 11700 | 11700 | 11700 | 11700 | 11700 | 11700 | 105300 |
| Production Cost (excl.Interest) | 0 | 5327 | 5327 | 5327 | 5327 | 5327 | 5327 | 5327 | 5327 | 5327 | 47943 |
| Interest | 0 | 502 | 437 | 372 | 307 | 242 | 210 | 210 | 210 | 210 | 2700 |
| Production Cost (incl.Interest) | 0 | 5829 | 5764 | 5699 | 5634 | 5569 | 5537 | 5537 | 5537 | 5537 | 50643 |
| Gross Profit | 0 | 5871 | 5936 | 6001 | 6066 | 6131 | 6163 | 6163 | 6163 | 6163 | 54657 |
| less: Tax | 0 | 1761 | 1781 | 1800 | 1820 | 1839 | 1849 | 1849 | 1849 | 1849 | 16397 |
| Tax - Relief | | | | | | | | | | | 0 |
| Profit after Tax | 0 | 4110 | 4155 | 4201 | 4246 | 4292 | 4314 | 4314 | 4314 | 4314 | 38260 |
| less: Repayment | 0 | 2050 | 2050 | 2050 | 2050 | 2048 | 1400 | 1400 | 1400 | 1400 | 15848 |
| Profit after Tax and repayment | 0 | 2060 | 2105 | 2151 | 2196 | 2244 | 2914 | 2914 | 2914 | 2914 | 22412 |
| Depreciation | 0 | 323 | 323 | 323 | 323 | 323 | 323 | 323 | 323 | 323 | 2907 |
| Cash-flow | 0 | 2383 | 2428 | 2474 | 2519 | 2567 | 3237 | 3237 | 3237 | 3237 | 25319 |
| Cumulative cash-flow | 0 | 2383 | 4811 | 7285 | 9804 | 12371 | 15608 | 18845 | 22082 | 25319 | |

The cumulative cash flow is almost 8 million USD for the case when bauxite raw material is used, and 25.3 million USD when aluminium trihydroxide is processed.

## Profitability

Some indicators for a steady state evaluation are the following:

| Item | Raw material | |
| --- | --- | --- |
| | Bauxite | ATH |
| Profit/capital cost, % | 30 | 111 |
| Profit/sales revenue, % | 35 | 51 |

These indicators are quite favourable. The disadvantage of using these indicators is that the time factor is not taken into consideration.

It is more informative, if the timing of expenditures and revenues are considered as a function of time. Let us assume that the duration of the project is 15 years for both process variants. The internal rates of return (IRR), i.e., the discount rate, when net present values give zero as a result of the difference of sales revenues and costs, are the following:

| | Raw material | |
| --- | --- | --- |
| | Bauxite | ATH |
| Internal Rate of Return (IRR),% | 7.6 | 47.0 |

A comparison with the average profitability of other investments, the interests of deposits and loans, and with the inflation rate should be made in order to decide, whether this particular project is viable or not.

## Sensitivity analysis

Various kinds of sensitivity analyses can be made as it has previously been described. These analyses are not included in this paper, because of the limited space.

The break-even point analysis was made as an example in this case. This reveals the impact of the utilization of the production capacity on the profitability/viability of the project. The following results were arrived at.

At least a 44.5 % utilization of the capacity should be attained in order to make any profit when bauxite is the raw material, while the respective figure is 24.2 % utilization for processing aluminium trihydroxide. The higher the utilization rate is above these figures, the greater gross profits can be made.

----------------------------------------------------------------

# References

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    Engineers, McGraw Hill Inc., 1981

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    Developing Countries. UNIDO, Vienna, 1986.

# CHAPTER 5

# MANAGING OF INFORMATION

# 5.1 ABOUT INFORMATION MANAGEMENT

É. Hidvégi

## 5.1.1 Importance of information management

Information is the primary source    Information is the primary source of
for todays technology, business and first of all for innovation.
Doing things better is doing things differently, more
imaginatively and not just once but repeatedly. Success in this
game depends on the application of information technology, what
is a rather new branch of the industry.

The appropriate knowledge of information being important in a
given question results in proper actions. It is essential
especially in our accelerated century when it is easy to react
too late to something, which the world has already determined.

Manufacturing could become a fruitless effort without information
on markets and customers need. The outcome is that customers get
not what they really want, but what the supplier thinks they
should have. Will they pay for it?

The main object of Information Management is to increase the
effectiveness of knowledge accumulated all over the world .
Therefore, information management is becoming an increasingly
important and responsible part of management.

In view of growing importance of information in research,
development, industry and/or commerce, all organizations, namely
for-profit corporations, non-profit enterprises or governmental
agencies do all efforts in order to strengthen their position in
information management.

Since the volume of data and information are increasing rapidly,
availability and access to modern information services taking
advantages of advanced technologies in data porcessing and
communications become of critical importance for the efficiency
of research and development activities, technology transfer, and
for the competitiveness of manufacturing industries.

Thus, the importance of this activity is quite obvious. It would
be irresponsible to ignore it.

The question of how to start or how to close up to already
existing information systems can not be answered in general.
Individual companies, countries and people should find their own
way taking into account their own advantages and disadvantages.
However, libraries could be filled with books and papers written

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on the subject, number of databanks are advertising their offers,
the hardware and software supply are tremendous and universities
start courses on information management lasting not less then
eight semesters.

## 5.1.2 Terms of information management

World around us is full of data and on the other hand, most
people is in want of information. The person, who possesses
information, is the winner. The question is, however, how to get
being informed? How to find our way in the dark forest of data?
Of course, it is impossible to entrust all this procedure to
individual's skill only, even if he/she is a genius. We need a
well trained team to go along with the task and this group should
be backed with appropriate hardware and software facilities.

The task of this group is first to be aware of the proper
**KNOWLEDGE ABOUT**

**WHOM, WHAT AND WHEN AN INFORMATION IS REQUIRED.**

Secondly, which is not less important, is

**TO MEET ALL THIS REQUIREMENTS.**

What is left, that is but the matter of details.

This all is the information management, and the Very Important
Person is the

**INFORMATION MANAGER.**

## 5.1.3 Tasks of information managing

Tasks are as follows:

- collecting data,
- storing data,
- managing data,
- transforming data into information,
- forwarding information to the right place in the right time.

**DATA COLLECTION** is supported by libraries, local and/or
international databanks and last but not least by personal
contacts.

The role of **LIBRARIES** went through a dynamic change in the last
decade, as dealing with literature has become computerised
basically. However, I strongly believe and declare it whenever
possible, that personal contact with books and journals is a
necessity as long as human beings exsist. Consequently, the
information manager should take the advantage of computerisation
by fast orientation in books and journals, and the library itself

should be a warm friendly and familiar place for people looking for new ideas.

**DATABANKS** are available in large quantities. One can reach contact with them through telecommunication networks or most conveniently and easily by **CD-ROM technique**. The most popular databanks are listed in Table 5.1-1 and some available CD-ROMs are given in Table 5.1-2. Databases are offered according to activities as it is given in Table 5.1-3. Beside databanks compiled by professionals, databases of our own are important tools as well. From data regarding to local circle of activities a privat databank or at least a database should be built.

