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United Nations Industrial Development Organization

GROUP TRAINING IN PRODUCTION OF ALUMINA

VOLUME 2

CHEMICAL BACKGROUND AND TECHNOLOGY OF PROCESSING BAUXITE TO ALUMINA

ALUTERV-FKI

BUDAPEST, 1979

VOLUME 2

CHEMICAL BACKGROUND AND TECHNOLOGY OF PROCESSING BAUXITE TO ALUMINA

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Printed in
ALUTERV-FKI's Printing Shop
in 1979/ 1012

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BAUXITE, THE RAW MATERIAL OF ALUMINA PRODUCTION

Bauxite was discovered in 1821 by a French professor, Pierre Berthier, near Les Beaux en Provence and it got its name from this French place.

Bauxite is a mixed rock of aluminium hydroxide minerals with varying amounts of hematite goethite, kaolinite, anatase, rutile, ilmenite etc. contaminants.

Characteristic Types of Bauxite

The composition of bauxite can - in general - be characterized by the data listed in Table 2.1 /1/.

Composition of Bauxite

Table 2.1

Chemical	Mineralogical
Al_2O_3: 40-65 per cent	Gibbsite $Al_2O_3.3H_2O$ Boehmite, Diaspore $Al_2O_3.H_2O$
SiO_2: 0.5-10 per cent	Kaolinite $Al_4/OH/_8.Si_4O_{10}$ Quartz SiO_2
Fe_2O_3: 3-30 per cent	Hematite Fe_2O_3 Goethite $Fe_2O_3.H_2O$
TiO_2: 0.5-8 per cent	Anatase, Rutile TiO_2
H_2O: 10-34 per cent	In gibbsite, boehmite, diaspore, kaolinite, goethite.
Trace elements: Mn, P, V, Cr, Ni, Ga, Ca, Mg etc.	
Organic matter	

On the basis of their mineral composition, bauxites can be listed into the following five types:

- pure gibbsitic bauxites
- gibbsitic bauxites containing quartz
- mixed bauxites /gibbsitic + boehmitic/
- boehmitic bauxites
- diasporic bauxites

With respect to the selection of the process technology, the mineral composition is of vital importance.

As regards quantitative distribution of the above 5 types, pure gibbsitic bauxites and gibbsitic bauxites containing quartz occur in the largest amount, the laterite bauxites falling basically into these two groups. Because of economical considerations, generally that type is called gibbsitic bauxite, in which the Al_2O_3 content in the monohydrates /boehmite + diaspore/ is less than 5 per cent.

Karstic bauxites are generally of boehmitic or diasporic type, though they can have considerable gibbsite content, too. The term diasporic bauxite is used in case when at least 5 per cent of the Al_2O_3 content is bound in diaspore.

Table 2.2 illustrates the mineral composition of some characteristic bauxite types: it gives the distribution of the main components between the mineral phases and states the type of the given bauxite from the point of view of the processing.

Mineralogical Composition of Bauxite Samples

/Data determined by ALUTERV-FKI/

Table 2.2

Component %	Bauxite Sample							
	No 1	No 2	No 3	No 4	No 5	No 6	No 7	No 8
Al_2O_3 in								
gibbsite	42.3	37.9	25.5	45.0	16.2	-	1.5	2.5
boehmite	3.1	2.0	1.0	7.8	24.5	17.2	49.5	2.8
diaspore	0.2	0.8	1.0	0.8	1.3	35.0	-	38.9
kaolinite	1.4	1.5	2.7	3.4	4.7	3.8	8.4	4.7
illite and cericite			trace				0.9	
goethite	0.5	1.4	2.7		2.1		0.2	0.6
hematite	0.6	0.4	1.0		0.4			
maghemite and magnetite			0.5					
chamosite			trace					1.2
corundum			0.5					
lithiophorite	0.2							
crandallite	0.1							
amorphous			4.0					
Al_2O_3 total	48.4	44.0	38.9	57.0	49.2	56.0	60.5	51.0
SiO_2 in								
kaolinite	1.6	1.8	3.2	4.0	5.5	4.5	9.9	5.5
illite and cericite	-	-	trace	-	-		1.5	-
chamosite	-	-	trace	-	-		-	1.1
quartz	0.5	0.7	8.5	1.0	-	0.1	-	0.7
SiO_2 total	2.1	2.5	11.7	5.0	5.5	4.6	11.4	7.3

Table 2.2 /cont./

Component %	Bauxite Sample No 1	No 2	No 3	No 4	No 5	No 6	No 7	No 8
Fe_2O_3 in								
hematite	15.1	15.3	10.5	6.0	9.7	18.5	3.1	15.2
goethite	4.2	10.2	11.0	1.0	10.2	2.5	5.5	7.6
maghemite	-	-	2.0	-	-			0.7
magnetite	-	-	3.5	-	-			-
chamosite	-	-	-	-	-			2.2
siderite	0.4	-	-	-	-			-
Fe_2O_3 total	19.7	25.5	27.0	7.0	19.9	21.0	8.6	25.7
TiO_2 in								
rutile	0.5	0.4	0.8	0.4	0.6	1.7	-	1.1
anatase	2.2	2.2	1.5	2.1	1.7	0.9	2.8	2.0
TiO_2 total	2.7	2.6	2.3	2.5	2.3	2.6	2.8	3.1

Origin of the bauxite samples:

No 1. South Manchester Jamaica /gibbsitic/
No 2. Aya-Nyinahin, Ghana /gibbsitic/
No 3. Gove, Australia /gibbsitic with quartz/
No 4. Weipa, Australia /gibbsitic + boehmitic/
No 5. Iszkaszentgyörgy, Hungary /gibbsitic + boehmitic/
No 6. Itea, Greece /diasporic/
No 7. Severoonieshk, Soviet Union /boehmitic/
No 8. Lang Son, Viet Nam /diasporic/

Bauxite Reserves and Quality

The world bauxite production in 1970 was 58.2 million tons, whereas the total amount of extracted bauxite up to 1970 reached 636 million tons /1/. The world consumption in 1976 increased to 80 million tons. Whereas De Weisse estimated the total ore reserve to be 8 billion tons only in 1972 /1/, Lotze /2/ in 1978 states already 38 billion tons for the same. This suggests as if the reserves were unexploitable. Lotze describes, however, that in case of an overall examination of the specific bauxite costs in the alumina production, moreover, the mining and transportation costs, merely 12 per cent of the total reserve fall into the most favourable cathegory of costs. As much as 95 per cent of this reserve is found in the territory of Jamaica, Guinea, Australia, Greece and Suriname. In several cases the specific costs of the - otherwise of very good quality - ore are significantly increased as a consequence of the geographical situation of the reserve, the poor infrastructure and the great transportation distance. This explains why most of the bauxite importing countries make efforts to process domestic raw materials with poorer quality and lower Al-content /3/.

Evaluation of Bauxites for Alumina Production

Evaluation of bauxites for alumina production is based on the fact that more than 90 per cent of the world's total alumina is produced by the Bayer technology in which Al_2O_3 and NaOH losses, at alkaline digestion of bauxite, are proportional to the reactive SiO_2 content of bauxite. The composition of the sodium-aluminium hydrosilicate formed can be given by the following summarized formula:

$$3/Na_2O \cdot Al_2O_3 \cdot 2SiO_2/ \cdot Na_2X \cdot aq$$

where: $X = CO_3^{2-}$; SO_4^{2-}; $2OH^-$; $2Cl^-$; $2AlO_3^-$; etc.

In case of producing bauxite for the market, investigations related to fulfilling of the qualitative requirements stated in the transport conditions are mostly restricted to the chemical analysis of the major components. The basis of transportation contracts is still formed by the basis number

$$B = Al_2O_3\,\% - 2SiO_2\,\%.$$

According to the data available during the period of 1955-1970 /4/, the price of bauxite could be determined by the following equation:

$$\text{Price of bauxite} = /B - 29/ \cdot 0.40 \text{ US \$ per ton}$$

The basis of evaluation in the USA is often not the total Al_2O_3 content, but only that part of it which is "available" /soluble/ under standardized conditions, moreover, distinction is made between the reactive /kaolinite/ and non-reactive /quartz/ SiO_2 content, too.

In certain countries, like in Hungary, too, where the content of contaminants in the bauxite is unfavourably high as regards alumina production, the basis number is used in a modified form: $B = Al_2O_3 - 2SiO_2 - CaO - MgO$.

Another widespread system - commonly used in the USSR, for example - is the classification of bauxites on the basis of their "module" defined as the quotient of the Al_2O_3 and SiO_2 content of bauxite /Al_2O_3 per cent/ SiO_2 per cent/.

The module emphasises the effect of SiO_2 content on the caustic soda consumption, but realistic value of the bauxite is given only by simultaneous determination of the Al_2O_3 content, too.

ALUMINIUMHYDROXIDES AND -OXIDES

Al-hydroxides and Al-oxides are of vital importance among the Al-minerals of bauxites and the compounds formed during alumina production. Their structural characteristics are illustrated in Table 2.3 based on the publications of ALCOA Research Laboratories /5/.

Aluminiumhydroxides

Al-hydroxides may occur in trihydrate form /gibbsite, bayerite, nordstrandite/, monohydrate form /boehmite, diaspore/ and as alumogel.

Alumogel plays a significant role principally during bauxite formation, it is a metastable state, which recrystallizes later on to gibbsite.

There is no natural bayerite occurrence, it is formed generally at low temperature in dilute, alkaline solutions. In case of being stored for a longer period or heating up of the solution, it is transformed into gibbsite.

Gibbsite is the main component of tropical laterite-bauxites, although it occurs in the North-American and European deposits, too. The crystal habit of natural gibbsite is generally pseudohexagonal, laminated, whereas artificial gibbsite may form elongated pseudohexagonal prisms. The grains of gibbsite precipitated in the course of the Bayer process are aggregates of laminar and prismatic crystals.

Nordstrandite was produced artificially by an American chemist, Nordstrand, only in 1956. It has been detected by several researchers in various bauxite deposits. Davis and Hill /6/ found it in Jamaican Bauxites. Its chemical characteristics are similar to those of the gibbsite.

Structural Properties of Oxides and Hydroxides

Table 2.3

Phase	Formula	Crystal system	Space Group	Molecules per Unit Cell	Unit Axis Length, Å			Angle	Density g/cm³	Reference
					a	b	c			
Gibbsite	$Al/OH/_3$	Monocline	C^5_{24}	4	8.68	5.07	9.72	94°34'	2.42	Saalfeld /1960/
Gibbsite	$Al/OH/_3$	Tricline	...	16	17.33	10.08	9.73	94°10' 92°08' 90°0'	....	Saalfeld /1960/
Bayerite	$Al/OH/_3$	Monocline	C^5_{24}	2	5.06	8.67	4.71	90°16'	2.53	Rothbauer et al
Nordstrandite	$Al/OH/_3$	Tricline	C^1_i	4	8.75	5.07	10.24	109°20' 97°40' 88°20'	....	Saalfeld and Jarchow
Boehmite	AlOOH	Orthorhombic	D^{17}_{24}	2	2.868	12.227	3.700	...	3.01	Swanson and Fuyat
Diaspore	AlOOH	Orthorhombic	D^{16}_{24}	2	4.396	9.426	2.844	...	3.44	Swanson and Fuyat
Corundum	Al_2O_3	Hexahonal /Rhombic/	D^6_{3d}	2	4.758	-	12.991	...	3.98	Swanson, Cook et al

Though of no practical importance, it should be noted here that Karsulin /7/ discovered a new mineral in a bauxite deposit near Montenegro of $2Al_2/OH/_6 \cdot H_2O$ composition, named tucanite by him.

Nemecz and Varjú /8/ detected the mineral scarbonite $12Al/OH/_3 \cdot Al_2/CO_3/_3$ composition in the Pilisvörösvár bauxite deposit.

Boehmite is the most important aluminium mineral of karstic bauxites. It can be easily produced artificially from gibbsite in digesters, at a temperature of 150 °C in water medium. Boehmite often forms small crystals dispersely mixed with iron minerals, so that it can not be identified even by optical methods. The particle diameters vary between 100 Å and 1000 Å. In certain deposits, however, it occurres in a well crystallized form. The significant deviation of the crystallization degree obviously affects its solubility.

Diaspore is the chemically least active form of aluminium-hydroxides. It is an important mineral of Greek, Rumanian, Ural /USSR/, Chinese, Viet-Namese etc. bauxites. It can be produced artificially by hydrothermal process from aluminium-hydroxide in water medium, by digesting it at 280-420 °C temperature and 140 bar pressure.

Aluminium Oxides

Several modifications of aluminium-oxides are known, the most stable of which is α-Al_2O_3, corundum, occurring in the nature, too. The alumina used for aluminium electrolysis is a mixture of α-Al_2O_3 and the so-called intermediate Al_2O_3-modifications, which are produced by ignition of gibbsite to a temperature higher than 1000 °C, sometimes in the presence of a mineralizator. By heating up any kind of aluminium-hydroxide to higher temperatures, α-Al_2O_3 /corundum/ is formed as a final product. Decomposition sequence of aluminiumhydroxides under the effect of heating is shown in Fig. 2.1 /5/.

IMPORTANCE OF THE BAYER TECHNOLOGY IN THE ALUMINA PRODUCTION

At present, more than 90 per cent of the world's alumina is produced by the Bayer process, a simple technology providing high purity final product. Apart from some exceptional local conditions, bauxite is processed almost solely by this technology.

As a beneficiation process, alumina production releases the Al_2O_3 content of bauxite from other accompanying oxides thus providing alumina suitable for electrolysis in a cryolite melt.

Characteristics of the Bayer Technology

The basic theory of the Bayer process was elaborated by K.J. Bayer and described in his patents in 1887 and 1892 /9/. The first patent refers to the desintegration of sodium-aluminate solutions with the aid of seed crystals of aluminiumhydroxide or of carbonic acid, that is, to the precipitation and carbonation processes. The second patent formulates the concept that the Al_2O_3 content of bauxites can be dissolved in sodium-hydroxide solutions, with the formation of sodium-aluminate, a process called digestion nowadays.

Industrial practice of the Bayer technology is based, up to this time, on the above two concepts which can be described by the following reactions:

a/ for gibbsitic bauxites:

$$Al/OH/_3 + NaOH \underset{<100\ ^{\circ}C}{\overset{>100\ ^{\circ}C}{\rightleftharpoons}} NaAl/OH/_4$$

CONDITIONS	CONDITIONS FAVOURING TRANSFORMATIONS PATH a	PATH b
PRESSURE	> 1 ATM	1 ATM
ATMOSPHERE	MOIST AIR	DRY AIR
HEATING RATE	> 1°C / MIN	< 1°C / MIN
PARTICLE SIZE	> 100 MICRONS	< 10 MICRONS

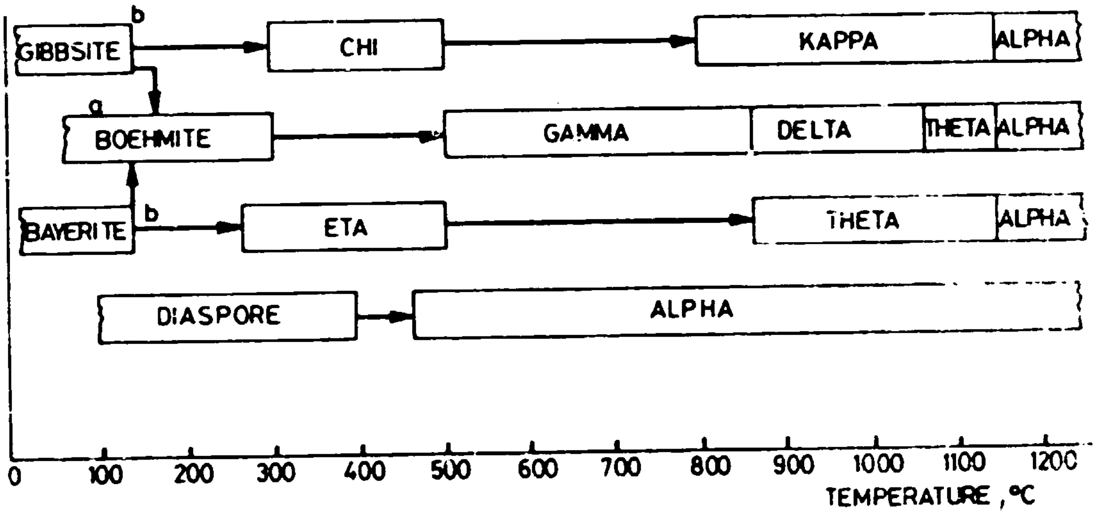


Fig.2.1

DECOMPOSITION SEQUENCE OF ALUMINIUM HYDROXIDES b/ for boehmitic bauxites:

$$AlOOH + NaOH + H_2O \xrightarrow{>200\ ^{o}C} NaAl/OH/_4$$

c/ for diasporic bauxites:

$$AlOOH + NaOH + Ca/OH/_2 + H_2O \xrightarrow{>240\ ^{o}C} NaAl/OH/_4 + Ca/OH/_2$$

In case of reaction c, $Ca/OH/_2$ can obviously not be regarded as final product, but undergoing subsequent reactions it will generally form calcium-aluminium-silicate.

The temperature of digestion in the above reaction equations is always determined by the solubility of the Al-mineral characterizing the given bauxite. On digesting diasporic bauxites, burnt lime is added in 2-6 weight per cent of the dry bauxite, to promote the total dissolution of diaspore.

In recent years the digestion technology of goethitic bauxites has been developed as new technology aiming at transforming the $Fe_{1-x}Al_xOOH$ - composition alumogoethite into hematite. The Al_2O_3 content built into the alumogoethite-lattice, approaching often the limit value /x = 0.33 molar per cent Al/, becomes soluble this way, and an easily separable, brown, hematitic type red mud is formed. The reaction equation in such cases is the following:

d/ for goethitic bauxites:

$$Fe_{1-x}Al_xOOH + NaOH \xrightarrow[\text{catalyzer}]{>220\ ^oC} Fe_2O_3 + xNaAl/OH/_4$$

At higher temperatures CaO /10/ is added as catalyzer, whereas at lower temperatures CaO, anions /SO_4^{2-}; Cl^-/ and cations /Fe^{2+}; Mn^{2+}/ are added simultaneously for the same purpose /11, 12/.

A simplified flow-sheet of the Bayer process is shown in Fig. 2.2 /13/.

The most important operations of the technology are bauxite preparation /crushing, grinding/, digestion, red mud separation /thickening, washing, filtration/, precipitation, calcination, evaporation.

Operational units of the Bayer technology are displayed in Fig. 2.3 /13/.

Variants of the Bayer Technology

Depending on the type of the bauxite to be processed two different variants of the Bayer process have been developed.

The Al_2O_3 content of gibbsitic /trihydrate/ bauxites can easily be dissolved: it is digested, consequently, at a temperature of maximum 140-145 ^oC, in a digestion liquor of relatively low concentration /120-140 g/l Na_2O_{caust}/, whereas boehmitic and diasporic /monohydrate/ bauxites are digested at a temperature of above 200 ^oC /at 240-250 ^oC in modern plants/ and at a higher liquor concentration /180-250 g/l Na_2O_{caust}/. The first technology is called the "American",

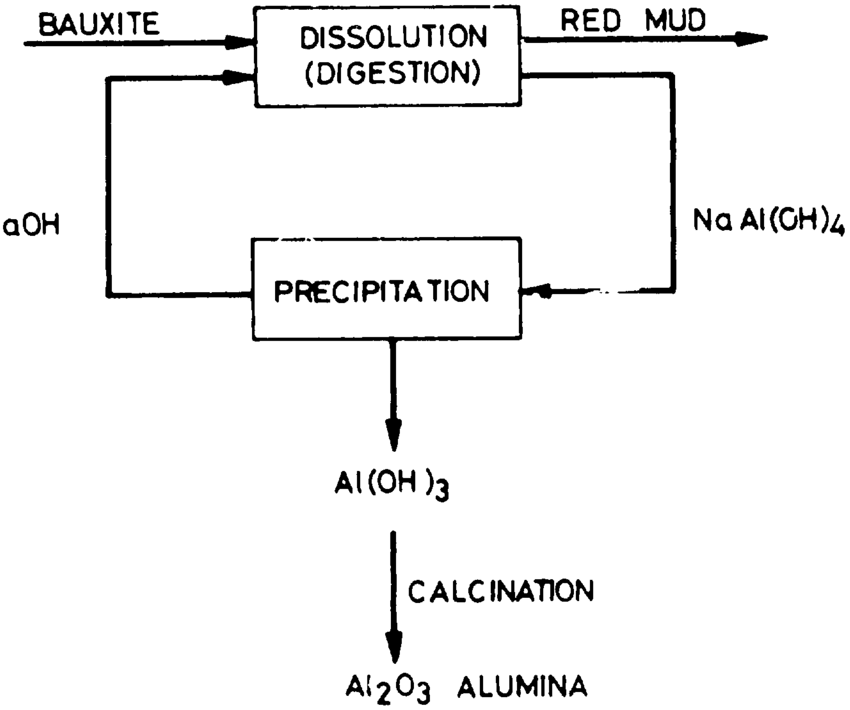


Fig. 2.2

SIMPLIFIED FLOW-SHEET OF THE BAYER PROCESS

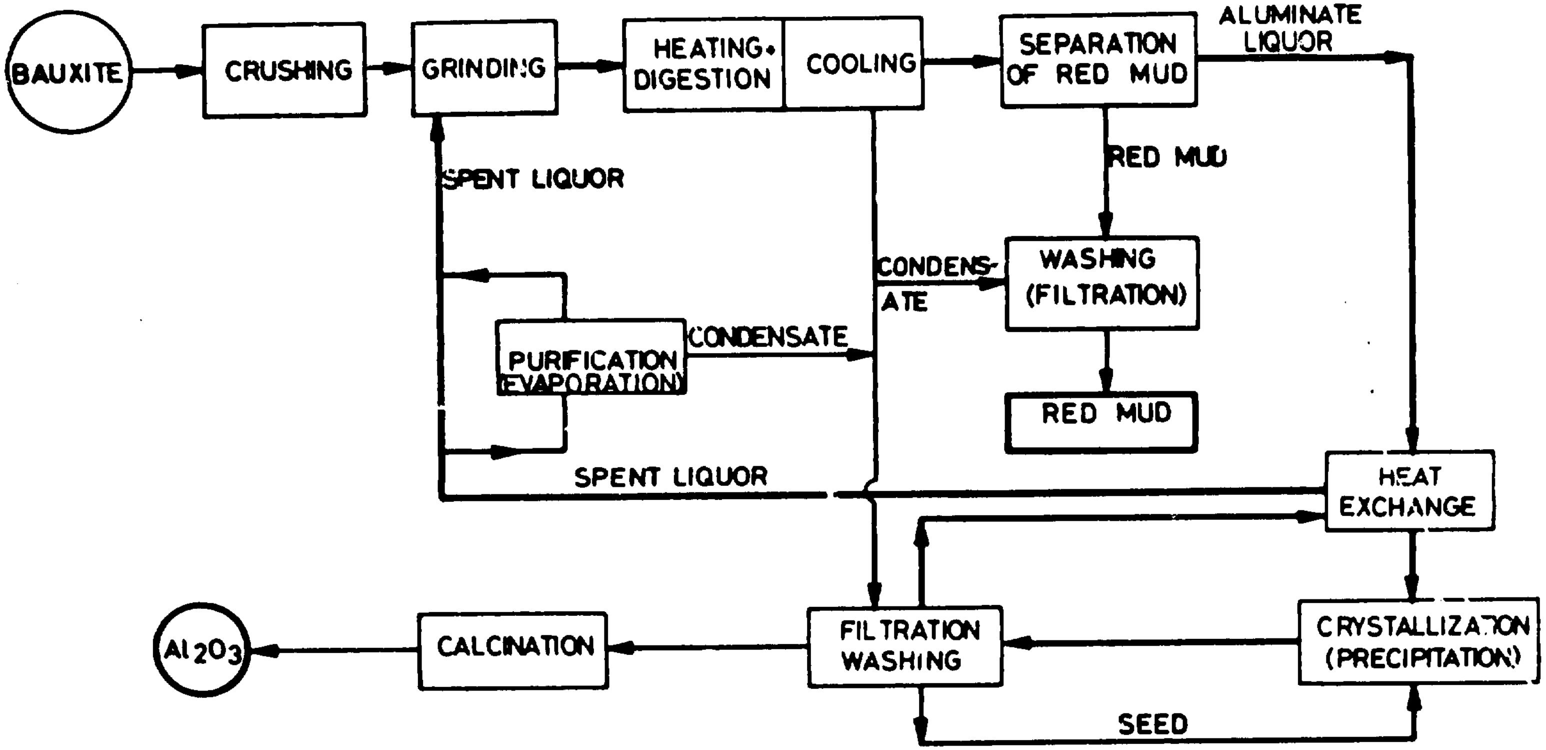


Fig. 2.3

OPERATION UNITS OF THE BAYER PROCESS

whereas the second one the "European" variant because, due to the deviating characteristics of the processed bauxites, the two technologies have developed separately on the two continents.

The most important characteristics are summarized in Table 2.4 /14/.

Recently, an approach of the two variants to each other can be experienced, as gibbsitic bauxites, containing some per cents of boehmite and a major amount of alumogoethite are also digested at a 240-250 °C temperature. In case of the "European" variant it is a definite endeavour to decrease the concentration of the digestion liquor even below 200 g/l Na_2O_{caust} content.

In case of the "American" technology, on the other hand, due to energy-saving considerations, there is an endeavour to increase the precipitation concentration, obviously in such a way that the coarse grain-size of hydrate would be retained.

Feasibility of the Bayer Process

The difficulties of the technology are inflicted by the reactions between the minerals of bauxites accompanying the Al-hydroxides and the digestion liquor. The most serious disadvantage of these reactions lies in the transformation of the SiO_2 content into Na-Al-hydrosilicates of sodalite or cancrinite structure, which are insoluble in the liquor and, when leaving the process together with the red mud, they cause Na_2O and Al_2O_3 losses. The caustic soda consumption vs. available alumina is illustrated in Fig. 2.4 /4/.

It was mentioned already that, due to the above facts, the reactive SiO_2 content determines the market price of bauxites. In addition to the SiO_2 content, TiO_2 content must also be tak-

Main Characteristics of the European and American Variants of Digestion

Table 2.4

Typical Parameters	European Bayer Variant	American Bayer Variant
Temperature at the end of digestion, °C	200-235 /250/	140-145
Temperature after recuperation, °C	135-185	110
Pressure of digesters, kg/cm²	12-30 /50/	4
Composition of solution after digestion:		
Caust. Na_2O g/l	200-300	120-140
Al_2O_3 g/l	190-300	125-150
Molar ratio	/1.40/1.50-1.75	1.50-1.60
Caust.Na_2O/total Na_2O %	90-93	60-80
Al_2O_3 produced of 1 m³ of digestion liquor, kg	90-150	50-80

Composition of Dry Bauxite and Red mud	Monohydrate Bauxite	Red Mud	Trihydrate Bauxite	Red Mud
Loss on ignition %	11.5-12.5	8-10	29-30	10
Total Al_2O_3 %	53-56	16-20	55-57	20-22
SiO_2 %	4.0-7.0	8-12	2.0-3.0	10-12
Fe_2O_3 %	24-26	40-50	7-9	36-40
TiO_2 %	2.5-3.0	5.5-6.5	2.5-3.0	10-11
CaO	0.2-0.4	-	0.1	-
Na_2O_{bound} %	-	5.0-8.0	-	4.0-5.5
Available Al_2O_3/$Al_2O_3-SiO_2$%/	49-52	-	52-55	-
Al_2O_3/Fe_2O_3 ratio	2.10-2.30	0.22-0.30	6.0-7.0	0.50-0.60

Specific red mud quantity kg/t Al_2O_3	1000-1400	350-450
Al_2O_3 digestion recovery, %	84-89	91-93
Recovery related to available Al_2O_3, %	95-96	96-98

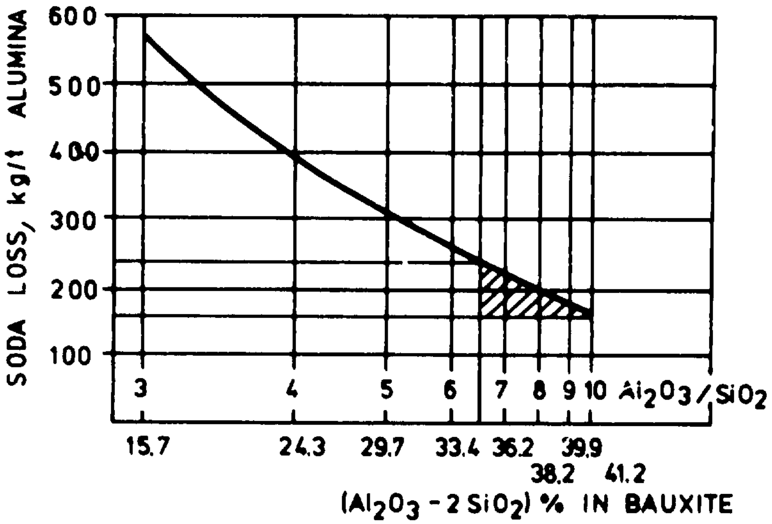


Fig. 2.4

SODA LOSS vs. BASIS NUMBER

en into consideration in the European variant of the Bayer technology, as it forms Na-titanates of various composition with the digestion liquor, thus increasing the NaOH consumption of the alumina production /15/.

The feasibility of the Bayer process is basically determined by economical considerations, the latter being the function of the raw material consumption - depending on the quality of bauxite -, of the technical level of technology and equipment, and of the economy of energy. The plant size is obviously a determinant factor, too. At present, the Bayer technology can be applied with favourable economy even for processing bauxites of 6.5-7 per cent SiO_2 content. Expressed by the basis number, the lower limit of economic operation is at 32-35, depending significantly on the fact whether the plant processes bauxite produced in its own industrial verticum or imported bauxite, on the capacity of the plant, on the technical level and on the depreciation rate. The tendency is to develop further the Bayer technology to make it suitable for processing bauxites of subsequently lower quality by increasing the proportion of recovered caustic soda and by approaching the theoretical alumina yield.

In case of processing imported bauxites, the condition of economic production in the long run is generally to use ores a minimum basis number of 40, whereas in case of processing local bauxites the required basis number is 30 to 32.

Expected Future Development of the Bayer Process

Future development of the Bayer process is characterized by further raising of the digestion temperature using tube digester units, and by the general prevalence of fluid bed calcining process. Considering the future development, greatest attention should be paid to the following technologies:

- Bayer hydrochemical process /16/
- Technology based on iron-hydrogranate formation /17/ and
- Complex processing of red mud /see page 2-28/.

The basis of the Bayer hydrochemical process is that by digesting at extremely high concentrations /about 500 g/l Na_2O_c, at a molar ratio above 11 and at high temperature, approximately 300 °C/ calcium-sodium-silicate is formed from the sodium-aluminium-hydrosilicate of the red mud, and most of its Na_2O and Al_2O_3 content is recovered by washing. Na_2O and Al_2O_3 recoveries from red mud may reach 90 per cent. The industrial realization of the technology elaborated by Ponomariov and Sazhin has not yet been solved because of the difficulties due to the use of extremely high liquor concentrations and high molar ratios, the problems of rapid red mud separation and those of the sodium-aluminate separation.

The essence of the technology based on the formation of iron hydrogranates is that sodium-aluminium-hydrosilicates may be transformed, under certain conditions, into calcium-iron-hydrosilicates. These compounds can be characterized by the following formula:

$$A_3B_2/SiO_4/_{3-x}\left[/OH/_4\right]_x$$

where: $A = Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}$

$B = Al^{3+}, Fe^{3+}, Cr^{3+}$

The production of an iron-hydrogranate type compound may be reckoned with both at bauxite and red mud processing.

Practical realization of the process for direct processing of bauxites is rather uncertain, as a consequence of the high molar ratio of the digestion liquor and the little amount of bauxite which can be processed in the unit liquor volume. Processing of red mud with the same technology seems to be more realistic.

SINTERING AND COMBINED PROCESSES

According to realistic forecasts, the Bayer technology will further be the dominant method for processing good quality bauxites of 3-6 per cent SiO_2 content.

The uneven distribution of bauxite reserves, the increase in the price of bauxite and in the transportation costs, the possibility of exhausting the present reserves of high quality ore, and the great reserves of the poorer quality bauxite and other aluminium containing minerals inspired several countries to elaborate an economical technology suitable to process poor quality bauxites, clayey bauxites, bauxitic clays and other aluminuous materials /nepheline, alunite, clay, fly ash, industrial wastes etc./.