**Table 5.1-1**
**Leading Databanks**

| Databanks | Headquarters | Number of databases |
|---|---|---|
| Dialog (Dialog Information Services | Palo Alto (USA) | >380 (260 million records) |
| Data-Star (Radio-Suisse) | Bern | >200 |
| STN (The Scientific and Technical | Karlsruhe | >100 (73 million citations and 14 million chemical structures or numeric records |
| ORBIT (Systyem Development) | Santa Monica (USA) | >100 (75 million citations) |
| BRS Information Technologies | Latham (USA) | >150 |
| Qestel | Paris | >50 (>60 million citations) |
| DIMDI | Koln | 98 |
| IMPADOC (Patent Family Service Patent Registry Service) | Vienna | 2 |
| ECHO (Commission of the European Commuties) | Luxemberg | 23 |
| Bertelsmann Information Service GmbH | Munchen | >130 |

Table 5.1-2
Possibilities of the most useful CD-ROMs

| Subjects: |
|---|
| **Patents**<br>    - European Patent Searching<br>    - Espace<br>    - Cassis/BIB<br>    - Claims/Patents CD |
| **Library**<br>    - The 1990 New Grolier Electronic Encyclopedia<br>      (MS-DOS Version)<br>    - Gabler Wirtschafts-Lexikon (WI-LEX) |
| **Science and technology**<br>    - CAB Abstracts on CD-ROM<br>    - Fine Chemicals Database<br>    - Standards Infodisk |
| **Business**<br>    - Europages CD-ROM<br>    - European Kompass on Disc<br>    - Standard & Poor's Corporations<br>    - F & S INDEX plus TEXT |

**PERSONAL CONTACT** is one of the most valuable source supposing that data collected by that way become common and public, possible as a part of the local database. Knowledge stored in drovers is very common and very useless. In long run storing does not pay even for the person who appreciate his/her value by the amount of hidden informations.

Table 5.1-3
Activities in databases

| BUSINESS | SCIENCE | SOCIAL SCIENCES & HUMANITIES |
|---|---|---|
| Business administr. | Agriculture | Anthropology |
| Company of directories | Astronomy | Architecture |
| Company news | Biology | Communications |
| Financial | Chemistry | Demography |
| International Business | Computer science | Economics |
| Products | Earth sciences | Fine arts |
| Trade | Electronics | History |
| | Energy | Information science |
| | Engineering | Linguistics |
| | Environment | Literature |
| | Food science | Philosophy |
| | Geology | Political science |
| | Materials | Psychology |
| | Mathematics | Religion |
| | Medicine | Sociology |
| | Pharmaceuticals | |
| | Physics | |
| | Space science | |

| LEGAL & GOVERNMENT | REFERENCE | GENERAL INFORMATION |
|---|---|---|
| Business law | Catalogs | Consumer information |
| Copyright | Directories | Culture |
| Criminal law | Encyclopedias,handbooks | Home & garden |
| Demographics | Statistics | Leisure & recreation |
| Employment rights | Standard & | People in the news |
| Patents | specifications | |
| Product liability | | |
| Regulations | | |
| Tax law | | |
| Trademarks | | |

| NEWS |
|---|
| Worldwide news |
| US regional news |
| Newspapers |
| Newswires |

Collected data are stored in **COMPUTERS** and we need computer
**PROGRAMS** to be able to manage the stored data. Several data and
text editing programs are available, however, among them ISIS is
the most fregnently used. The program is provided free of charge
by UNESCO. In the Information Centre of HUNGALU Mini/Micro ISIS
2.3 version is used with full satisfaction. ISIS is a
multilanguage system and popular not only for its low cost but
because of the continuous improvements of the program and
advicing the users by UNESCO specialists. Today the program is
applied by more that 5000 users in nearly 50 countries, from

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South-Africa to the Far-East.

Transforming data into information is the most difficult part of
the whole procedure. It is common saying, that the way of making
an atomic bomb is written down in the databases, the question is
how to find it?

The problem in question should be understood, formulated and
expressed with words and commands understandable for the
computer. Beside adequate technical knowledge a great deal of
skill and intelligence are needed to meet these requirements.

The best way to understand the problem and give an inside how to
handle it, is to see an example.

### 5.1.4 An example: about alumina

In this case we would like to know everything written about
alumina in databanks, we can select the database. The index
section of **DIALOG** shows us the offer in Table 5.1-4.

Table 5.1-4a
Search in DIALGG

--------------------------------------------------------------------
Welcome to DIALOG

DIALINDEX(tm)
   (Copr. DIALOG Info.Ser.Inc.)
--------------------------------------------------------------------
?set files allscience
?s alumina
 Your SELECT statement is:
   s alumina
           Items    File
           -----    ----
           12000      `: INSPEC 2_69-91/9111B2
            1660      5: BIOSIS PREVIEWS_69-91/SEP BA9209:BARRM4109
            4161      6: NTIS_64-91/9111B2
           15045      8: COMPENDEX PLUS_1970-1991/OCT
              42     10: AGRICOLA_1979-91/OCT
             550     14: ISMEC: MECHANICAL ENGINEERING_1973-91/AUG
            5209     16: PTS PROMT_- 72-91/October 21
            2087     18: F & S INDEX _ 1980-91/Oct, Week 3
            3032     19: CHEM. INDUSTRY NOTES_1974-914142
              44     28: OCEANIC ABSTRACTS _ 64-91/OCT
               8     29: MET/GEOASTRO ABSTRACTS - 70-90/NOV
            5037     32: METADEX_66-91/OCT
            8399     33: WORLD ALUMINUM ABSTRACTS _ 68-91/OCT
            1177     35: DISSERTATION ABSTRACTS ONLINE_1861-NOV 91
             158     40: ENVIROLINE_70-91/SEP
--------------------------------------------------------------------

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**Table 5.1-4b**
**Search in DIALOG**

------------------------------------------------------------

| | |
|---:|:---|
| 338 | 41: POLLUTION ABSTRACTS _ 70-91/SEP |
| 14 | 42: PHARMACEUTICAL NEWS INDEX_74-91/OCT, WEEK 4 |
| 97 | 44: AQUATIC SCIENCE ABSTRACTS _ 78-91/SEP |
| 1292 | 45: APTIC _ 66-78/OcT |
| 2 | 48: SPORT DATABASE_1977 - OCT 91 |
| 294 | 50: CAB ABSTRACTS_1984-91/SEP |
| 610 | 51: FSTA _ 69-91/SEP |
| 20 | 52: TSCA Chemical Substances Inventory (Jan. 1991) |
| 344 | 53: CAB ABSTRACTS_1972-1983 |
| 341 | 58: GEOARCHIVE _ 74-91/AUG |
| 11 | 60: CRIS USDA _ AUG 1991 |
| 500 | 62: SPIN _ 75-91/SEP |
| 184 | 63: TRIS _ 70-91/JUN |
| 305 | 65: SSIE CURRENT RESEARCH_78-82/FEB |
| 239 | 67: WORLD TEXTILES_70-91/SEP |
| 105 | 68: ENVIRONMENTAL BIBLIOGRAPHY _ 74-91/AUG |
| 113 | 69: ENERGYLINE_70-91/SEP |
| 4 | 70: SEDBASE _ SEP 1991 |
| 1174 | 73: EMBASE (EXCERPTA MEDICA)_74-91/ISS42 |
| 51 | 74: INTERNATIONAL PHARMACEUTICAL ABS. _ 70-91/SEP |
| 293 | 76: LIFE SCIENCES COLLECTION _ 78-91/JUL |
| 951 | 77: CONFERENCE PAPERS INDEX - 73-91/NOV |
| 22 | 79: FOODS ADLIBRA _ 74-91/AUG |
| 27 | 80: PTS A/DM&T _ - 82-91/Oct.22 |
| 78 | 86: MENTAL HEALTH ABSTRACTS _ 69-91/AUG |
| 1240 | 89: GEOREF_1785-1991/JUL |
| 108 | 92: IHS INTERNATIONAL STANDARDS AND SPECIFICATIONS_ |
| 459 | 96: FLUIDEX _ 73/90 - DEC |
| 1386 | 98: F & S Indexes _ 1972 Thru 1978 |
| 21 | 110: AGRICOLA _ 70-78/Dec |
| 28 | 113: STANDARDS & SPECIFICATIONS_OCT91 |
| 282 | 117: WATER RESOURCES ABSTRACTS _ 68-91/NOV |
| 872 | 118: Nonferrous MeTals AbsTracTs _ 61-83/Dec |
| 129 | 119: TEXTILE TECHNOLOGY DIGEST_1978-91/SEP |