Raw materials, which can not be processed economically by the Bayer technology are processed to alumina by sintering and Bayer sintering combined processes on a large industrial scale. Research work for developing acid methods is carried out in laboratories and pilot plants, principally with the objective to process aluminium-silicates /clays, kaoline/ of low iron content /18, 19, 20/.

Sintering Processes

The first sintering method which can be considered as the first industrial alumina production process, was elaborated in 1856-1860 /Saint-Claire Deville/ /14/. The mixture of ground bauxite and soda was sintered at a temperature of 1000 to 1100 °C, the produced sodium-aluminate was dissolved, separated from the insoluble residue, and then the aluminium-hydroxide, precipitated by CO_2 gas, was calcined. Later on the more economical Bayer process took the place of the above technology in the industry.

Attempts were made to substitute soda with sodium-sulphate and a reducing agent /Peniakov/, but, due to the complicated reactions principally, this method has not spread in the industry /21/.

Müller's patent specification submitted in 1880 /22/ was a significant advancement. Apart form the soda he recommended to add magnezite for binding the silica, but he calculated the CaO, to be added on the basis of the Al_2O_3 content of the raw material. Pakard stated in 1902 that limestone must be calculated on the basis of the SiO_2 content. He considered the molar ratios:

$$\frac{CaO}{SiO_2} = 2 \text{ and } \frac{Na_2O}{Al_2O_3} = 2$$

to be optimal /23/. The amount of CaO is calculated basically the same way even at present, but the amount of Na_2O was modified on the basis of composition of the resulting compounds clarified later.

The method was further developed in the Soviet Union, and a large scale industrial technology was developed for bauxite sintering and for complex processing of nepheline /21, 24, 25/.

The technology consists basically of the following phases:

- production of sodium-aluminate at high temperature, above 1000 °C /sintering/
- dissolution of sodium-aluminate from the sinter product /leaching/
- decreasing the SiO_2 content of the solution /desilication/

- separating $Al/OH/_3$ from the solution by introducing CO_2 gas /carbonization/
- calcining of $Al/OH/_3$ /calcination/

The process is outlined in Fig. 2.5.

As the lime bounds SiO_2 in form of insoluble dicalcium-silicate, the sintering method theoretically can be used for processing raw materials of high silica content. Its economic utilization is limited, however, by the fact that whereas 2.0-2.5 tons of bauxite, about 0.3 ton of standard equivalent of fuel oil and about 300 kWh energy is required to produce 1 ton of alumina by the Bayer technology, in case of sintering poor quality bauxites, about 3 tons of bauxite, 2-3 tons of lime and soda, 1.5-2 tons of standard fuel and about 900 kWh energy is required. Accordingly, the material flow is 2.5 to 3 times higher than that of the Bayer process /26/. The total investment costs are about double of those of the Bayer process.

Combined Bayer and Sintering Processes

Aiming at decreasing the drawbacks and utilizing the advantages of the Bayer and sintering processes resp. the so-called combined processes had been developed. Two variants are known, the parallel- and the series-combined process /90/.

Parallel-Combined Process

The essence of the process is to establish, beside the Bayer line processing good quality bauxite, a sintering line processing lower quality /of higher SiO_2 content, and contaminated/ bauxite and to mix the aluminate liquors formed in the two lines before precipitation. This method makes possible to use cheaper Na_2CO_3 and soda salt removed from the Bayer circuit for making up caustic soda losses. Utilization of the Bayer soda salt in the sintering process is suit-

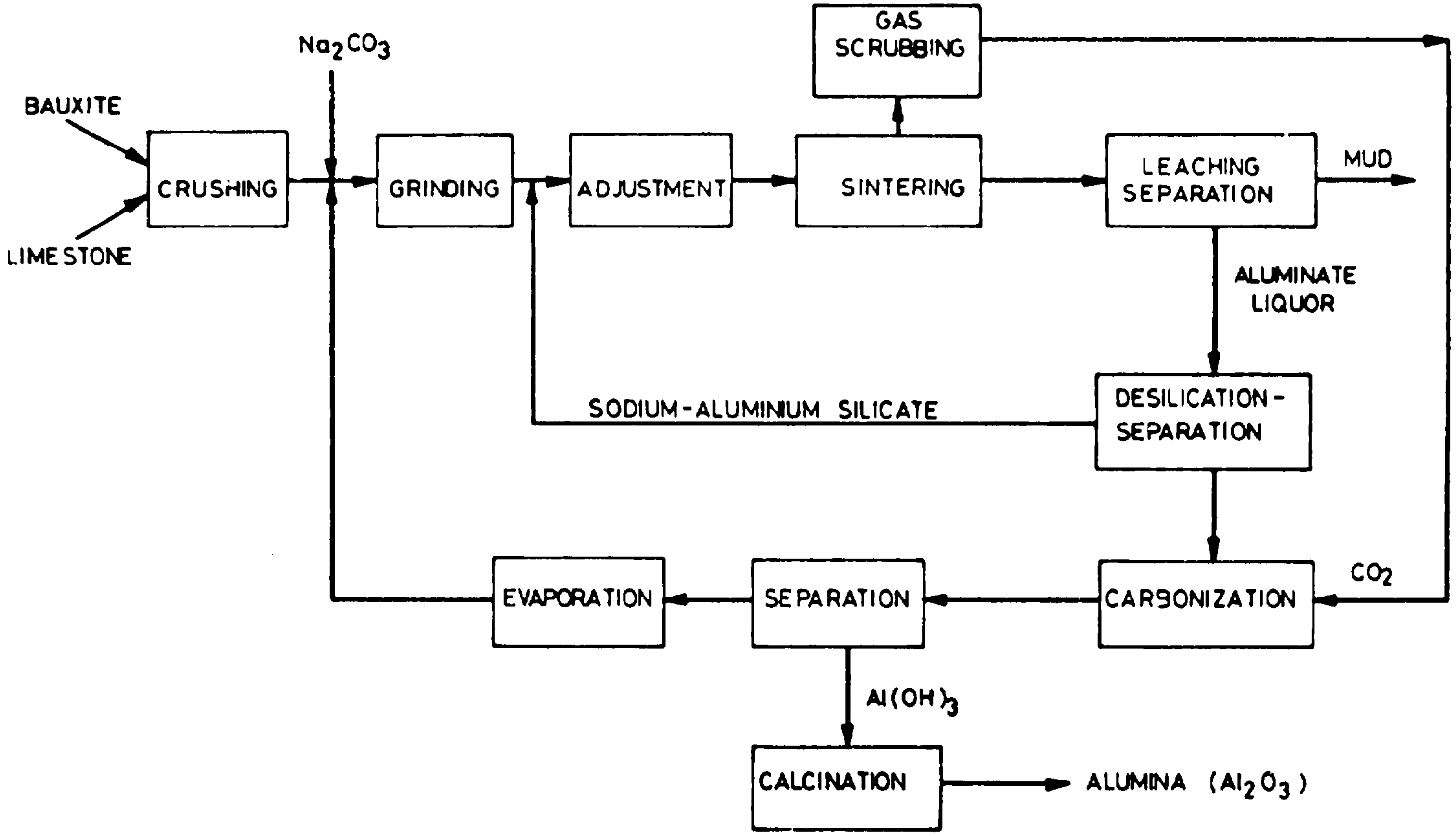


Fig. 2.5

SINTERING PROCESS

able to remove certain contaminants of the circuit, too, e.g. organic matter etc. The aluminate liquor of low molar ratio formed in the sintering branch also affects favourably the precipitation process. The scheme of the process is shown in Fig. 2.6.

This process is the most economic one in case the bauxite can be mined selectively into two qualities with a higher and a lower SiO_2 content, respectively, or the two qualities are found separately. The proportion of the sintering branch, however, may not generally exceed 10 to 15 per cent of the total production, otherwise the soda balance can only be maintained by carbonizing part of the aluminate liquor.

Series Combined Process

The essence of the process is that a considerable proportion of the Al_2O_3 content of the bauxite of relatively low quality, 3-6 module, is dissolved by the Bayer technology, the red mud formed is sintered by the use of limestone and the aluminate liquor obtained after leaching the sinter product is mixed and precipitated with that of the Bayer line.

The technology is illustrated in Fig. 2.7.

The series combined process is advantageous first of all for processing bauxites of an iron content of 17 to 18 per cent Fe_2O_3, max., as by sintering the red mud of higher iron content, ferrites of relatively low melting point are formed and, consequently, the sintering temperature interval will decrease. To avoid this, attempts are made to perform sintering by charging bauxite or reducing agent to the red mud before sintering.

In case the major part of Al-minerals in the poor quality bauxite is gibbsite, the economy of the technology may approach that of the Bayer process, as a consequence of the cheap atmospheric digestion.

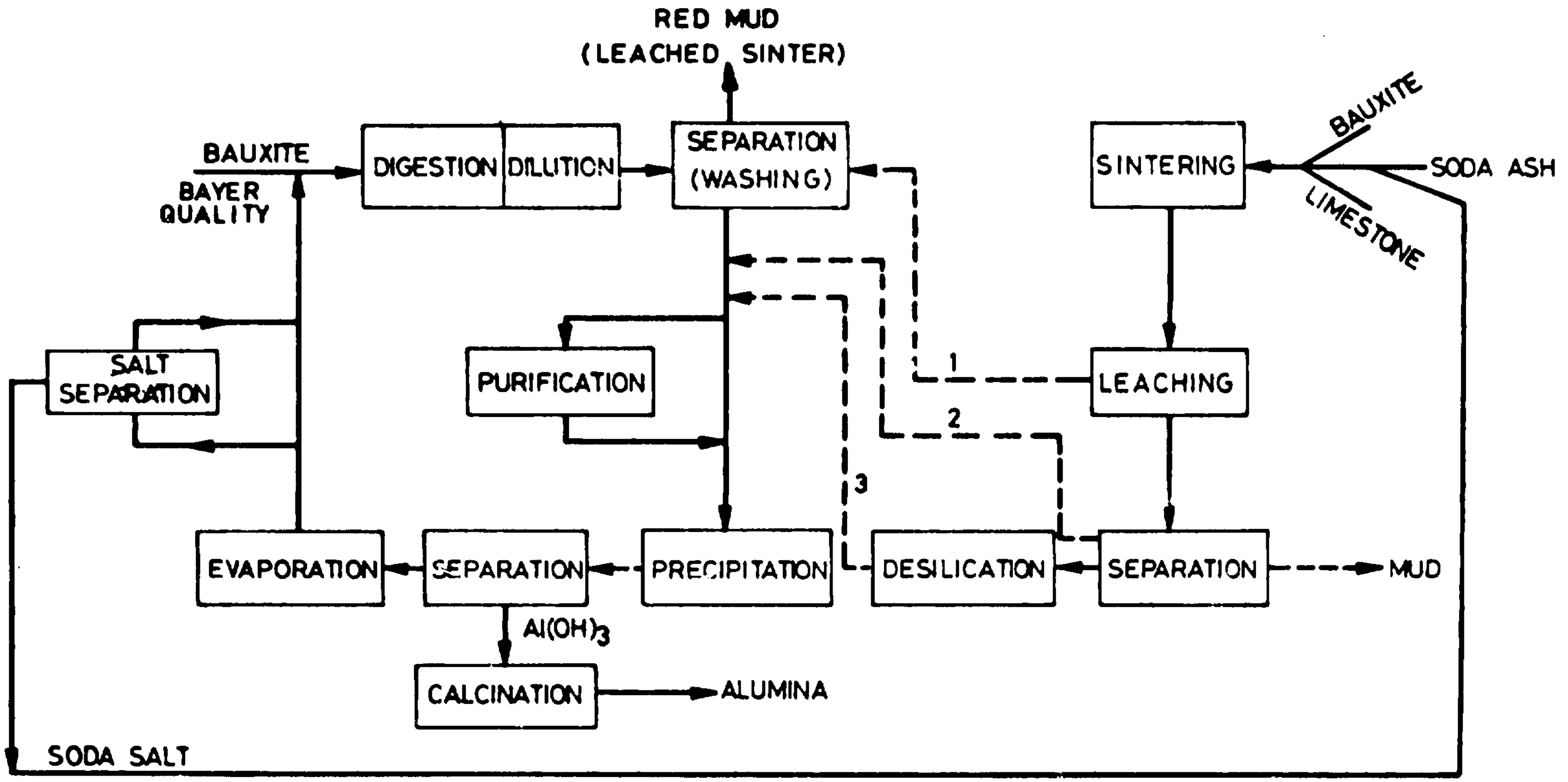


Fig. 2.6

PARALLEL COMBINED PROCESS

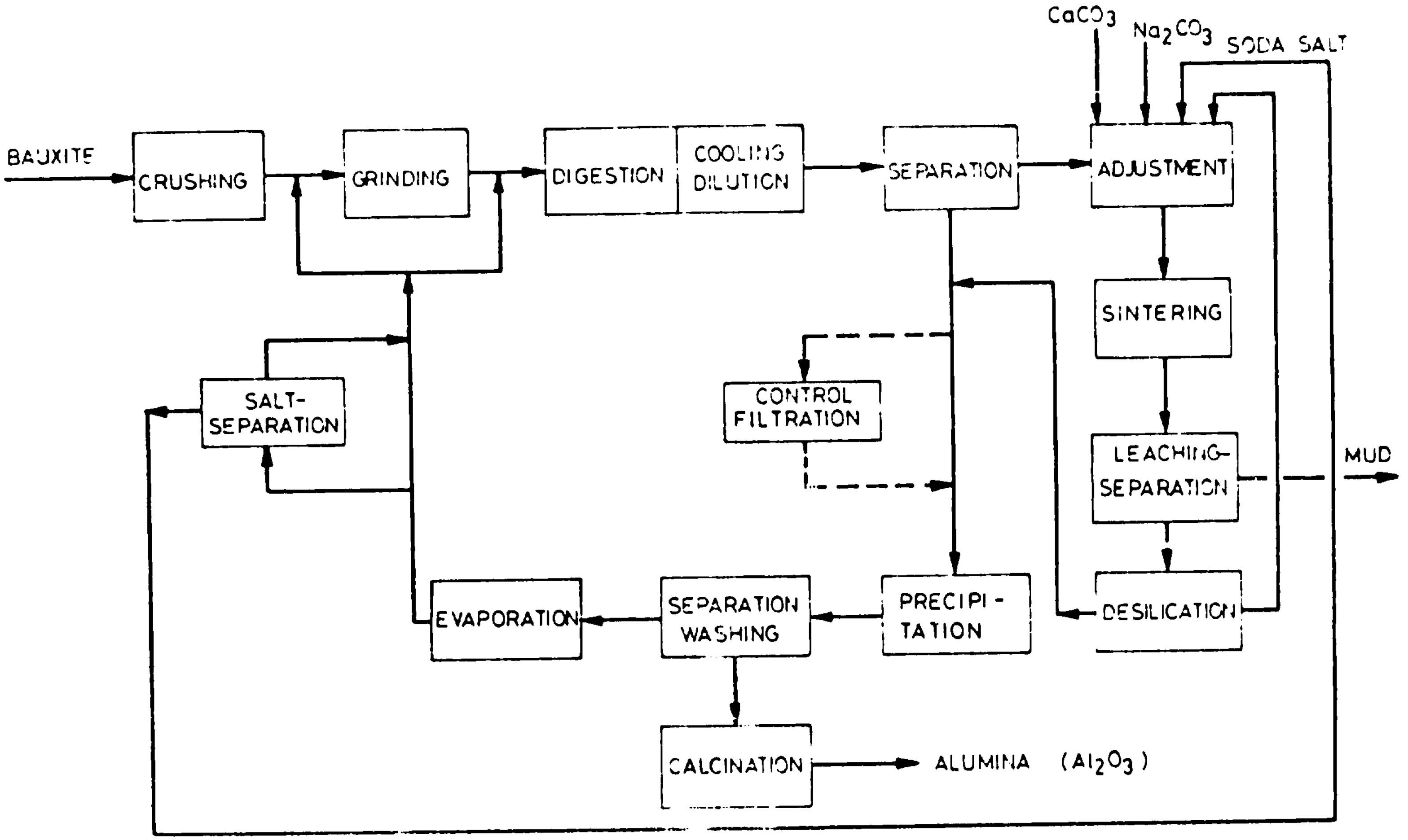


Fig 2.7
SERIES COMBINED PROCESS

An overall evaluation of the series-combined process as against the Bayer and sintering process is illustrated in the table below /27/:

Comparison of the Bayer, Bayer-Sinter and Sinter Processes

Table 2.5

Parameters	Bayer Process	Combined Bayer-Sinter Process	Sinter Process
Investment per unit production, %	100	150	190
Production cost, %	100	146	182
Labour per ton Al_2O_3, %	100	136	163

Complex Processing of Red Mud

The complex processing of Bayer red muds can be considered as a modified variant of the series-combined process in which the extraction of Al_2O_3 and Na_2O content of red mud is preceeded by the removal of iron.

At present, separated smelting of mud to pig iron and self-desintegrating calcium aluminate slag subsequent to its reduction can be considered as the most elaborated process. Alumina can be leached out from the slag and the remaining secondary mud can be utilized for cement production. Industrial realization of the process is hindered at present because of its high investment costs /28/.

Sintering Process with the Formation of Calcium Aluminate

Raw materials of high silica content - generally above 15 per cent - can best be processed by means of the methods based on calcium aluminate production. Processing of bauxite with sintering by limestone was firstly introduced in the

Gardanne plant, France /14/. Later on the so-called "self-desintegrating" sinter producing process was elaborated based on intensive research work in several countries, like Poland /29/, the Soviet Union /30/ and Hungary /31/, which provides advantageous processing possibilities for raw materials /clay kaoline, slate, fly ash etc./ comprising at least 30 per cent Al_2O_3, and SiO_2 and Fe_2O_3 corresponding to the following minimal weight ratios:

$$\frac{SiO_2}{Al_2O_3} \leq 2 \quad \text{and} \quad \frac{Al_2O_3}{Fe_2O_3} \geq 5$$

In case of higher Fe_2O_3 content, reductive sintering by coal or reductive smelting is performed /24/.

The essence of the method is that at a high temperature /above 1200 °C/ calcium-aluminate and calcium-silicate are formed in the mixture of the raw material and calcium-carbonate. In the course of the controlled cooling process the sinter pulverises by itself i.e. it becomes "self-desintegrated" due to polimorph transformation of dicalcium-silicate. Calcium-aluminate is leached with a weak soda solution and a sodium-aluminate solution, is formed from which $Al/OH/_3$ is precipitated by CO_2 gas. Alumina is produced from aluminium-hydroxide by calcination. Leached sinter is used for cement production. Na_2CO_3 solution is recycled.

Na_2O - Al_2O_3 - H_2O SYSTEM

Equilibrium diagram of the Na_2O-Al_2O_3-H_2O system at 30 °C is shown in Fig. 2-8 /32/.

Despite the fact that this figure shows the equilibrium of pure components, basic relationships are valid in tendency for industrial solutions comprising several contaminants, too, though the numerical values may differ significantly. It

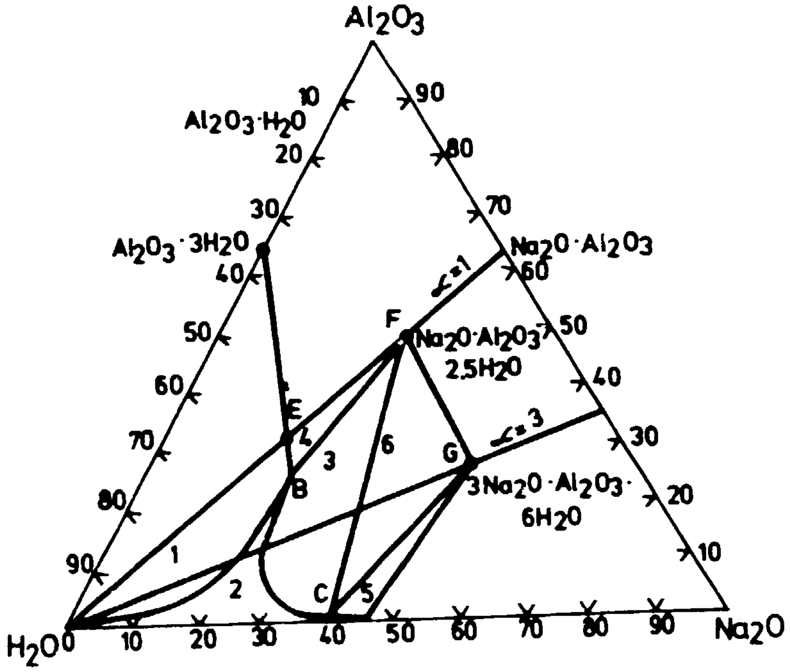


Fig. 2.8

EQUILIBRIUM DIAGRAM OF THE $Na_2O-Al_2O_3-H_2O$ SYSTEM AT 30° C follows that the actual $Na_2O-Al_2O_3-H_2O$ equilibrium diagram of the solutions of a given alumina plant will always deviate from the values given in the literature. First of all let us mention here the effect of soda and organic material on the equilibrium solubility.

Stability ranges of the equilibrium phases are also displayed in Fig. 2.8.

Equilibrium Solubility of Al_2O_3

The triangle diagram describes the entire system, but, as regards alumina production, only the range up to 30 per cent Na_2O content has practical importance, consequently the equilibrium marked by the OB curve is especially important. This fact explains that in lieu of the triangle diagram, the Al_2O_3-Na_2O rectangular co-ordinate system is preferably used. This diagram is shown in Fig. 2.9 /21, 33/ where equilibrium isotherms and the straight lines corresponding to caustic molar ratios /α_c/ are displayed. The term caustic molar ratio means the quotient of numbers of moles of caustic Na_2O and Al_2O_3:

$$\alpha c = \frac{\frac{Na_2O_{caust} \quad g/l}{62}}{\frac{Al_2O_3 \quad g/l}{102}} = 1.645 \cdot \frac{Na_2O_{caust} \; g/l}{Al_2O_3 \quad g/l}$$

Na_2O_{caust} represents the sum of free NaOH and of bound in sodium-aluminate. This definition corresponds to the European practice, whereas in the American /English-written/ technical literature the Na_2O content is expressed in terms of Na_2CO_3 and the A/C /alumina g/l per caustic soda g/l/ quotient is used, instead of α_c molar ratio. An advantage of the latter quotient lies in the fact that it provides

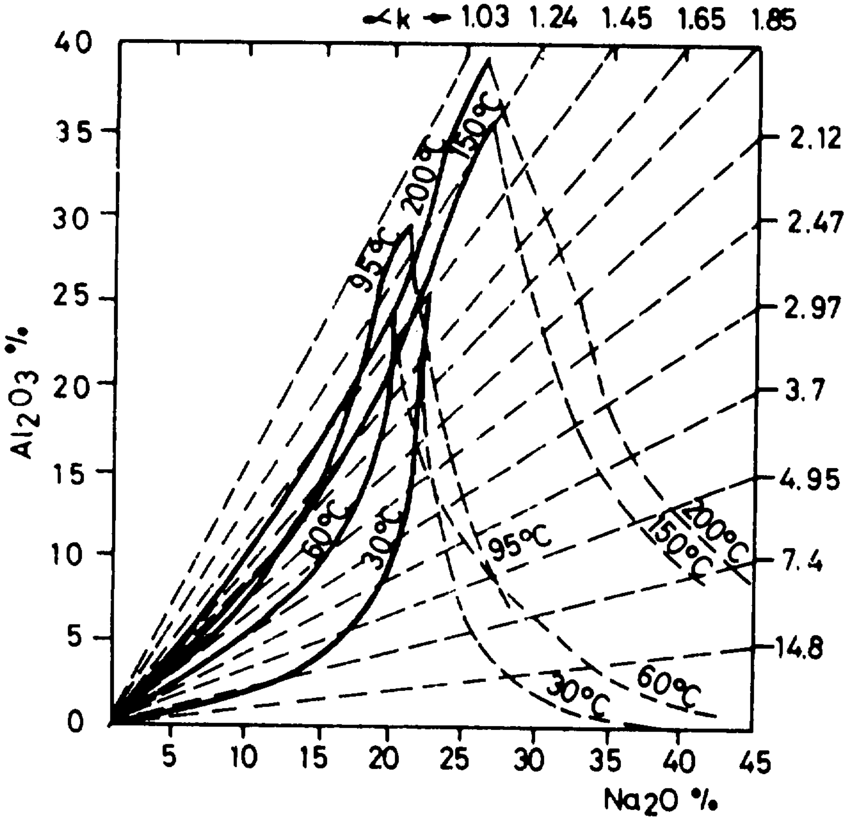


Fig. 2.9

EQUILIBRIUM ISOTHERMS OF THE Na_2O-Al_2O_3-H_2O SYSTEM AT 30, 60, 95, 150 AND 200°C direct information about the changes of Al_2O_3 content in case of similar Na_2O concentration. Conversion: $\alpha_c \cdot A/C = 0.96$.

The α_c molar ratio, however, determines the deviation of the system from the theoretical sodium-aluminate composition.

In the European practice even the carbonate soda content of liquors is expressed in terms of Na_2O. In Europe the Al_2O_3/Na_2O weight ratio is also used at certain plants /e.g. Pechiney/.

Fig. 2.10 illustrates the equilibrium solubility of tri- and monohydrates /34/. By recalculating the same data Fig. 2.11 was obtained, where α_c molar ratio is also marked on the equilibrium curves. This figure illustrates the fact that between 140-160 °C, gibbsite is transformed into boehmite of significantly lower solubility.

Bayer Process Circuit in the Na_2O-Al_2O_3-H_2O System

For the representation of the Bayer process circuit the Na_2O-Al_2O_3 and Al_2O_3-H_2O rectangular co-ordinate systems are generally used in practice as being easy to handle. They can favourably be applied for comparing the technologies of various plants or to record the development in the technology of a given plant. For example, Fig. 2.12 and Fig. 2.13 illustrate the technological development of the Almásfüzitő Alumina Plant between 1955-1975 /35/.

Lines between single points represent the following processing stages:

0-1: adjustment of digestion liquor by the mixing of strong liquor, spent liquor and fresh caustic soda;
1-2: desilication of bauxite slurry;

EQUILIBRIUM RATIOS FOR TRIHYDRATED ALUMINA OVER A TEMPERATURE RANGE OF 100 TO 140°C

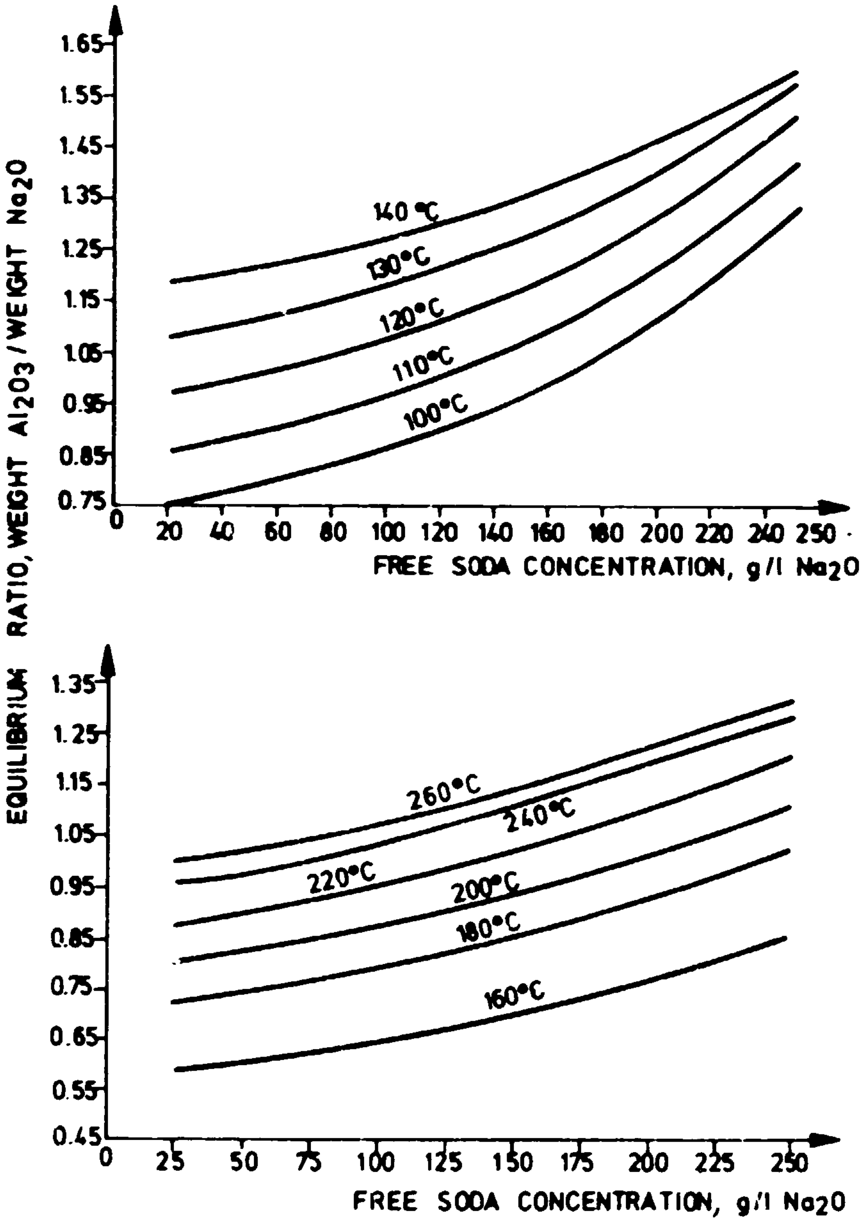
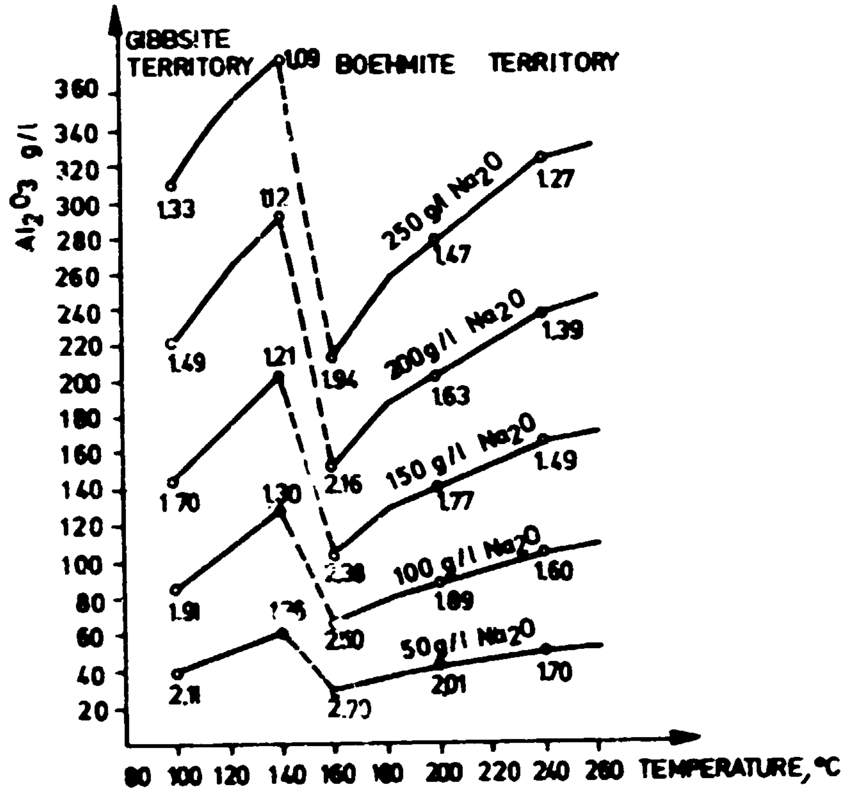