Examined  50 files

| | |
|---:|:---|
| 6 | 123: CLAIMS/REASSIGNMENT & REEXAMINATION_ |
| 31 | 124: CLAIMS/REFERENCE_ |
| 138 | 125: CLAIMS/U.S. PATENT ABSTRACTS WEEKLY_ |
| 17 | 129: PHIND (ARCHIVAL)_SEP 1991 |
| 5 | 141: MARTINDALE ONLINE_1989 |
| 502 | 142: CURRENT TECHNOLOGY INDEX_81-91/JUN |
| 7890 | 144: PASCAL_1983 - 1991 SEP |
| 212 | 148: TRADE AND INDUSTRY INDEX_81-91/OCT |

------------------------------------------------------------

## Table 5.1-4c
## Search in DIALOG

```
   20    149: HEALTH PERIODICALS DATABASE_1976-91/WEEK 41
    6    151: HEALTH PLANNING AND ADMINISTRATION - 1975-91/NOV
  914    155: MEDLINE _ 66-91/DEC (9112W2)
 1112    156: TOXLINE _ 1965-1991/OCT
   18    158: DIOGENES_1976 - OCT. 15, 1991
  104    159: Cancerlit_1963-91/Oct
   42    160: SMOKING AND HEALTH _ 70-89/Dec
  374    161: OCCUPATIONAL SAFETY & HEALTH (NIOSH)_73-91/SEPT
    5    164: COFFEELINE(SM) _ 73-91/AUG
   11    174: Chemical RegulaTions and Guidelines SysTem - Nov
              1982
    2    178: AVERY ARCHITECTURE INDEX_1979-91
   10    179: ARCHITECTURE DATABASE_SEP 1991
    3    185: ZOOLOGICAL RECORD_78-91 V.127 I.09
    5    187: F-D-C REPORTS_1987-OCT. 14, 1991
    2    198: HEALTH DEVICES ALERTS_77-91/OCT WK2
   43    203: AGRIS INTERNATIONAL_74-91/JUN
    2    211: NEWSEARCH_WK=41, 10/18/91
    3    226: TRADEMARKSCAN OG:10/08/91 AP:09/16/91
    2    229: DRUG INFORMATION FULLTEXT - DEC 1990
   51    236: AMERICAN MEN & WOMEN OF SCIENCE 17TH ED.
    6    238: SUPERTECH _ 1973-1991/SEP
    1    239: MATHSCI_59-91/OCT MR,CMP91:10;80-89 CIS
  704    240: PAPERCHEM _ 67-91/DEC
   88    241: ELECTRIC POWER DATABASE_72-91/OCT
    5    242: CLAIMS/COMPOUND REGISTRY
   49    245: WATERNET _ 71-91/SEP
    2    252: PACKAGING SCIENCE & TECHNOLOGY ABSTRACTS_1991 OCT
   43    257: API Energy Business News Index (APIBIZ)_75-91/Oct
              17
Examined 100 files
   78    265: FEDERAL RESEARCH IN PROGRESS_SEP 1991
    3    267: DE HAEN DRUG DATA _ 1980-91
 1246    269: MATERIALS BUSINESS FILE_85-91/OCT
  255    270: Soviet Science & Technology
   26    275: COMPUTER DATABASE_83-91/ISSUE40
  206    285: BIOBUSINESS_1985-1991/OCT WEEK 4
    2    286: BIOCOMMERCE ABS & DIRECTORY_81-91/SEP 30
  488    292: GEOBASE_1980 - AUG  91
 3079    293: ENGINEERED MATERIALS ABS_86-91/OCT
  206    295: WORLD TRANSLATIONS INDEX_1984 - SEP 1991
  680    302: Kirk-OThmer Encyc of Chem Technology
   36    303: Chapman&Hall Chemical Database_11/89
   14    304: MERCK INDEX ONLINE(sm)  UD=90S2
 1068    305: ANALYTICAL ABSTRACTS ONLINE_1980-91/NOV
 1446    315: CHEM ENG & BIOTECH ABSTRACTS_1971-91/OCT
```

### Table 5.1-4d
### Search in DIALOG

```
     15    317: CHEMICAL SAFETY NEWSBASE_1981-91/SEP
      2    318: CHEM-INTELL  UD=9110
    537    319: CHEM BUS NEWSBASE_1984-91 ISS41 /UD=9141
    133    322: POLYMER ONLINE
   4637    335: CERAMIC ABSTRACTS_(1976-AUG 91)
      9    336: RTECS - Registry of Toxic Effects of
  13457    340: CLAIMS/U.S. PATENT ABS FOR FILE INFO,TYPE ?NEWS340
    116    344: CHINESE PATENTS ABSTRACTS IN ENGLISH
   3126    345: INPADOC/Family & Legal Status_
  15821    350: WORLD PATENTS INDEX_1963-1980_
  26897    351: World Patents Index Latest_
   8021    353: APIPAT_- 1964-Jul 1991
  10424    354: APILIT_- 1964-Aug 1991
    466    357: BIOTECHNOLOGY ABSTRACTS_1982-1991/Oct
     56    358: CURRENT BIOTECHNOLOGY ABS_1983-91/OCT
    224    360: FINE CHEMICALS DATABASE UD=9004
     18    390: Beilstein Online -3,837,837 Substances Oct 1991
    107    398: CHEMSEARCH(TM)1965-1991/Sep 10,570,791 Subs
  68193    399: CA SEARCH_1967-1991 UD=11514
  12393    434: SCISEARCH_1974 - 9110W1
   2207    440: CURRENT CONTENTS SEARCH_1990-199110W2
     12    465: ARAB INFORMATION BANK_1983-9109W4
    116    536: New Industrial Products_85-91/Oct Wk 3
   1703    545: INVESTEXT_82-91/OCT 18
     96    563: ICC IBR_10/Oct/91
      3    581: AGRIBUSINESS U.S.A._85-90/Jul 31
   1005    582: JAPAN TECHNOLOGY _ 1985-1991 SEP
      6    587: Jane`s Defense & Aerospace News/Analysis_ 10/17/91
Examined 150 files
    134    609: KNIGHT-RIDDER FINANCIAL NEWS - 89-91/Oct 22
    373    621: PTS NPA _ 85-91/Oct Week 3
    426    624: McGraw-Hill Publications Online_85-91/Oct 21
     56    635: Business Dateline _ 1985-Wk 3 Oct 1991
    986    636: PTS NEWSLETTER DATABASE_87-91/Oct. 22
    136    637: JOURNAL OF COMMERCE_1988 - 21 Oct 1991
   1640    648: TRADE AND INDUSTRY ASAP_83-91/OCT
      7    655: BNA DAILY NEWS_06/01/90 - 10/21/91
     71    669: FEDERAL REGISTER_04 JAN 88 - 17 Oct 1991
     50    675: COMPUTER ASAP_83-91/ISSUE 40
```

Several databases write about alumina, for example, about market or price data or may be some miscellenous technical information is hidden in local newspapers, however we should decide. Let us suppose, that technical details of production and the use of alumina for different purposes is the question of interest. Our selection is either World Aluminium Abstract or Chemical Abstract.