Fig. 2.10

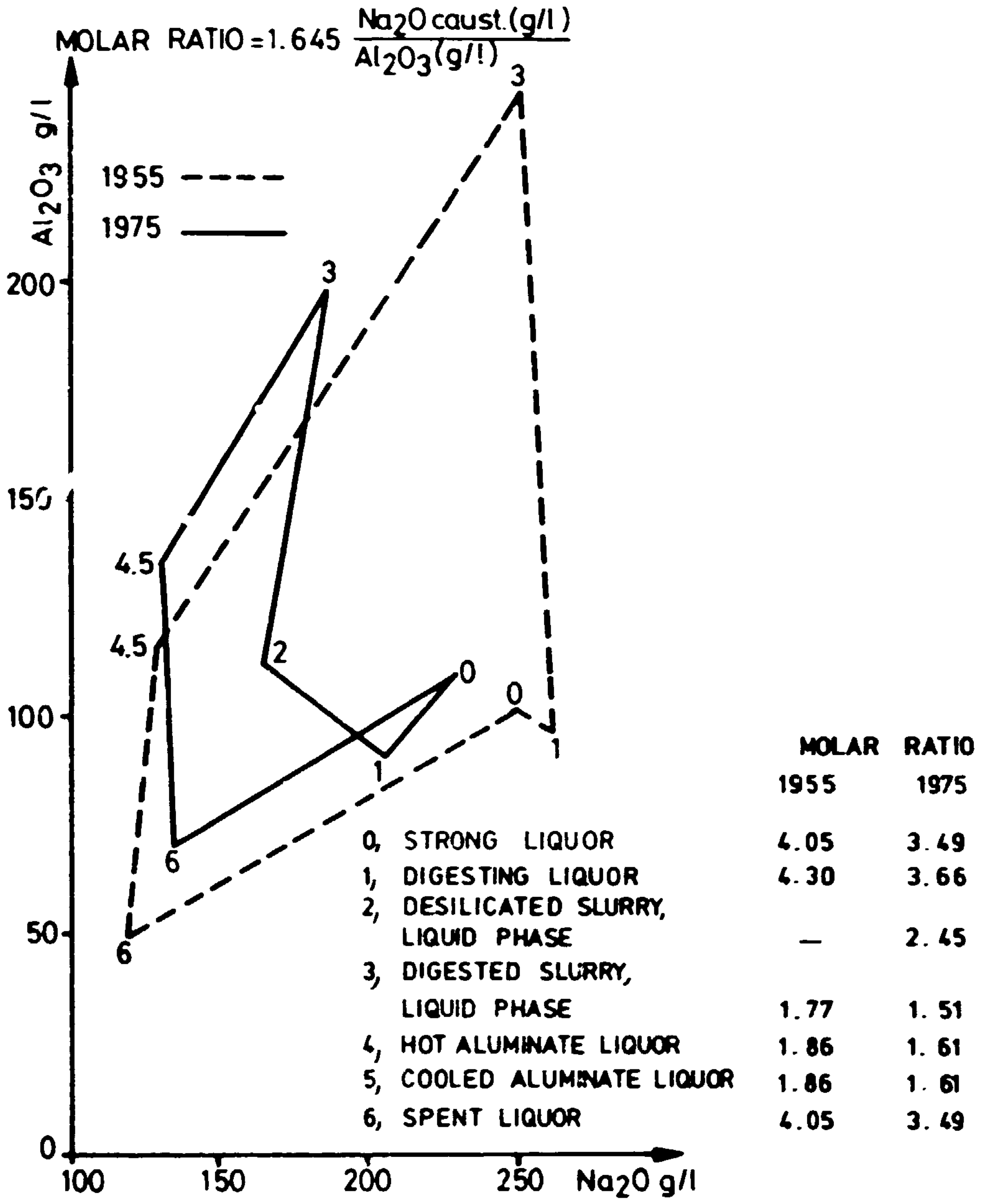
EQUILIBRIUM RATIOS FOR MONOHYDRATED ALUMINA OVER A TEMPERATURE RANGE OF 100 TO 260°C



(INSCRIPTIONS ON THE CURVES MEAN EQUILIBRIUM MOLAR RATIOS)

Fig. 2.11

EQUILIBRIUM SOLUBILITY OF GIBBSITE AND BOEHMITE



	MOLAR RATIO	
	1955	1975
0, STRONG LIQUOR	4.05	3.49
1, DIGESTING LIQUOR	4.30	3.66
2, DESILICATED SLURRY, LIQUID PHASE	—	2.45
3, DIGESTED SLURRY, LIQUID PHASE	1.77	1.51
4, HOT ALUMINATE LIQUOR	1.86	1.61
5, COOLED ALUMINATE LIQUOR	1.86	1.61
6, SPENT LIQUOR	4.05	3.49

Fig. 2.12

BAYER CYCLE IN $Na_2O - Al_2O_3 - H_2O$ DIAGRAM
(ALMÁSFÜZITŐ PLANT)

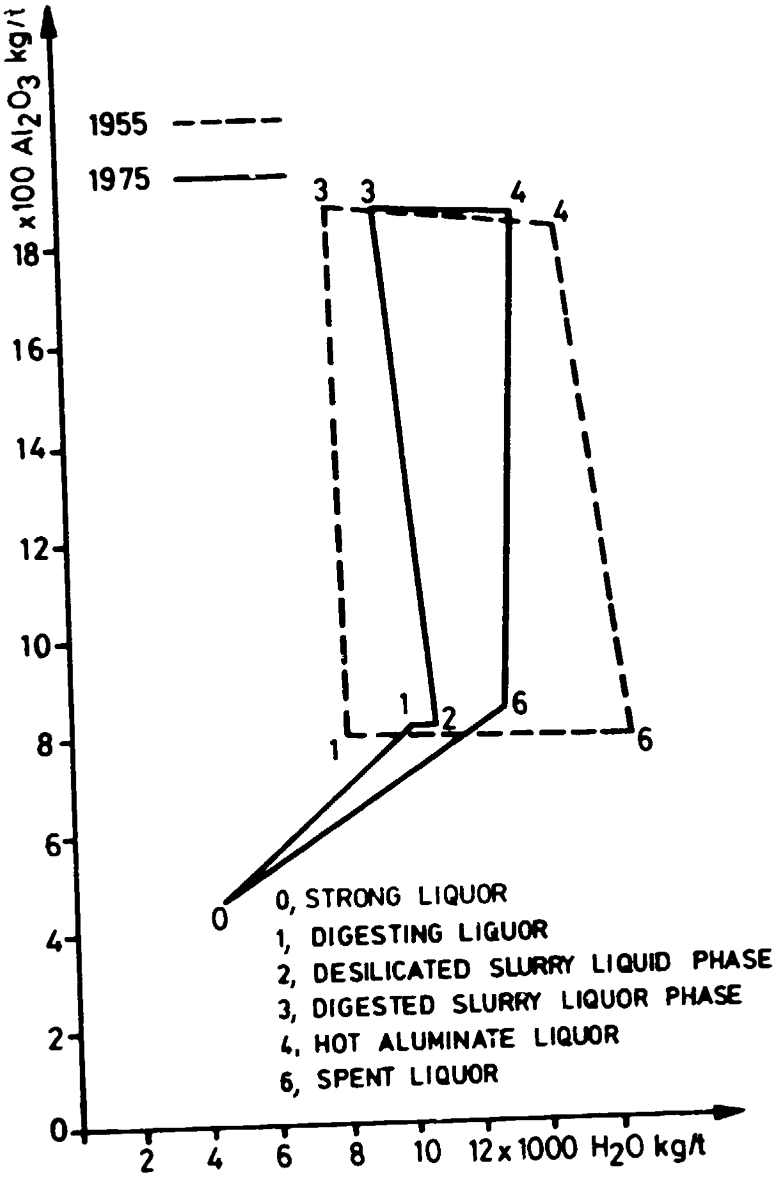


Fig. 2.13

BAYER CYCLE IN $Al_2O_3 - H_2O$ DIAGRAM

(ALMÁSFÜZITŐ PLANT)

2-3: digestion;
3-4: dilution and mud separation;
4-5: cooling of the aluminate liquor;
5-6: precipitation and hydrate filtration;
6-0: evaporation of spent liquor.

By comparing the states for 1955 and 1975, the most characteristic visible change is the approach of digestion and precipitation concentrations to each other. As a consequence, the amount of water to be removed by evaporation was considerably reduced.

Lower caustic concentration for extraction was balanced by higher digestion temperature.

Shifting of positions of points 0 and 1 to each other indicate that in 1955 soda losses were made up by adding caustic soda to the strong liquor to increase the concentration of digestion, whereas in 1975 only part of the spent liquor was evaporated, although to higher concentration than required for digestion: soda- and vanadium-salts were removed from this concentrated liquor, then it was diluted with spent liquor to attain at suitable caustic concentration for digestion.

Step 1-2 again appears as a significant change showing causticization prior to digestion. Essentially sodium-aluminium-silicate formed during desilication of slurry is partly transformed into calcium-aluminium-silicate by lime addition. Thus caustic soda losses are lowered and silicate scaling in preheaters and digesters is reduced at the same time.

Generally, the up-to-date technology is characterized by the diminishing of the area enclosed by points 0-6 in Fig. 2.12 and Fig. 2.13.

STRUCTURE AND CHARACTERISTICS OF SODIUM-ALUMINATE LIQUORS

In spite of its great significance as regards the complete Bayer technology, the structure of sodium-aluminate solutions has not been cleared up definitely yet. There is, in fact, no definite explanation for why the reaction

$$Al/OH/_3 + NaOH \rightleftharpoons NaAl/OH/_4$$

can not be reversed by higher efficiency than 50 to 55 per cent, achieved in the industrial practice.

Efficiency of the precipitation process is expressed by the following formula:

$$\text{Precipitation efficiency, } \% = \left[1 - \frac{\alpha_{starting}}{\alpha_{final}}\right] \cdot 100$$

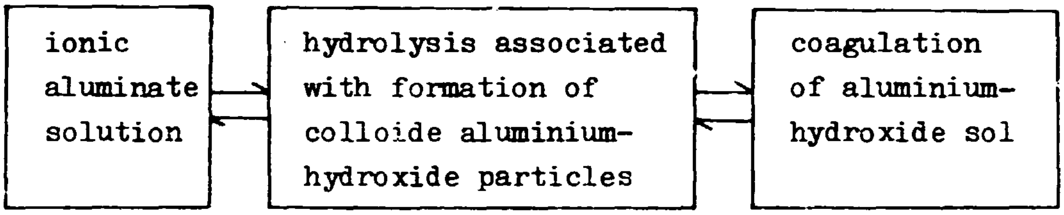
where: $\alpha_{starting}$ and α_{final} are the molar ratios of the aluminate liquor at the beginning and at the end of the precipitation process, respectively. This efficiency determines the effectiveness of the total Bayer process, too, representing the amount of Al_2O_3 produced in a cycle with the unit-amount of sodium-hydroxide.

Three theories have been developed regarding the structure of aluminate solutions: concepts supposing colloide, composite or ionic structures /32/.

Theories Relating to the Structure of Aluminate Solutions

According to the supporters of the colloide structure, sodium-aluminate solution is built up from aluminium-hydroxide particles in the sodium-hydroxide, and there is no sodium-aluminate compound in the solution. Precipitation of aluminium-hydroxide is considered as the coagulation of a sol out of the colloide solution.

According to the theory of composite structure, both colloide aluminium-hydroxide and sodium-aluminate dissociated to ions are present in the aluminate solutions. Their proportion is a function of the concentration, temperature and molar ratio of the solution. Precipitation of aluminium-hydroxide is described, for example, as follows:



Ionic theory regards aluminate solutions to be real solutions, in which aluminium is present in the form of sodium-aluminate. Analysis of physical characteristics of different sodium-aluminate solutions proved with absolute certainly the ionic character. Fig. 2.14 /32/ illustrates the density, viscosity and conductivity of sodium-aluminate solution and NaOH + Na_2CO_3 solution. The similar characteristics of the curves indicate the ionic structure of the sodium-aluminate solution.

Recent Results of Research on the Structure of Aluminate Solutions

Hungarian researchers have studied recently the structure of aluminate solutions with new examination methods /36/. A secondary mercury - mercury-oxide electrode was modified for measuring hydroxide ion activity, up to a concentration of

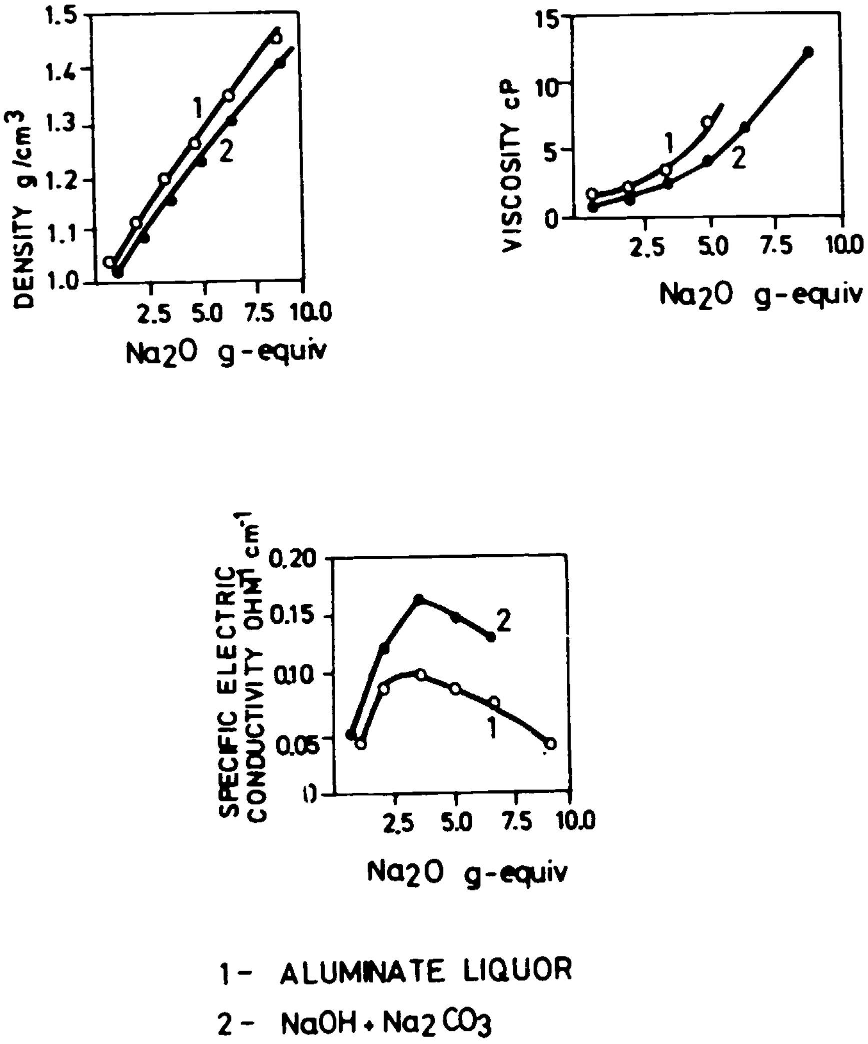


Fig. 2.14

DENSITY, VISCOSITY AND CONDUCTIVITY OF ALUMINATE LIQUOR AND NaOH + Na_2CO_3 SOLUTIONS

10 M/dm^3. The change in the structure of aluminate solutions was also studied by measuring the activity of the water with the aid of isopiestic method. Conductivity measurements have also been utilized to determine the particle-concentration in the solution.

On the basis of these investigations, aluminate solution systems can be modelled as follows:

$$\begin{tikzcd}[column sep=huge, row sep=huge]
\mathrm{Al/OH/}_4^- \arrow[r, shift left, "+\ OH^-"] \arrow[d, shift right, "-\ H_2O"'] & \mathrm{Al/OH/}_4^- \cdot OH^- \arrow[l, shift left, "-\ OH^-"] \\
\mathrm{Al_2O/OH/}_6^{2-} \arrow[u, shift right, "+\ H_2O"'] \arrow[r, shift left, "+\ OH^-"] \arrow[d, shift right, "-\ H_2O"'] & \mathrm{Al_2O/OH/}_6^{2-} \cdot OH^- \arrow[l, shift left, "-\ OH^-"] \\
\mathrm{Al_6O_n/OH/}_{24-2n}^{6-} \arrow[u, shift right, "+\ H_2O"'] \arrow[r, squiggly, "-\ OH^-"] & \mathrm{Al/OH/}_3
\end{tikzcd}$$

Based on the above model, the optimal course of the precipitation process can be described by the following scheme:

$$\mathrm{Al/OH/}_4^- \xrightarrow{-\ H_2O} \mathrm{Al_2O/OH/}_6^{2-} \xrightarrow{-\ H_2O}$$

$$\longrightarrow \mathrm{Al_6O_n/OH/}_{24-2n}^{6-} \xrightarrow{-\ OH^-} \mathrm{Al/OH/}_3$$

The first two stages are obviously water-producing processes, and only the last irreversible stage brings about a decrease in water activity, due to the more intensive hydratation of hydroxide ions. Formation of $Al/OH/_4^- \cdot OH^-$ and $Al_2O/OH/_6^{2-} \cdot OH^-$ ions works against precipitation as it pushes the equilibrium in undesirable direction.

Characteristics of Aluminate Solutions

Most data available regarding the characteristics of the aluminate solutions refer to the density, viscosity and conductivity as illustrated already in Fig. 2.14 /24/. These data are important from the point of view of the practical technology, too /e.g. material transportation, dimensioning of equipment, etc./, moreover, they can also be used for indirect determination of the composition of solutions.