----------------------------------------------------------------------

Starting with both, the result is frightening. Nearly 100
thousands of papers should be read to learn the answer. A search
and the results are shown below:

Welcome to DIALOG

```
    ?b 33 ,399
        File 33: WORLD ALUMINIUM ABSTRACTS 68-91/OCT
        FILE 399: SEARCH1967-1991 UD=11514
```

```
?s alumina?
     S1          90073 ALUMINA?
```

Next decision is, that we see only WAA and we deal only with
alumina used for special purposes. Let's see, what about this?
The expression "special alumina" is unknown in the world
literature.

```
    ?s special(w)alumina
                     1 SPECIAL
                 76592 ALUMINA
         S2          0 SPECIAL(W)ALUMINA
```

Our first question covered a too bright area and the second was
not understood. Now we locate the questioning either on area of
production or of using alumina. The bunch of hits is more
friendly, however still to much to read.

```
?s alumina and production
                 76592 ALUMINA
                176734 PRODUCTION
         S3        7274 ALUMINA AND PRODUCTION
```

```
?s alumina and use
                 76592 ALUMINA
                219024 USE
         S4        2276 ALUMINA AND USE
```

Going further the news about the production by Bayer technology
can be obtained.

```
?s alumina and bayer
                 76592 ALUMINA
                  2526 BAYER
         S1        1892 ALUMINA AND BAYER
```

Hits could be decreased further adding new aspects of production
as for example morphology or we could give time limitations.

```
?s alumina and morphology
              76592 ALUMINA
              29787 MORPHOLOGY
      S6        185 ALUMINA AND MORPHOLOGY
```

To have some more ideas to limit data on the production of
alumina see Table 5.1-5.

<div align="center">

**Table 5.1-5**
**Production of alumina**

</div>

| RAW MATERIALS | METHODS |
|---|---|
| - Improvement of Bayer technology | - Surface treatment |
| - Bauxite with low modulus | - Sintering techniques |
| - Nepheline | - Carbonization |
| - Clays | - Calcination |
| - Alkali aluminate | |
| - Aluminium chloride | |
| - Alkoxide | |
| - Aluminium sulphate | - Quality control |

| SPECIAL FEATURES | | |
|---|---|---|
| - Structural state | - gel | |
| | - sol | |
| | - hydroxide | |
| | - pseudo-boehmite | |
| | - boehmite | |
| | - special calcined | |
| | - tabular | |
| - Morphology | - specific surface area | |
| | - spherical | |
| | - mouldable | |
| | - size | - direct |
| | | - subsequent grinding |
| | - porosity | |
| | - purity | |
| | - surface quality | |

To have a look into the forest of the other question, namely the
use of alumina for other than metallurgical purposes we select
the use in ceramics. The results show that we should go further.

```
?s alumina and ceramic?
              76592 ALUMINA
             205151 CERAMIC?
      S7      21002 ALUMINA AND CERAMIC?
```

Developments in high strength ceramics is a very important
question nowadays. Reading the offered 45 papers in literature is

not an impossible task anymore.

```
?S alumina and high(w)strength(w)ceramic?
              76592 ALUMINA
             612316 HIGH
             128122 STRENGTH
             205151 CERAMIC?
                180 HIGH(W)STRENGTH(W)CERAMIC?
   S8             45 ALUMINA AND HIGH(W)STRENGTH(W)CERAMIC?
```

Of course, alumina could have been used in several more areas. A comprehensive overlook is given on Table 5.1-6.

<div align="center">

**Table 5.1-6**
**USE OF ALUMINA**

</div>

| CERAMICS | FILLERS |
|---|---|
| - Electronic and optoelectronic<br>   - fiber optics<br>   - thin layer<br>   - cosmetics<br>   - illumination<br>- High strength<br>   - solid electrolyte<br>   - electronic substrat<br>   - cutting, grinding tools<br>   - abrasives - optic (Lucalox)<br>   - high alumina content s icas ceramics<br>   - propants<br>- Bioceramics<br>- Porous ceramics (filters) | - plastic industry<br>- building industry<br>- textil industry<br>- chemical industry<br>  (medicines)<br><br>- polishing agents<br>- artificial marble |

| CATALYST, CATALYST CARRIER | INSULATORS |
|---|---|
| - Sevage treatment<br>- Petroleum industry<br>- Gas purification coatings | - Refractories<br>- Radiation absorbing<br>- Plasma sprayed layer<br>- Composites |

| SYNTHETIC MINERALS |
|---|
| - Zeolites<br>- Semi-precious stones |

The demonstrated procedure could be repeated in **CA** database and about 50-60% new hits could be observed.

More important, that patent information databanks INPADOC, HUNPADOC and DERWENT should be searched thoroughly.

In possession of all available data the information manager is

----------------------------------------------------------------

supposed to give reports as short as possible. Condensed and
comprehensive tables are very welcome. Example is given in Table
5.1-7

Table 5.1-7a
Electronics and optoelectronics

| USE/ADVANTAGE | DESCRIPTION | PARTICLE SIZE | PATENT ASSIGNEE | PRIORITY NO . |
|---|---|---|---|---|
| Light transmission of a light transmissive alumina sintered compact, which is used for luminescence bulbs such as high temp. Na-lamps, can be improved. | The light transmission is improved by treating light transmissive alumina sintered compact at 1000-1450 deg.C in oxidising atmos. (Pref. combined with steam flow). | | SHOWA DENKO KK | JP 85255782 |
| Light transmissive aluminous tube having high diffusion tranmissivity and improved strength is produced. | An aluminous tube which is prepd. so as to have diffusion transmissivity of light higher than 95 %, mean crystalline particle size 20-40 microns and variance of particle size (i.e., ratio of the max. crystalline particle size) lower than than 4.0. | 20-40 μ | TOSHIBA CERAMICS KK | JP 8593901 |
| In e.g. high pressure discharge lamps. Presence of Er provides a regular crystal size distribution and eliminates beta-aluminate structure. | Gas-tight sintered translucent $Al_2O_3$ having a density of at least 99.5 % contains at most 2000 ppm MgO (by wt.), pref. below 500 ppm MgO, and 20-200 ppm pref. 20-130 ppm Er as $Er_2O_3$. Article is formed by shaping an $Al_2O_3$ powder contg. an MgO cpd.; impregnating the shape with an Er soln., pref. Er acetyl acetonate in alcohol; and sintering in $H_2$ or a vacuum of 0.13 Pa max. at 1800 deg. C max. | - | PHILIPS GLOEILAMPEN NV | NL 852457 |

Table 5.1-7b
Electronics and optoelectronics (cont)

| USE/ADVANTAGE | DESCRIPTION | PARTICLE SIZE | PATENT ASSIGNEE | PRIORITY NO . |
|---|---|---|---|---|

The sinter tubes are used in high pressure gas discharge lamps. The sintered articles have the following claimed properties: average crystallite size 20-40 microns, surface roughness 0.1-1 (0.2) microns, mechanical strength at least 320 N/sq·mm and in-line light-transmission over 64 %. The tubes require no further processing; energy- and time consumption in sintering is small; smooth surfaces are obtd. and the prods. are dimensionally stable.

The sintered tubes are prepd. from more than 99.5 wt.% $Al_2O_3$ powder having grain-size below 1 mu and opt. admixed with small amts. of MgO and $ZrO_2$ the mixt. is worked up with binders and lubricants and extruded to shaped articles, annealed at 900-1200 deg. C and fired at 1750-1900 deg. C in $N_2$ or vacuum.

0.1 μ    ROSENTHAL TECH AG 83108397 HOECHST CERAMTEC

Esp. in high intensity discharge lamp envelopes (claimed): Body has high optical transmission.

Transparent sintered polycrystalline $Al_2O_3$ body has a major surface glaze-polished to reduce surface high spots without introducing low spots so optical transmission is increased and surface is free of contamination on removal of the glaze. Pref. polycrystalline $Al_2O_3$ body may contain up to 0.5 wt.% MgO; or consist of uniform equiaxed grains of $Al_2O_3$ contg. no more than 150 ppm Mg, less than 1 % pore vol. and ave. grain dia. 20-35 micron (26 micron); alternatively the body compsn. $Al_2O_3$, Mg and Zr and/or Hf, esp. (in wt.%): Mg 0.03-0.15, Hf 0.003-0.12 and Zr 0.002-0.07, each calculated as oxide. In a typical process, the glaze material comprises an alkali metal borate (other than Li borate) with alkali metal oxide to B oxide wt.% ratio of 1:2-4, deposited on the $Al_2O_3$ surface as a liq. suspn.