By measuring the density and electric conductivity, for example, the composition of digestion liquor and the molar ratio after digestion can be determined; the precipitation process can be followed up and the solids content of the various slurries can also be checked /37, 38/.

As for the technology, highest importance is attributed to the equilibrium and stability conditions of aluminate solutions. Several data have already been referred to them in the previous chapters. For the sake of supplementation, attention is called to the fact that the stability of aluminate solution is sometimes given in the literature by the degree of oversaturation, as expressed for a given solution by the following formula:

$$\eta = \frac{\alpha \text{ equilibrium}}{\alpha \text{ oversaturated}} = \frac{Al_2O_3 \text{ oversaturated}}{Al_2O_3 \text{ equilibrium}}$$

Na_2O - Al_2O_3 - SiO_2 - CaO - H_2O SYSTEMS

SiO_2 content of bauxites brings about not only significant Na_2O and Al_2O_3 losses in the alumina production but, due to its solubility in liquors and to its complicated reactions, it may contaminate the alumina, it forms scalings at various points of the circuit, moreover, it may considerably affect the technological behaviour of red mud, too /91/.

CaO takes part in the different phase-transformations either as a desintegration product of contaminating minerals of bauxite /calcite, dolomite/ or as burnt lime, charged on purpose.

As regards the most important phase transformations, titanium and iron minerals of bauxite have to be taken into consideration, too.

The Partial System Na_2O - Al_2O_3 - SiO_2 - H_2O

The composition of sodium-aluminate hydrosilicates forming in the Bayer process in case of high temperature digestion /200 - 240 °C/ can be summarized as: $3/Na_2O \cdot Al_2O_3 \cdot 2SiO_2/ \cdot Na_2X \cdot aq$. This formula may obviously undergo minor changes, depending on the conditions of the formation of the compound and on the composition of the solution. Formation of mineralogically different Na-Al-hydrosilicates must generally be reckoned with, and even their relative proportion is varying. For the illustration of the above, Fig. 2.15 shows the effect of addition of NaCl and Na_2SO_4, resp. to digestion liquor, and the distribution of sodium-aluminium-hydrosilicates of different types /39/. The phenomenon that the addition of NaCl or Na_2SO_4 may bring about chloride-sodalite or nosean formation against hydroxide-sodalite, creates the possibility of making up part of the caustic soda losses by NaCl or sodium-sulphate /40/.

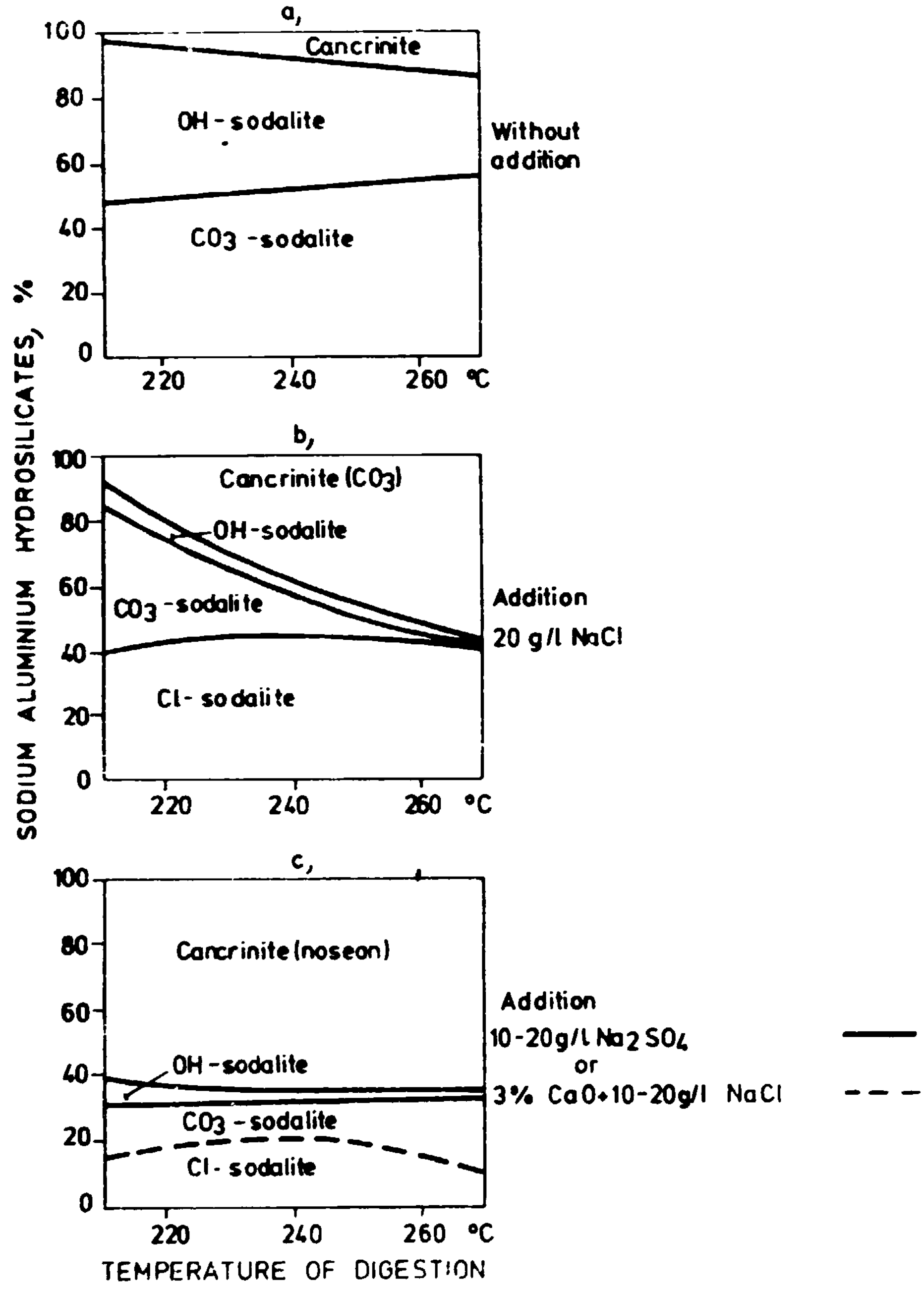


Fig. 2.15

EFFECT OF ADDITIVES ON THE COMPOSITION OF SODIUM ALUMINIUM HYDROSILICATES

(DIG. TIME 0.5 HOURS)

For the determination of various sodium-aluminium-hydrosilicates, X-ray diffractometry can be used to differentiate between the phases displayed in Table 2.6 /41/.

Digestion Tests at Different Parameters

Table 2.6

	SAMPLE	
Digestion Conditions	240^{o}C-60' 3 % CaO	240^{o}C-60'
Phase Denomination	Al_2O_3 %	
Distribution of sodalites		
$3/Na_2O.Al_2O_3.2SiO_2/Na_2CO_3.2H_2O$	1.1	2.0
$3/Na_2O.Al_2O_3.2SiO_2/Na_2SO_4.2H_2O$	1.1	2.9
	2.2	4.9
Distribution of cancrinites		
$\begin{Bmatrix} 3Na_2O/NaHCO_3/CaO. \\ 4Al_2O_3.9SiO_2.2H_2O \end{Bmatrix}$	2.4	2.8
$3/Na_2O.Al_2O_3.2SiO_2/Na_2CO_3.2H_2O$	0.7	2.3
$3/Na_2O.Al_2O_3.2SiO_2/Na_2SO_4.2H_2O$	0.9	1.6
	4.0	6.7
$3CaO.Al_2O_3.kSiO_2./6-2k/H_2O$	1.9	0.3
$Na_2O.8CaO.3Al_2O_3.5SiO_2$	1.8	traces
$CaO.2Al_2O_3.2SiO_2.H_2O$	1.8	traces

Independently from the condition that, subsequent to grinding of bauxites, the structure of sodium-aluminium-hydrosilicate precipitating from the solution in the course of preheating /due to dissolution of the caolinite/ may be of the zeolite and sodalite structure, all compounds would transform into sodalites and cancrinites described above during digestion.

Solubility of the forming sodium-aluminium-hydrosilicates decreases significantly, as the temperature increases /42/: this practically brings about the precipitation of sodium-aluminate-hydrosilicates in the course of digestion /or preheating and digestion/ or, in certain cases, it may cause scaling.

Special attention should be devoted to the behaviour of the SiO_2 content of bauxites in a tube digester unit. VAW experimental data are shown in Fig. 2.16 and Fig. 2.17 /43/. Fig. 2.16 illustrates the change of SiO_2 content in the tube digester, in the function of temperature. The figure clearly shows that the SiO_2 content remaining in the solution decreased from 3.2 g/l to 0.4 g/l, between temperatures of 140 and 200 °C, and it was not higher after digestion, than in a system of conventional digesters, even if processing bauxite of 8 per cent SiO_2 content.

Fig. 2.17 illustrates the reaction products of quartz and caolinite minerals after tube digestion of 150 seconds, in the function of the temperature. The figure shows that, owing to the short residence time, not only a significant part of quartz remained unchanged even if achieving a final temperature of 270 °C, but the same applies to a small portion of caolinite, too. SiO_2 content of the solution represents a minor value.

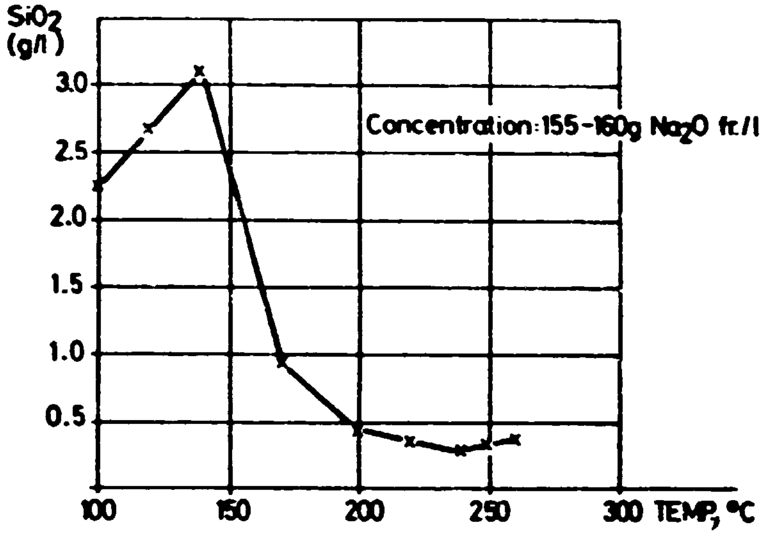


Fig. 2.16

SiO_2 CONTENT OF DIGESTION LIQUOR AS A FUNCTION OF TEMPERATURE

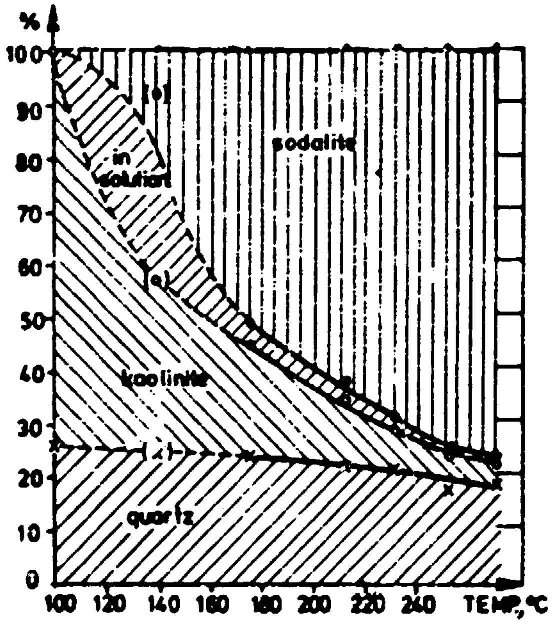


Fig. 2.17

REACTION PRODUCTS OF SiO_2 AFTER 150 SEC. TUBE DIGESTION AS A FUNCTION OF TEMPERATURE

The Whole Na_2O - Al_2O_3 - SiO_2 - CaO - H_2O System

Depending on the degree of crystallization and on the temperature of digestion, calcite and dolomite content of bauxites desintegrates forming carbonate soda. In case of Hungarian bauxites, 70 per cent of calcite and 92 per cent of dolomite desintegrates already at a temperature of 210 °C. The formed phases are listed in Table 2.7 /44/.

Phases Formed During Digestion

Table 2.7

	Phases	ASTM Code Number
1.	$3CaO.Al_2O_3.6H_2O$	3-0125
2.	$Ca_3Al_2O_3 . 8\text{-}12H_2O$	2-0083
3.	$CaAl_2O_4$	1-0688
4.	$Ca/OH/_2$	4-0733
5.	$CaCO_3$	5-0586
6.	$3CaO.Al_2O_3.kSiO_2./6\text{-}2k/H_2O$	3-0125
7.	$Na_2O . 8CaO.3Al_2O_3.5SiO_2$	8-186
8.	$CaTiO_3$	9-365
9.	$MgAl_2O_4$	10-62
10.	$Mg/OH/_2$	7-239
11.	$MgCO_3$	8.479
12.	$Mg_6Al_2CO_3/OH/_{16}.4H_2O$	14-91
13.	$Mg_4Al_2/Al_2Si_2/O_{10}/OH/_8$	11-157
14.	$Mg_2Al_4Si_5O_{18}$	12-244
15.	$NaCa_2Mg_5Si_7AlO_{22}$	10-431
16.	/Ca, Mg/ titanates	13-552
17.	$MgTiO_3$	6-0494

Quantitative distribution of Ca- and Mg-containing phases formed in the red mud at a temperature of 210 °C is shown in Fig. 2.18 /44/.

Formation of Ca-Al-hydrosilicates, which can be described by the hydrogranate structure of

$$3CaO.Al_2O_3.kSiO_2/6-2k/.H_2O$$

composition is essentially important in this system. Practically the value of k determines the rate of Na_2O regeneration and of Al_2O_3 losses opposite in direction. In the course of digestion the value of k is generally 0.8–0.9 and the value of k = 2 can be approached only by treating the red mud with burnt lime /causticization/. SiO_2 content of Ca-Al-hydrosilicates as compared to the Na-Al-hydrosilicates is only about 50 per cent. CaO addition to diasporic and goethitic bauxites must be optimized, therefore, so that no significant excess Al_2O_3 losses occur.

Phase Transformations During Digestion

In the course of the digestion process of the Bayer technology simultaneous and consecutive reactions take place between the mineral components of bauxite and the digestion liquor. With regard to the reactions detailed in the above, typical phase transformations are illustrated in Table 2.8 /45/.

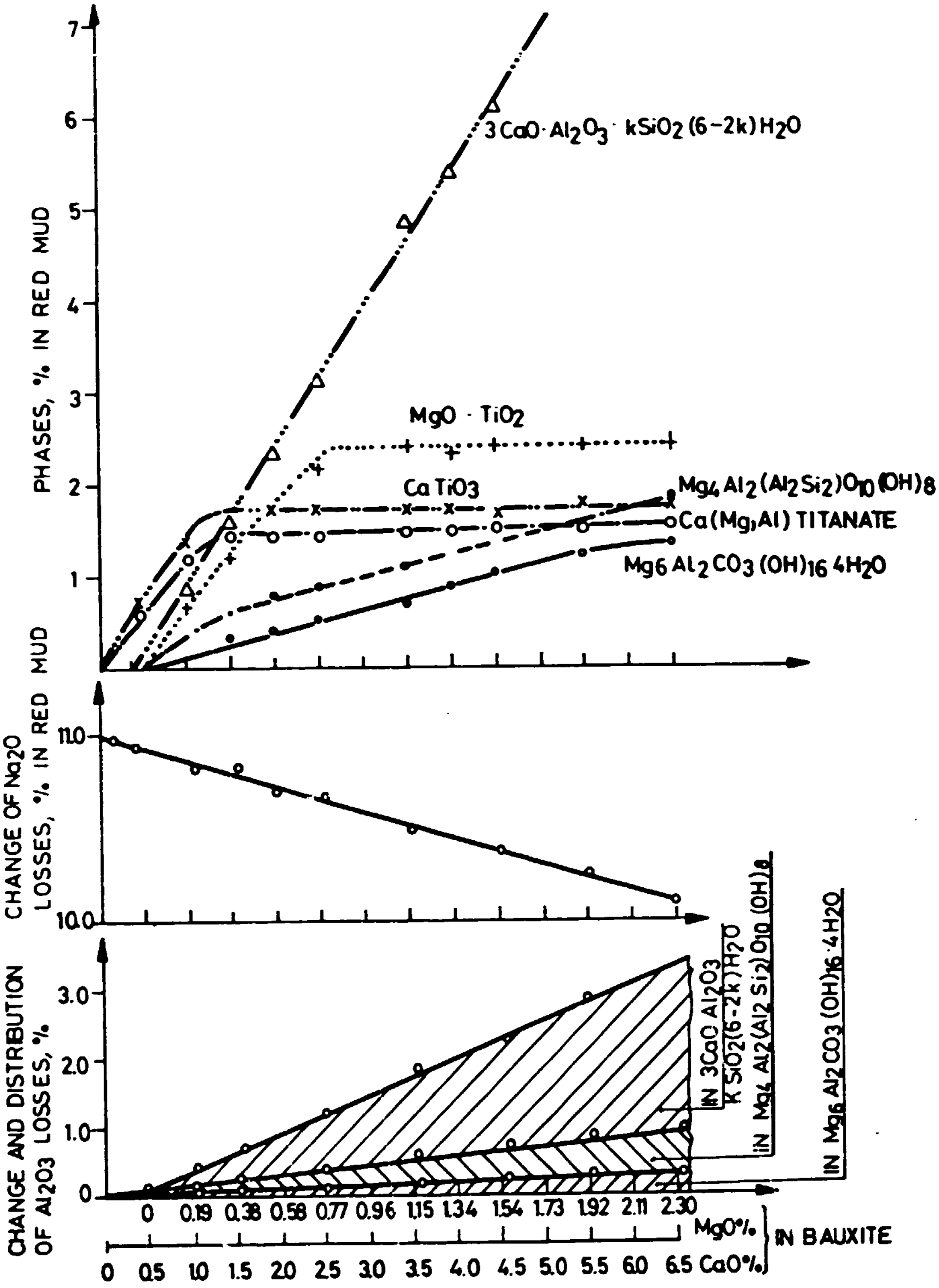


Fig. 2.18

Na_2O AND Al_2O_3 LOSSES, AND LOSSES DUE TO THE FORMATION OF MINERALOGICAL PHASES vs. CaO AND MgO CONTENT

Characteristic Phase Transformations During Digestion /45/

Table 2.8

Bauxite Minerals	Reaction Products Formed Without Additives		Reaction Products Formed With CaO-Addition
Gibbsite, Boehmite, Nordstrandite		$Al/OH/_4^-$	/CA/
Diaspore		$/Al/OH/_4^-/$	/CA/, $Al/OH/_4^-$
Quartz, Kaolinite, Halloysite	NAS		CAS
Chamosite	NAS	Fe^{2+}	CAS
Hematite	$Fe_{2-x}Al_xO_3$		$/Fe_2O_3 + Al/OH/_4^-/$
Goethite	$Fe_{1-x}Al_xOOH$		$Fe_2O_3 + Al/OH/_4^-$
Ilmenite	$FeTiO_3$		$FeTiO_3$
Anatase, Rutile	Na-titanates		$CaTiO_3$
Calcite, Dolomite	Ca- and Mg-compounds	CO_3^{2-}	Ca- and Mg-compounds
Siderite		CO_3^{2-} Fe^{2+}	
Crandallite, Apatite	$Ca_3/PO_4/_2$	PO_4^{3-}	$Ca_3/PO_4/_2$
Alunite		$Al/OH/_4^-$ SO_4^{2-}	
Pyrite		Fe^{2+} S^{2-}, SO_3^{2-}	
Lithiophorite, Todorokite		Mn^{2+} Mn^{4+}	

The table shows the most important minerals of bauxite, and their reaction products in case of digestion performed without or in presence of lime, resp. The rate of the individual reactions and the quasi equilibriums ar determined by the conditions of concentration, temperature and duration of the digestion. Selection of the digestion parameters provides a possibility to avoid certain unfavourable reactions, such e.g. in case of low digestion temperature, short digestion time and low liquor concentration smaller or more considerable amounts of quartz, chamosite, anatase, rutile, calcite, dolomite and siderite may get unchanged into the red mud.

Another possibility is the transformation of certain unfavourable phases by lime-addition, when, for example, Na-Al-hydrosilicates, Na-titanates and Na-phosphates transform into calcium-compounds.

Finally, the conversion of iron minerals can also be realized in the digestion process by adding burnt lime and catalyzers /11/: alumogoethite and - under certain conditions - alumohematite, too, can be transformed into hematite by simultaneous dissolution of the isomorphically built-in Al-content.

Consequently by the selection of technological parameters, the composition of the forming compounds can be influenced, thus affecting the NaOH and Al_2O_3 losses of the Bayer process, moreover, the separation and washing conditions of red mud.

Equilibrium diagram of Na-titanates forming from the titanium minerals of bauxites is shown in Fig. 2.19, based on Wefers' data /15/.

In the Na_2O-CaO-Al_2O_3-TiO_2-H_2O system the perovskite becomes the most stable phase, especially at higher temperatures /46, 47/.

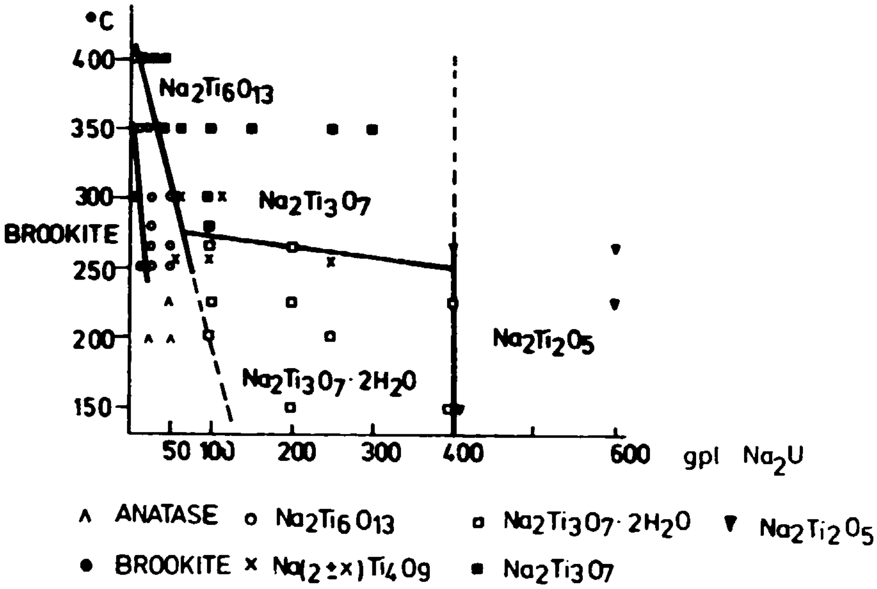


Fig. 2.19

EQUILIBRIUM DIAGRAM OF Na - TITANATES

Wefers had also studied the $Na_2O-Al_2O_3-Fe_2O_3-H_2O$ system /48/. Based on his data the kinetics of the transformation of goethite to hematite, taking into consideration various digestion temperatures, is illustrated in Fig. 2.20. The figure clearly shows that the transformation of goethite, used as model material, is promoted by the presence of hematite in the base substance, and that its rate increases parallelly with the rise of the temperature.

It is mentioned, however, that the alumogoethite present in bauxites is a much more stable phase, than the model materials of the above tests.

BAUXITE PREPARATION, CRUSHING AND GRINDING TECHNOLOGY AND EQUIPMENT

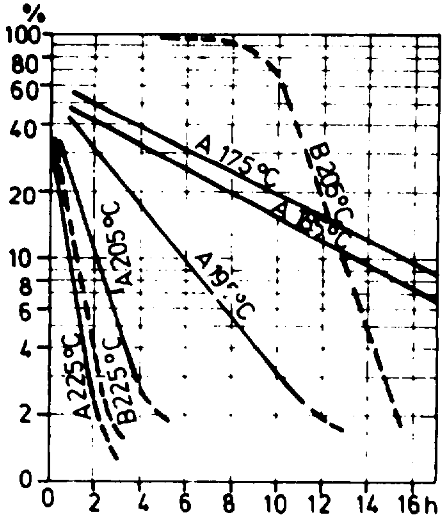
Bauxite Preparation

The mined bauxite is transported to the alumina plant either in its original state, or after being washed or crushed in the mine.

In case the alumina plant is situated right in the vicinity of the mine, the bauxite can be carried to the plant by belt conveyor /Fria, Guinea/, but it can also be transported by 20 /Ajka, Hungary/ to 50 ton capacity trucks, light railway /Linden, Guyana/, normal-gauge railway /Almásfüzitő, Hungary/ or by ropeway /Korba, India/.

Railway transport is especially suitable for spanning greater distances, though some example can be found when bauxite is carried by belt conveyor even for 18 km-s /Gove, Australia/.

Naturally, if the alumina plant and the bauxite mine are situated on two different continents, the bauxite is shipped



A : BOTTOM BODY 50 % FeOOH + 50 % α-Fe_2O_3

B : BOTTOM BODY 100 % α - FeOOH

Fig. 2.20

DECOMPOSITION OF α-FeOOH IN SODIUM ALUMINATE SOLUTION OF 150 gpl Na_2O AND 100 gpl Al_2O_3 CONCENTRATION from the port of the mine to that of the alumina plant /from Australia to Protoscuso, Sardinia, to Stade, GFR etc./. Seventy per cent of the bauxite is transported in ships of less than 40,000 t DW. Some of the bauxite producers have a fleet of their own /Jamaica, Guyana, etc./.

Several proposals have already been made concerning the hydraulic transporation of bauxite, yet it has not been adopted in practice up to this time, as separation of the dispersed fine bauxite from the conveying medium /water/ would surely inflict problems.

The bauxite reaching the plant area is generally discharged from the conveyor belt into bins or it is immediately delivered to the storage area. Bauxite delivered in railway trucks is discharged either by cranes /Magyaróvár, Hungary/, or it is unloaded from self-discharging railway trucks into hoppers situated by the rails or below them /an old system at Ajka, Hungary/ or the waggon is taken to the rotary waggon tipper the angle of swing of which can come close to 180° /Almásfüzitő, Hungary/.

Bauxite arriving by ships is generally unloaded by cranes and carried by belt conveyor to the plant area.

The amount of bauxite stored on the plant area is determined first of all by the duration of shortages in the course of delivery. Where the mine is situated close to the alumina plant /Fria, Guinea, or the alumina plants in Jamaica/ a 2-3 days' stock is sufficient. In case of ship delivery at least an amount corresponding to one and a half or two ships has to be stored; if the transportation is retarded as a consequence of bad weather-conditions in wintertime or the monsoon period, the accumulation of 2-3 months' stock may be necessary.

Bauxite is stored in its original state /lump size max.

300 mm/, generally in an open-air storage area. Crushed bauxite can also be stored; this is advantageous for the homogenization /Almásfüzitő, Hungary/. At monsoon areas part of the dry bauxite is stored in covered store-houses and it is mixed with the wet bauxite during the monsoon period in order to reduce adherent moisture.

One of the advantages of storing greater stock of bauxite is the possibility of homogenization. According to the basic principle of homogenization bauxite is deposited in horizontal layers /e.g. from the conveyor belts located above the storage area, Ziar, Czehoslovakia/, and is picked up vertically by shovel crawler loaders, or pushed by bulldozers through the grating into the hopper and rubber belt system located below the storage area /Obrovac, Yougoslavia/.

In the plant at Almásfüzitő the homogenization of bauxite takes place in a 100 thousand tons capacity circular storage area. In the plant at Ajka, where the bauxite is delivered by trucks, calculations during the course of design showed that the bauxite delivered in small lots gets homogenized to such an extent, without adapting any particular storage regulations, that the fluctuation of the Al_2O_3 to silica ratio /module/ remains within two units.

In a commonly used storage system the storage area is divided into two rectangular parts; the bauxite is stratified horizontally on the first and processed in vertical cuts from the second.

Together with the bauxite several different mining-contaminants reach the plant: fractures of wood, iron and limestone, pieces of blasting wire etc. Great lumps of limestone and oversized fractures of bauxite can be separated by covering the bins with wire screens and thus, when tilting the screen-cover periodically, the great fractures fall beside the bins. For removing the great limestone fractures the wobbler "grizzlies" consisting of finger-biscuit shaped elements proved to be satisfactory. The fine-grain bauxite falls through the openings, while the limestone advances and thus it can be removed /a common system in Jamaica/. Pieces of iron are removed after crushing but before grinding by a magnetic separator.

In cases when the moisture content of the bauxite is high and/or the major part of the product is transported for a longer distance, the bauxite is dried. The drying procedure takes place in oil-fired rotary kilns, the drying temperature is abt. 150-200°. Flue-gas can also be used for drying /e.g. Ludwigshafen, GFR/. Dried bauxite is processed later by dry or wet grinding.

In the past bauxite was dried partly for the purpose of dry grinding. Bauxites with goethite-content were generally dried at about 400 °C. This promoted better digestibility and settling, and, at the same time, the organic matter content of bauxite had been also decreased.

Bauxite Crushing

The purpose of crushing the bauxite is to prepare it for the grinding process. Generally it is advisable to feed bauxite with a maximum grain-size of 50 mm into the grinding mill. As the grain-size of certain bauxites in extracted form is smaller than 50 mm, it is unnecessary to crush them /Weipa, Australia/.

Bauxite is crushed in roller-, jaw- or hammer mills. An up-to-date equipment is the differential cylindric crusher, which is suitable first of all for processing softer bauxites /Fig. 2.21/. Hammer mill is a simple means for crushing harder bauxites, while the softer ones often stick to the wall of the mill. For removing the adhered bauxite the wall is equipped with a moving belt or revolving rollers /Fig. 2.22/. /Ajka,

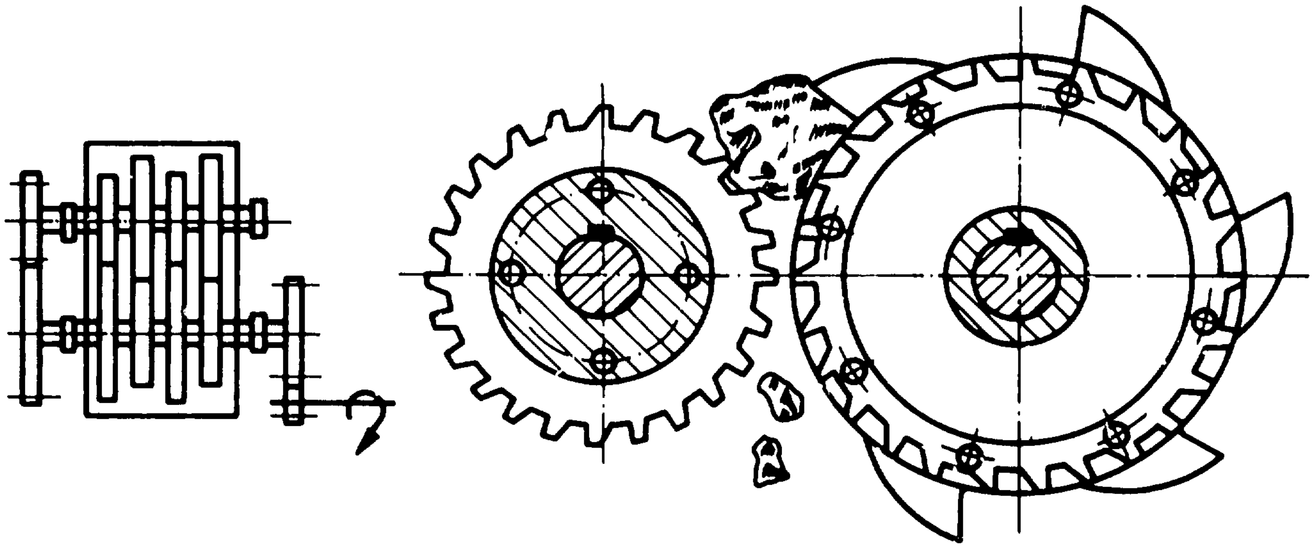


Fig. 2. 21

DIFFERENTIAL CYLINDRIC CRUSHER

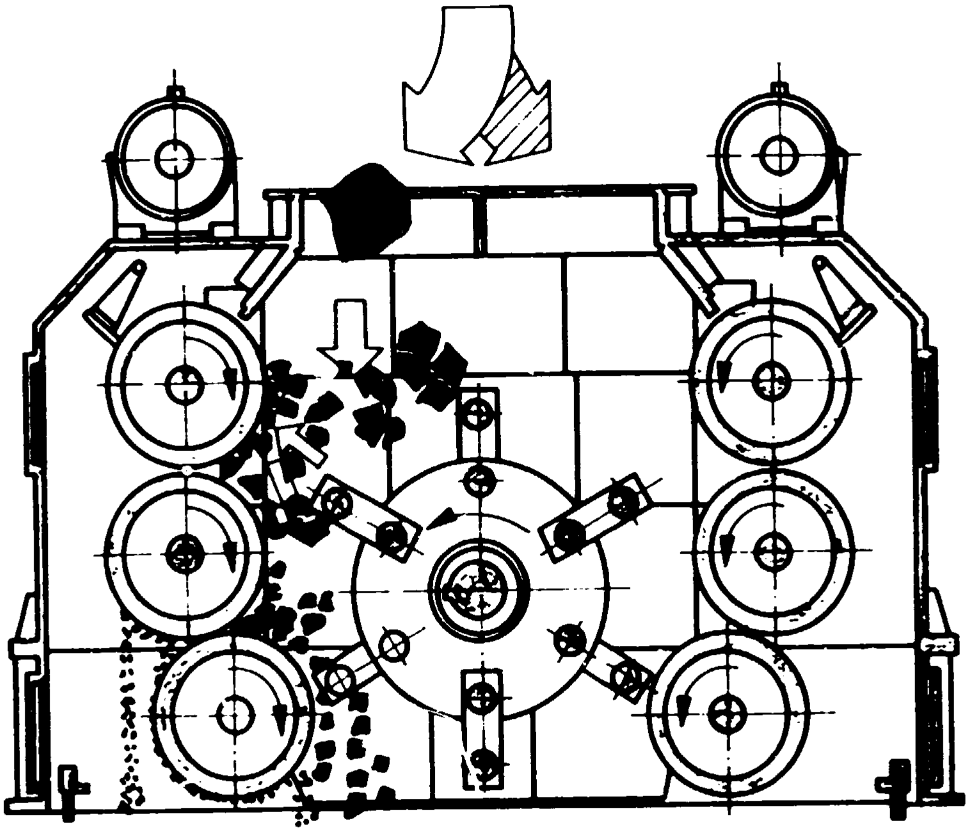


Fig. 2. 22

HAMMER MILL (AJKA)