25-35 μ  GENERAL US ELECTRIC 666858 CO

# LIST OF FIRMS
# INVOLVED IN THE WORKSHOP

HUNGALU Group incorporates one bauxite prospecting company, one bauxite mine, three alumina plants, two smelters, two semis production and two finished products manufacturing plants, moreover it owns a machine construction factory for the aluminium industry and a trading company. They are listed below:

### Bakonyi Bauxit Mines Ltd.
Tapolca, Hősök tere 5.
H-8301 Tapolca P.O.B. 61
Telex:          032-225
Telefax:        (0036)-87-12-813

### Ajka Aluminiumindustrial Ltd.
Ajka,
H-8401, Ajka P.O.B. 45.
Telex:          032-234 or 032-366
Telefax:        (0036)-88-11-634

### Balassagyarmat Metal Working Ltd.
Balassagyarmat
H-2661, Balassagyarmat, P.O.B. 130
Telex:          028-2218

### KÖFÉM Light Metal Works of Székesfehérvár Ltd.
Székesfehérvár, Verseci út 1-15
H-8005, Székesfehérvár, P.O.B. 1
Telex:          021-322 or 021-357
Telefax:        (0036)-22-14-120

### Tatabánya Aluminium Co. Ltd.
Tatabánya
H-2801, Tatabánya, P.O.B. 192
Telex:          027-319
Telefax:        (0036)-34-11-789

### Mr. Róbert Jelinkó BSc, MSc, PhD.
Research Institute for Technical Chemistry of the Hungarian Academy of Sciences,
Veszprém

Graduated at University of Chemical Engineering, Veszprém, Hungary in 1978. His special fields were chlorination of aluminium-oxide at high temperature and mobilizing and mixing of solid systems. He made a procedure to determine local concentration and rate of flowing solid systems. Recently he has been investigating new inorganic processes, use of zeolites and properties of intensive gas-solid/gas-liquid systems.

### Mrs. Erzsébet Juhász, BSc
ALUTERV-FKI Ltd
Research Fellow

Chemical engineer, experienced in halogen metallurgy and in plasma technologies. Main fields of activity: production of metal chlorides, chlorination of aluminuous ores, preparation of ceramic raw materials in plasmas.

### Mrs. Éva Kálmán, BSc, MSc. PhD.
ALUTERV-FKI Ltd.
Head of the Laboratory for Wet Chemistry and Ion-chromatography

Since 1975 she has been working at ALUTERV-FKI in the Materials Science Department. Her main activities are the investigation of

## GEOPROSPECT Prospecting and Drilling Company Limited
Balatonalmádi
H-8221 Balatonalmádi, P.O.B. 28
Telex:          032-251

## Inota Aluminium Works Ltd.
Várpalota
H-8104 Várpalota, P.O.B. 8.
Telex:          032-230
Telefax:        (0036)-80-71-889

## ALUTERV-FKI Ltd. HUNGALU Engineering and Development Centre Ltd.
Budapest, XIII. Pozsonyi út 56
H-1389, Budapest, P.O.B. 128.
Telex:          22-6029
Telefax:        (00361)-1850-153

## Machine Factory of Aluminium Processing Industry Ltd.
Zalaegerszeg
H-8901 Zalaegerszeg. P.O.B. 207
Telex:          033-295
Telefax:        (0036)-92-11-083

## ALOXID Almásfüzítő Alumina Limited Co. Ltd.
Almásfüzítő
H-2931 Almásfüzítő, P.O.B. 2
Telex:          027-378
Telefax:        (0036)-34-80-569

## HUNGALU Trading Co. Ltd.
Budapest, XIII. Pozsonyi út 56
H-1388 Budapest P.O.B.63
Telex:          22-5471 or 22-805
Telefax:        (00361)-140-2723

Mr. Péter Lukács, BSc, PhD, CSc.
ALUTERV-FKI Ltd.
Head of Department for New Materials and Technologies

Graduated on metalphysics and powder metallurgy at the Kiev Technical University (Ukrania). His CSc dissertation work was on the influence of rare earth metaloxides on the behaviours of soft ferrites. Main fields of interest are plasma technologies, advanced ceramics and high purity metals.

Mrs. Eleonóra Molnár, BSc
ALUTERV-FKI Ltd.
Senior Process Engineer

Graduated at the University of Chemical Engineering, Veszprém, Hungary in 1972. 3. She took part in the detailed engineering and process design works of the reconstruction of the digestion of Lauta Alumina Plant, GDR, and in Ajka Gallium Plant, 1985. She was involved in preparing various feasibility studies on different alumina plants, in energy conservation projects and in several studies for the improvement of the alumina production technology.

Mrs. Zsuzsanna Porkoláb, BSc, MSc,
ALUTERV-FKI Ltd.
Head of Economics Section

# ALUTERV-FKI Ltd.

**Hungalu Engineering and Development Centre** (ALUTERV-FKI Ltd.) is a member company of the Hungalu Group (HUNGALU).

**ALUTERV-FKI Ltd.** is the research, development, engineering, contracting and intellectual product centre of the HUNGALU Group. The Institute members about 400 employees, near half of them with the highest qualification, and a considerable number of experts having more than one university or scientific degrees. Majority of the research workers, designers and sales experts has firm industrial background and experience, too.

**ALUTERV-FKI Ltd.** was established in 1976 by uniting two legal predecessors of great past, namely the Research Institute for Non-Ferrous Metals (acronym: FKI) founded in 1948 and the Design Company of the Aluminium Industry (acronym: ALUTERV) established in 1955.

Experts of ALUTERV-FKI are closely cooperating with the manufacturing companies of the parent company and with other research institutes in the non-ferrous metals industry. In possession of profound technological knowledge and experience gained through practice our Institute undertakes:

- research and investigation tasks,
- elaboration of feasibility studies for complete projects, selecting and elaborating process technologies including economic evaluation,
- engineering of new projects, modernization, updating and intensification of existing plants, and erection as main contractor cooperating with local or third country sub-contractors,
- technical supervision,
- training of staff, start-up and commissioning the plant,
- long-term technical assistance,

in the following fields:

- prospecting of bauxite and other mineral resources,
- qualitative and quantitative analysis of explored mineral resources,
- bauxite and other mines,
- bauxite beneficiating plants,
- alumina plants, development of technologies and production facilities,
- plants for producing aluminium sulphate and special aluminium oxides,
- production and processing of by-products resulting from the alumina production,
- plants for artificial corundum (fused alumina),

- plants for aluminium semis and finished products,
- architectural light structures and civil engineering.

**Research activity**

In the well-equipped scientific laboratories of ALUTERV-FKI Ltd.,
the research and development activities covering all fields of
the aluminium industry are carried out by highly qualified
experts of international experience, who have gained
acknowledgements in several countries of the world.

**Organization**

**ALUTERV-FKI Ltd.** is organized according to the verticality of the
aluminium industry in order to meet all the requirements in the
field of research, development, engineering and investment tasks.
Our highly qualified experts grant for the quality of our work.
These colleagues with a great number of scientific and
postgraduate degrees have successfully proved itself in various
jobs.

We should like to draw your kind attention to some outstanding
topics in the field of alumina plants established in foreign
countries, to the reconstruction and expansion works done in the
Hungarian semis-fabrication plants and to the realizations in the
field of aluminium ready-made products and structures. The works
realized abroad were mainly organized by our Foreign Trading
Division and by our Prime Contracting Division.

There are specified divisions not only for the research and
technological tasks, but for the detailed engineering as well
(civil eng. div., electrical and control div., various mechanical
divisions).

A special organization serves for the Prime Contracting and for
the Foreign Trade.

# Ajka Aluminiumindustrial Co., Ltd.

The aluminium works set up in Ajka consist of different plants which are involved in a vertical aluminium industrial system.

Main producing units of the works are the following:

- alumina refinery 500,000 tpy capacity
- aluminium smelter 22,000 tpy capacity
- die-casting plant 5,000 tpy capacity
- various plants producing special products: gallium, zeolite, ground alumina hydrates.

The factory is based on local bauxite deposits and coal mines and situated near the Budapest-Graz railway and road.

The alumina plant operates by the classical Bayer-process. The bigger part of the product is metallurgical alumina, but it is produced for refractories and ceramics, too. Hydrates, zeolites and gallium are processed from aluminate liquor of the Bayer cycle.

Smelter and die-casting plant manufacture a smaller quantity of the alumina product. The rest of alumina and aluminium products are exported.

The direction of strategic development is determined by world economical position: producing products with high quality and low cost.

Changing of the market demand is recognized to produce individual, mainly non-metallurgical alumina products in smaller quantity.

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### HUNGAMOLA Ltd.

HUNGAMOLA Ltd. was founded by Ajka Aluminiumindustrial Co., Ltd. and ALUTERV-FKI Ltd. for producing ground fine products.

# HUNGALU ALOXID (Almásfüzitő Alumina) Ltd.

The plant is affiliated to HUNGALU group. The 300.000 tons/year amina production capacity is based on domestic bauxite by Bayer process. Beside metallurgical grade alumina the ALOXID Ltd. produces special aluminas for special purposes as well.

As a result of many years' research the following branches of special aluminas have been developed:

- ceramic aluminas
- abrasive and polishing aluminas
- gamma-aluminas
- adsorbent and catalyst carriers
-- amorphous aluminium-hydroxide (gel)

The main types of these aluminas are available ground in air jet mill. This method of grinding makes possible breaking up the particles without contamination and they can achieve grain size under 6 um of the 95 percent of the material.

Efficiency of development and quality control are guaranteed by laboratories equiped with modern devices.

The plant offers cooperation to manufacturers and users in the realization of their developments connected to products on aluminium oxide and aluminium hydroxide basis.

# Alumina and Electrocorundum Factory of Mosonmagyaróvár (MOTIM)

In Hungary mining of bauxite, raw material of alumina production was launched in 1925.

The installation works of Mosonmagyaróvár alumina factory were started 18th June, 1934. Its starting capacity was of 1000 tons/year of alumina-hydrate, later on, in 1950 expanded up to 35.000 tons/year.

The 1st of January, 1951 the Alundum factory operational since the last year only had also been attached to the alumina one, and in August the vanadium producing unit was put into service. Production of cast refractory materials was started 6 years later, in 1957.

Section for the production of artificial cryolith was ready in 1963, while the most recent section of the whole factory, the aluminum sulfate plant became operational in 1971.

One year later, in 1972 the extension works of the alumina factory were over, resulting in an overall capacity of 75.000 tons/year.

Meanwhile, development of the plants, the widening choice of products the factory offers made the MOTIM an important exporting company, which products are selled nearly in every country of the world.

# Central Research and Design Institute for Silicate Industry

(Budapest, III. Bécsi út 126-128
H-1300 Budapest, P.O.B. 122
Telex: 22-5269, 22-4376)

The **Central Research and Design Institute for Silicate Industry** (hereinafter SZIKKTI) is the complex research-, development-, technical design- and direct concracting (engineering) organization of the Hungarian building material's industry. The fundamental organizational units of SZIKKTI are: Research Main Department, Design Main Department and Direct Concracting Main Department. Commissioned by Hungarian and foreign partners SZIKKTI displays research-, design- and direct concracting activity in the following fields:

    concrete industry
    cement-, lime- and asbestos cement industry
    stone, quarrying, gravel and clay digging and processing
    brick and tiles industry
    fine- and structural ceramics industry
    glass industry
    special ceramics
    heat-, sound- and water insulating materials
    organic building materials
    silicate chemistry
    power engineering (energetics)
    automatization
    environmental protection, dust collection technologies
    computer control technique
    maintenance and construction of side tracks

# LIST OF CONTRIBUTORS

# LIST OF CONTRIBUTORS
## (in alphabetical order)

### Mrs. Márta Altrichter, MSc.
ALUTERV-FKI Ltd.
Research Engineer

Completed her studies at University of Chemical Engineering, Veszprém in 1974. She worked for Almásfüzitő Alumina Plant from 1976 to 1984 as head of laboratory for special aluminas. She has been working for ALUTERV-FKI since 1984 where her main topics are as follows: Bayer precipitation, technological testing of bauxites, developing new technologies for special alumina production, application of different chemicals in the Bayer-process.

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### Mr. György Baksa, BSc, MSc, PhD.
Hungalu Ajka Aluminiumindustrial Ltd.
General Manager

After finishing his studies he got his MSc degree on chemical engineering at University of Veszprém in 1968. Later on he took part in a postgradual education at Budapest Technical University and got his second MSc degree on economical engineering in 1982. He has been working for HUNGALU AJKA ALUMINIUMINDUSTRIAL Ltd. since 1968. His special fields were the development of alumina production technology especially the lime chemistry of Bayer process and the precipitation of aluminium-trihydroxide. This latter was the subject of his dissertation for PhD.

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### Mr. Zoltán Balogh, BSc.
Hungalu Ajka Aluminiu mindustrial Ltd.
Head of Products' Development Department

graduated at University of Chemistry in Veszprém in 1980. He has been working for Hungalu Ajka Aluminiumindustrial Co., Ltd. since 1981. His special field has been the development of alumina technology.

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### Mr. György Bánvölgyi BSc, MSc.
ALUTERV-FKI Ltd.
Senior Process Engineer

Got MSc. degree at the University of Chemical Engineering, Veszprém, Hungary in 1972. He was involved in the optimisation of the process technology of the Hungarian alumina plants and took part in the elaboration of several relating Feasibility Studies.

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### Mrs. Magdalena Borsodi, BSc, MSc, PhD.
ALUTERV-FKI Ltd.
Research Fellow

Graduated at ELTE University, Budapest as a chemist. She has different tasks of researching, developing and data service in the AAS Laboratory of the Department. She is engaged in chemical and analytical examination of different materials, including determination of main and impurity components of bauxite, red mud, alumina, pure and alloyed aluminium metal.

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Mrs **Ágnes Csanády,** BSc, MSc, PhD, CSc.*
ALUTERV-FKI Ltd.
Scientific Councillor

Graduated at ELTE University in chemistry. She is experienced in
material science as well as in aluminium and aluminium based
alloys, as in the morphology structure and composition of
bauxites, ATH, and aluminium oxides. Recently her special fields
are the surface reactions of bulk and thin film materials. Member
of     the     board     of     the     International     Federation     of
Electronmicroscopic Societies and some other international and
Hungarian Scientific Committees.

Miss **Anna Csordás Tóth** BSc, MSc, PhD.
ALUTERV-FKI Ltd.
Head of the Laboratory for Electron Microscopy

As physicist her main activities are the investigation of non-
metallic materials, SEM and TEM, microanalysis and image analysis
of particular materials. In 1990 she was elected secretary of the
Hungarian Society on Electron Microscopy.

Mrs. **Margarita Dimitrova-Lukács,** BSc, PhD.
Central Research and Design Institute for Silicate Industry (SZIKKTI)
Senior Researcher

In 1969 graduated as engineer in powder metallurgy at the Kiev
Technical University (Ukraina). She studied the influence of rare
earth oxides on the magnetic and electrical properties of some
soft and hard ferrites. She has been working as a senior
researcher at the Special Ceramics Department (SZIKKTI) in the
field of zirconia based advanced ceramics and high temperature
ceramic superconductors. Field of interest: advanced ceramics.

* CSc. = Candidate of Sciences, special Hungarian scientific
degree between PhD. and DSc.

Mr. **Attila Farkas** M.Sc.
ALUTERV-FKI Ltd.
Head of Instrumental Chemical Laboratory


Graduated at Budapest Technical University on Chemical Engineering Faculty in 1970. Since 1988 he has been working for the ALUTERV-FKI in Instrumental Laboratory. His tasks were here: analyses of slurries by ICP-OES technique, investigation of microwave digestion, the control of producing Standard Reference Materials from highly alloyed aluminium.


Mrs. **Judit Fekete** BSc.
ALUTERV-FKI Ltd.
Research Fellow


Graduated Heavy Industrial University, Miskolc, as metallurgist. Her main interesting fields are the morphology of different powders and surface chemistry. She is involved the development of ceramic powders.


Mrs. **Krisztina Fodor,** BSc, MSc.
Ajka Aluminiumindustrial Co., Ltd.


Graduated at Chemical University of Veszprém in 1978. She is interested in the instrumental material tests out of the analytical methods. She directs the research work as a group leader at the Laboratory of Ajka Aluminiumindustrial Co., Ltd.


Mrs. **Mária Földvári,** BSc.
Ajka Aluminiumindustrial Co., Ltd.

Mr. **László Gillemot,** BSc, MSc, PhD.
ALUTERV-FKI Ltd.
Head of Department for Material Science

Graduated at Technical University of Budapest, as mechanical engineer. His special fields are mechanical testing and forming of semis, and application of aluminium products. Acting as short term expert for UNIDO.

Mr. **József György,** BSc, MSc, PhD.
Szikkti,
Head of Department

He graduated for chemistry at ELTE TTK, Budapest. From 1965 on he has been fellow researcher with Szikkti. His area of activity has been the development of aluminium oxide basic materials in order to produce ceramics of predetermined properties.

Mrs. **Éva Hidvégi,** BSc, MSc, PhD.
ALUTERV-FKI Ltd.
Head of Information Centre

Mechanical engineer, received her PhD in 1970 in metallurgy and material testing at the Technical University of Budapest. As the organiser of the Information Centre, her present main field of interest is the collection and evaluation of technical and trading information.

Mr. **Aladár Imre** BSc, MSc, PhD, CSc
ALUTERV-FKI Ltd.
Head of Laboratory

Chemist, head of the Research Department of New Materials and Technologies. Main fields of activity: surface chemistry of products of the aluminium industry, production of vanadium chlorides and aluminium chloride, production of special alumina.

Mr. **István E. Sajó**, BSc.
ALUTERV-FKI Ltd.
**Research Fellow**

He graduated from the Science University of Budapest [ELTE] in 1973. As an X-ray crystallographer works in the Materials Science Department of ALUTERV-FKI Ltd. He is involved in the development of phase analytical methods.

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Mrs. **Judit Sasvári**, BSc, PhD.
ALUTERV-FKI Ltd.
**Head of Laboratory for X-ray diffraction**

Physicist, she has been working in X-ray field. Her main activities are the investigation of poly- and single-crystal materials (qualitative and quantitative phase analysis of minerals, bauxites, red muds, high temperature superconductors etc.).

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Mr. **Károly Solymár**, Bsc, PhD.
ALUTERV-FKI Ltd.
**Head of section of Alumina Technology**

Graduated as chemical engineer (Inorganic chemical technologies, specialized for electrochemistry) in 1957 at Veszprém University, Hungary. Main fields of activity: gallium recovery, Bayer process development, especially digestion with catalytic additives and lime chemistry (causticization procedures), co- and by-products, contribution to preparation of techno-economic studies for alumina plants. Short term consultant for UNIDO. Organizer (lecturer and supervisor) of technical programs of UNIDO Group Trainings on alumina production held in Hungary in 1979 and 1983, in China in 1984, in Vietnam in 1989.

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Mr. **István Somogyi**, BSc.
Ajka Aluminiumindustrial Co., Ltd.
**Technical Specialist**

Finished his studies at Chemical University of Veszprém in 1970 as a chemist engineer, since he has been working for Ajka Aluminiumindustrial Co., Ltd. He was the head of Ajka Gallium Plant for years.

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Mr. **István Somosi**, BSc, MSc, PhD, CSc.
Ajka Aluminiumindustrial Co., Ltd.
Supreme Councillor

Has graduated at Natural Science Faculty of Kossuth Lajos University, Debrecen (Hungary) as a chemist engineer. He got PhD degree with "Study of features of the impurities at the recovery of gallium by electrolysis from aluminate liquor", and CSc degree with "Intensification of home production and refinement of gallium".

Mrs. **Éva Szabados**, BSc, MSc.
ALUTFRV-FKI Ltd.
Economic Councillor

Got M.Sc, degree at the Industrial Faculty of the University for Economics, Budapest, Hungary, in 1975 and a degree as specialist in finance in 1985. As analytical economist her job is to prepare economic and financial analyses for various investments in the Hungarian aluminium industry. She prepared the economic and financial calculations of various Feasibility Studies on alumina plants for foreign countries.

Mr. **Bálint Szabó** BSc, MSc
HUNGAMOLA Ltd.
Director

Mr. **István Szabó**, BSc, PhD, CSc.
Research Institute for Technical Chemistry of the Hungarian Academy of Sciences,
Veszprém
Scientific leader of Dep. Chemical Processes

Graduated at University of Chemistry in Veszprém. His special field was the intensification of organic reactions. Subject of his CSc paper was the haloid-metallurgical processing of metal-oxides. His research areas are developing and intensification of inorganic technologies, gas-solid processes, haloid-metallurgy and production of zeolites and fillers.

Mr. **Tibor Szalai**, BSc.
Magyaróvár Alumina and Fused Alumina Mfg.Ltd.
Plant Unit Manager

Graduated for technology of inorganic chemistry at Veszprém University for Chemical Industry in 1964. Initially he has been engaged as research engineer in the Research laboratory. From 1972 on he has been taking care of the production of the vanadium pentoxide and the aluminium sulphate plant units as Chemical Plant Unit Manager.

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Mr. **Géza Szalay**, BSc, MSc.
Ajka Aluminiumindustrial Co., Ltd.
Technical Director

Got his degree on chemical engineering at the Chemistry University of Veszprém and another degree on electrical engineering at Budapest Technical University. His special fields have been the mathematical modelling and the computerized process control of the alumina production and the aluminium electrolysis in Hungary. In his activity special importance is given to the improvement of the quality of alumina for metallurgical purposes and the development of the product based $Al_2O_3$ for non-metallurgical purposes.

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Mrs. **Mária Tóth**, BSc, PhD.
HUNGALU ALOXID (Almasfuzito Alumina) Ltd.
Head of Research and Quality Control Department

Graduated in 1969 at Faculty of Natural Sciences of ELTE University, Budapest, as chemist. Employed as research chemist at Almasfuzito Alumina Plant since 1969. At present she works as leader of research and development activities of special aluminas. Leading member of the local organization of Hungarian Mining and Metallurgical Society (OMBKE)

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Mrs. **Mariann Tóth-Gyutai**, BSc.
Ajka Aluminiumindustrial Co., Ltd.

Graduated at Dep. Chemical Technology of Veszprém University. Her special field was the production of special aluminium-hydroxides and gallium. Recently she deals with development of zeolite production and forming.

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Mr. **Ferenc Valló**, BSc, MSc, PhD.
Ajka Aluminiumindustrial Co., Ltd.
Head of Technical and Innovation Dept.

Graduated at University of Chemistry in Veszprém. He is leader of
the company's R&D activity. His special fields are Bayer alumina
technology, development of production technology of silica based
products, mainly zeolites. He is member of several scientific
societies.

Mr. **János Vitéz**, BSc. MSc, PhD.
Ajka Aluminiumindustrial Co., Ltd.
Head of Laboratories

Got his degree at Leuna-Meseburg Chemical Faculty of the
Technische Hochschule für Chemie "Carl Schorlemmer" in 1965. He
got PhD degree at Chemical University of Veszprém with "Study of
spectrometric testing results in aluminium industry". He is
interested in material tests, production of high purity gallium.

Mr. **József Zábráczki**, BSc, PhD.
HUNGALU ALOXID (Almasfuzito Alumina) Ltd.
Chief Technical Councillor

Graduated in 1971 at Faculty of Natural Sciences of ELTE
University, Budapest, as physicist. Formerly university
assistant, later research fellow at ALUTERV-FKI and head of
laboratory at Almásfüzitő since 1984. Member and legal specialist
of Hungarian Mining and Metallurgical Society (OMBKE) and Eotvos
Physical Society (ELFT).

Mr. **József Zöldi**, BSc, PhD.
ALUTERV-FKI Ltd
Head of Alumina Laboratory

Completed his studies at the Budapest Eötvös Lóránd University
(ELTE) as chemist. Main fields of research activity: decreasing
of caustic soda losses in Bayer-process, removal of different
impurities from Bayer-process, precipitation of coarse alumina
hydrate, special alumina production, technological evaluation of
bauxites.

# ATTACHMENT


## DETAILED PROGRAM AND TIMETABLE

## OF

## WORKSHOP

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**WORKSHOP**
on
**Co-products and By-products of
the Bayer Alumina Production**
Budapest, Hungary, 25 November - 6 December 1991.
**ALUTERV-FKI Ltd.**

**TIMETABLE**

**25. Nov 1991 Monday**

 8.30  Start from the Hotel to ALUTERV-FKI Ltd. (return about 17.30)

**26. Nov 1991 Tuesday**

 8.30  Start from the Hotel to ALUTERV-FKI Ltd. (return about 19.30)

**27. Nov 1991 Wednesday**

 7.30  Start from the Hotel tc MOTIM (return about 18.30)

**28. Nov 1991 Thursday**

 8.30  Start from the Hotel to ALUTERV-FKI Ltd. (return about 16.30)

**29. Nov 1991 Friday**

 8.30  Start from the Hotel to ALUTERV-FKI Ltd. (return about 16.30)

**30. Nov 1991 Saturday**

13.30  Sightseeing (start from the Hotel, return about 17.30)

**1. Dec 1991 Sunday**

 9.00  Visit to Danube curve (all day excursion) (start from the Hotel, return about 18.00)

**2. Dec 1991 Monday**

 8.30  Start from the Hotel to ALUTERV-FKI Ltd. (return about 16.30)

**3. Dec 1991 Tuesday**

 7.30  Start from the Hotel to AJKA Works (return about 18.30)

**4. Dec 1991 Wednesday**

 8.00  Start from the Hotel to Research for Silicate Industry. (return about 18.30)

**5. Dec 1991 Thursday**

 8.30  Start from the Hotel to ALUTERV-FKI Ltd. (return about 16.30)

**6. Dec 1991 Friday**

 8.30  Start from the Hotel to ALUTERV-FKI Ltd. (return about 16.00)

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**WORKSHOP**
on
Co-products and By-products of
the Bayer Alumina Production
Budapest, Hungary, 25 November - 6 December 1991.
ALUTERV-FKI Ltd.


**TIMETABLE**


| | |
|---|---|
| **25. Nov 1991** | **Monday** |
| 9:00 - 9.45 | Opening of the meeting |

- Statements of the representatives    of UNIDO
- Statements of the representatives    of UNIDO Hungarian
  National    Committee
- Statements of the representatives    of HUNGALU Rt
- Statements of the representatives    of ALUTERV-FKI Ltd.

| | |
|---|---|
| 10:00 - 12:00 | **Lectures** |
| | Main trends of the further development of the alumina production: geographical and product restructuring |
| 12:00 - 14:00 | Lunch brake |
| 14:00 - 17:00 | **Lectures** |
| | Production, use and market for co-products and by-products in connection with Bayer alumina production |
| | General overview of the techniques of quality control in the field of special products |


| | |
|---|---|
| **26. Nov. 1991.** | **Tuesday** |
| 9:00 - 12:00 | **Lectures** |
| | Development and production of non-metallurgical grade aluminas in Hungary |
| | Ceramic aluminas and their characteristics |
| | Production of aluminium sulphate and vanadium pentoxide |
| 12:00 - 13:00 | Lunch brake |
| 13:00 - 16:00 | **Lectures** |
| | Plasma materials for ceramics. |
| | Production of special aluminium-hydroxides and aluminas based on the Bayer cycle |
| | Consultation. |
| 17.00 - 19.00 | WELCOME party |


| | |
|---|---|
| **27. Nov. 1991.** | **Wednesday** |
| 7:30 - 18:00 | **Plant visit** to MOTIM Works |

| 28. Nov. 1991. | Thursday |
|---|---|
| 9:00 - 12:00 | Lectures |
| | Phase analysis of the transition aluminas |
| | Major, minor and trace element analysis by chemical methods: |
| 12:00 - 13:00 | Lunch brake |
| 13:00 - 16:00 | Lectures |
| | Major, minor and trace element analysis by chemical methods: (cont) |
| | - X-ray Fluorescence Spectrometry |
| | - Atomic Absorption Spectrometry |
| | - Analytical spectroscopy |
| | Consultation on material testing |

| 29. Nov. 1991. | Friday |
|---|---|
| 9:00 - 12:00 | Demonstration in laboratories |
| | (X-ray, AAS, Information Centre) |
| 12.00 - 13:00 | Lunch brake |
| 13:00 - 16:00 | Demonstration in laboratories (cont.) |
| | (ICP, Ioncromatograph+wet chemistry, test evaluation) |

| 2. Dec. 1991. | Monday |
|---|---|
| 9:00 - 12:00 | Lectures |
| | Gallium recovery from the Bayer cycle. |
| | Production of zeolite in Ajka |
| | Production of aluminium trihydroxide based products at the Ajka Aluminiumindustrial Co. Ltd |
| 12:00 - 13:00 | Lunch brake |
| 13:00 - 15:00 | Demonstration on test system of model grinding system (grinding system, Technological Laboratories for Alumina and Special Alumina Production) |
| 15:00 - 16:00 | Consultation on technologies |

| 3. Dec. 1991. | Tuesday |
|---|---|
| 7:30 - 18:00 | Plant visit to the Ajka Works |

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| 4. Dec. 1991. | **Wednesday** |
|---|---|
| 8:30 - 11:15 | **Visit to Engineering and Developing Centre for Silicate Industry** |
| | **Lectures** |
| | Ceramic aluminas and their characteristics |
| 11:45 - 12:30 | Lunch brake |
| 12:30 - 18:00 | **Plant visit** to Alumina Plant of Almasfuzito |

| 5. Dec. 1991. | **Thursday** |
|---|---|
| 9:00 - 12:00 | **Lectures** |
| | Some aspects of engineering in a development project: a case study |
| | Surface analysis and morphological studies of special products |
| 12:00 - 13:00 | Lunch brake |
| 13:00 - 16:00 | **Lecture** |
| | Porosity, grain size analysis and surface area determination. |
| | **Demonstration** in laboratories |
| | (SEM, Laboratory for Ceramics, particle size analysis) |

| 6. Dec. 1991. | **Friday** |
|---|---|
| 9:00 - 11:00 | **Consultation** |
| 11:00 - 12:00 | **Closing session** |
| 12:00 - 15:00 | **Lunch** |