Hungary/. In case of extremely wet bauxites, however, this kind of crusher gets often plugged. As the energy requirement of crushing is rather high /1-3 kW/t/, it is advisable to classify the bauxite before crushing. Classifying can be done, among other methods, by vibrating screens.

While adhesion makes the crushing of wet bauxites difficult, in case of dry bauxites the dust formation is considerable. Care must be taken for the exhaustion, and the dusty air must be forced through a scrubber. It is advisable to re-circulate the water used in the scrubber and, when the efficiency of dust precipitation worsens, to spray the slurry over the stored bauxite.

Bauxite Grinding

Bauxite grinding is necessary first of all because of mechanical engineering aspects, since in the course of the subsequent procedures the coarse fraction of bauxite settles on the bottom of the vessels, cloggs the preheating tubes, deposits in the return chambers of the preheaters, and wears out the stirring equipment and bearings. The question of favourable digestibility can not be neglected either: decline in the digestion output caused by coarse grinding may exceed 10 % in case of hard, diasporic bauxites. It is expedient therefore, to grind such kind of bauxites to below 60 µm grain-size.

Recently dry grinding of bauxites is driven into the background, even those dried for transportation purposes undergo wet grinding before digestion.

In case of extremely soft bauxites, grinding may have a repulping nature /Jamaica/: rotating the mixture of bauxite-digestion liquor in drums covered by screen, the bauxite disaggregates and passes through the holes of the screen in the form of small grains.

Harder bauxites are ground in single or multichamber ball-mills or rod-mills. Rod-mills provide more uniform granulometry of the ground bauxite. In case of fine grinding of hard bauxites, the ratio between the length and diameter of the mill /L/D ratio/ is 3 to 4, while in case of coarse grinding of soft bauxites it is about 1.4 to 1.7.

In the "multichamber" ball-mills individual chambers are separated by slotted discs allowing thus only the fine product to pass into the next chamber. The concentration of the ground slurry in the individual chambers may range between 300 and 1000 g/l.

Soft bauxites can generally be ground with lower solids concentration, because the disaggregated part can increase the viscosity of the slurry to such an extent that the striking effect of the balls will diminish when considering harder lumps of ore.

Balls of different sizes are placed into the mill /50-100 mm/. While grinding the balls gradually wear off /the ball-loss can amount to 5 kg-s for 1 ton of alumina/ and larger balls are charged in order to make up for this loss.

Grinding is performed in open or closed circuits. Open-circuit grinding requires reduced equipment, but the risk is greater that the coarser grains would proceed and bring about operating troubles as it had been described above.

Closed circuit grinding demands less energy consumption, however, the recycled coarse grains usually cause significant abrasion in the classifying systems, the equipment is rather complicated and part of the saved energy must be invested in the pumping procedure. Classification can be performed in hydrocyclones or trommel screens /Fig. 2.23/.

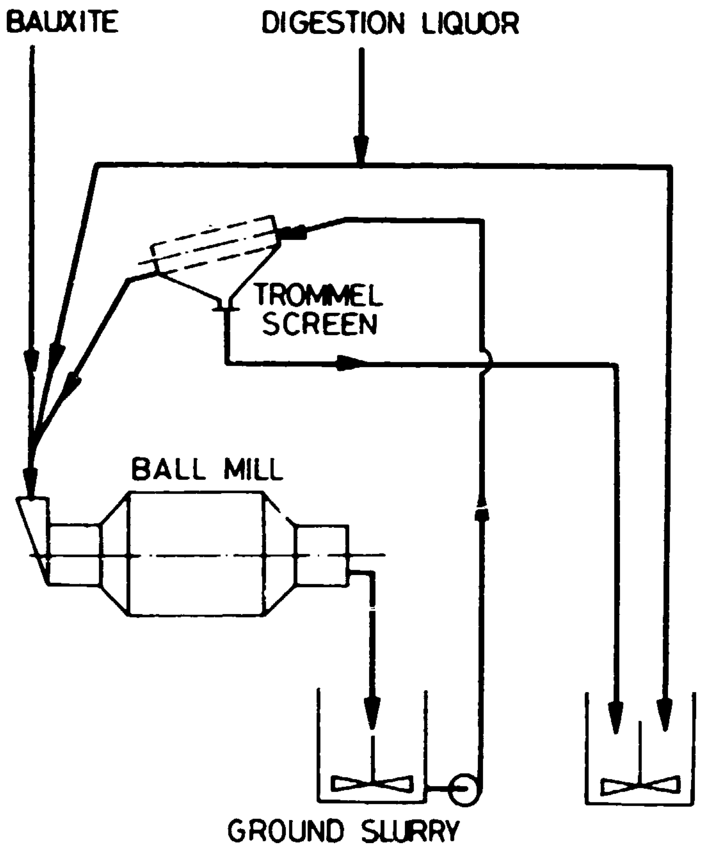


Fig. 2.23
CLOSED CIRCUIT GRINDING

Hard bauxites can inflict a significant abrasion of the hydrocyclones or of the impellers of the pumps.

Several experiments have been performed in the field of autogenous grinding /i.e. grinding without balls/ of bauxites. Experiments with harder bauxites showed more favourable results, however, in the practice it is necessary to classify and to use an additional mill for grinding the coarse part of the raw material. Therefore, when working with harder bauxites, it seems to be safer to use two series-connected ball mills.

On the basis of the above, designing of an alumina plant must be preceeded by the correct analysis of the grindability of bauxite, since the grinding energy forms a significant part of the plant's energy-demand and, at the same time, insufficient grinding would cause serious operating difficulties in the course of the further procedures.

Two qualifying methods are used for characterizing the grindability of bauxite:

The Hardgrove-index can be calculated from the result of grinding test carried out in the laboratories; the Hardgrove-index of hard bauxites is low /50-60/ while that of the soft bauxites, e.g. that of the Hungarian bauxites, is about 100-120.

The Bond working-index is very useful for application as on the basis of the grinding test it determines the energy requirement of grinding 1 ton of bauxite. This value is 9-11 kWh/t for soft bauxites and can exceed 15 kWh/t in case of harder bauxites.

The efficiency of grinding under plant conditions can be controlled by wet screening of the bauxite slurry. The result of the screening /"R" residue curve/ gives generally a straight line in the Rosin-Rammler diagram. The slope of this line gives the grindability of the matter, and the grain-size belonging to the 36.8 % residue gives the average grain-size. Every ground material can properly be characterized by these two numbers and the grinding curve can be determined from some screening data /Fig. 2.24/.

When classifying, the two products give two deviating curves in the diagram, providing a possibility for evaluating the efficiency of the classification.

PREDESILICATION TECHNOLOGY AND EQUIPMENT

After grinding - and, in some cases, adjusting by digestion liquor - the bauxite slurry is preheated to the digestion temperature. During this heating, part of the bauxites reactive silica content /in case of higher temperature the total silica content and part of the quartz/ is dissolved in the digestion liquor. The silica content of the solution first shows a sudden increase, then a fast decrease as sodium-aluminium silicates separate from the solution, finally it approaches asymptotically the equilibrium value.

On the basis of Leiteizen's formula /49/, in the first approach the equilibrium value is independent from the temperature:

$$S_e = 26 \cdot 10^{-6} \cdot N \cdot A$$

where: N = caustic Na_2O concentration, and A = Al_2O_3 concentration in g/l-s.

Desilication is a reaction of the first order

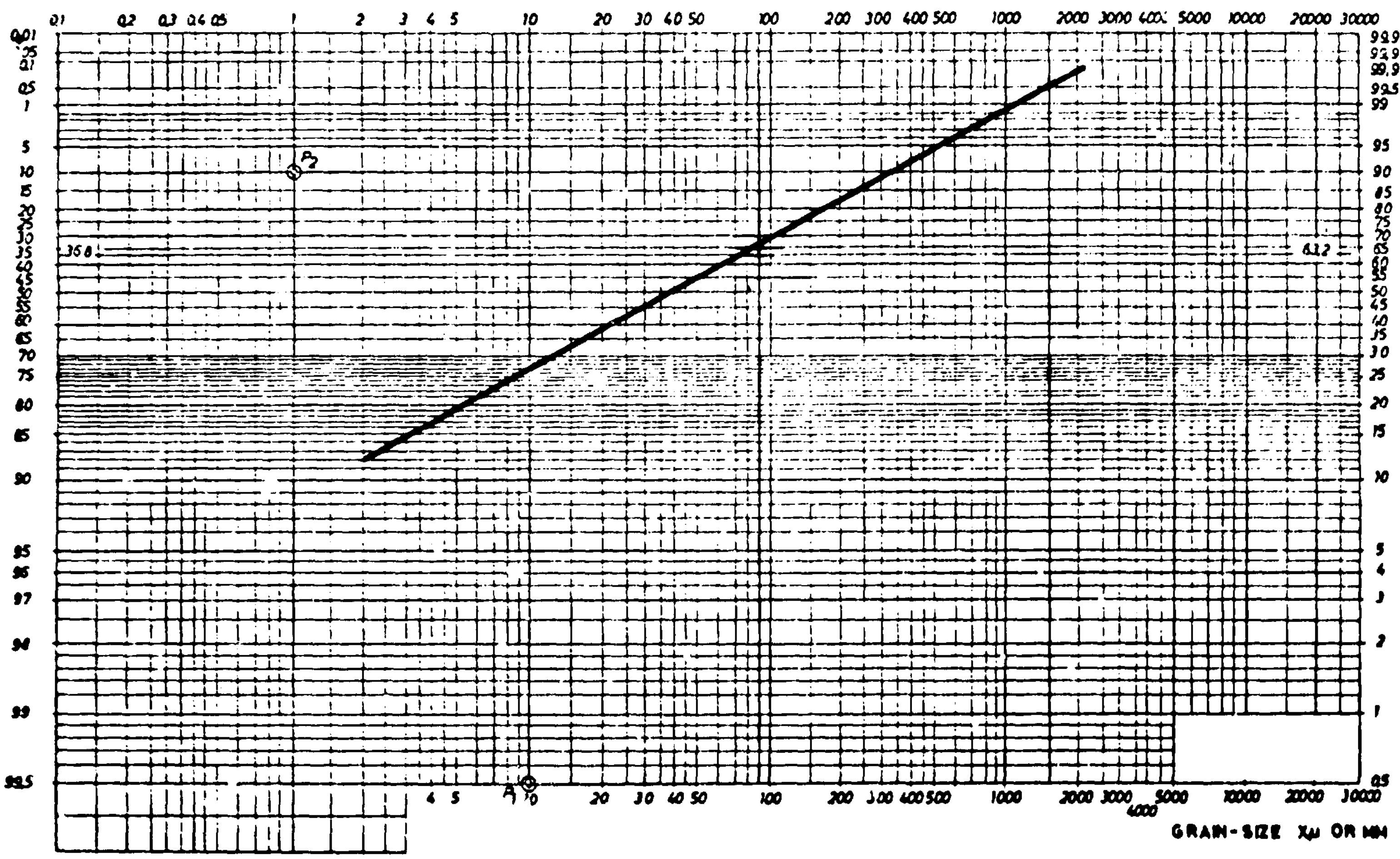


Fig. 2.24

R-CURVE OF GROUND BAUXITE

$$-dS/dt = k' /S - S_e/, \quad \text{or}$$

$$\log/S - S_e/ = -kt + C$$

where: t = time in hours.

The value of k can be calculated from the following formula:

$$\log k = B-2000/T-1.5 \times \log Al_2O_3$$

where: T means the temperature in K^0, the value of B depends on the sodalite "seed" present. The formulas show that as the slurry is heated in preheaters to the digestion temperature, more and more silica precipitates from the solution in the form of sodalite and forms scales on the heated tube-walls, worsening by that significantly the heat transfer coefficient. The heat transmission capability of the preheaters decreases in time and, therefore, the preheaters must be taken off-stream and cleaned after a certain period of run.

In case of similar digesting conditions a low digestion molar ratio would increase the equilibrium silica concentration thus, when processing gibbsitic bauxites the silica level is always higher than in case of diasporic bauxites.

To prevent sodalite precipitation and scale formation in the preheaters it is advisable to preheat the bauxite slurry already before digestion to the highest possible temperature. This process is called predesilication. The efficiency of predesilication may be increased by extending its duration. According to the experiments of processing Hungarian bauxites the practical equilibrium in predesilication is reached in 5-6 hours' time.

Decreasing of the silica content of the liquid phase of the digestion slurry may be promoted by performing the aesilication at high solids concentration. Therefore, it is expedient to dilute the slurry by the digestion liquor only after desilication. Another advantage of this method is that significantly less material has to be handled in the desilication. The high solids concentration after grinding can generally be achieved in case of harder tropical bauxites /up to 1000 g/l/, while the softer boehmitic ones can often be ground only at a solids concentration of 300 to 400 g/l.

In practice, it is advisable to perform the desilication at the highest admissible temperature /100 °C or above/.

Desilication can also be promoted by adding desilicated, filtered product or filtered red mud as seed to the desilication process /50/. Desilication is generally performed in large tanks; it must be taken into consideration, however, that part of the matter overtakes the bulk and, therefore, after a given retention time the efficiency of desilication is always less as compared to that achieved under laboratory conditions. To eliminate this effect desilication is performed instead of a single large tank in more smaller tanks, where the effect of overtaking decreases. For security purposes 8-10 hours of retention time is maintained. In case of indirectly heated tanks silica scales will deposit on the heating surface so the heating surface and the heat transmission coefficient decrease to a very low degree. It is a routine process, therefore, to preheat the slurry going to desilication in tube-bundle preheaters by flash steams and to provide spare preheaters.

Finally, desilicated slurry can be heated directly in flash condensers with waste steam drawn, for example, from the last flash tank or from the steam-operated slurry pumps. Obviously in case of direct heating the slurry is diluted by the condensating steam, and this requires a surplus evaporation.

Desilication tanks are series-connected. Their stirring with air-lift pumps is partly favourable, as in this case transfer of the slurry from a tank in to the other is simple, though the treatment causes the cooling of the slurry. Therefore, it is advisable to apply mechanical agitation, and to transfer the slurry by cascade arrangement of the tanks, or by pumping.

The term predesilication has been used here above because this process is performed before digestion. Desilication process, however, may also be inserted in the course of digestion, in an intermediate retention tank, where the higher temperature accelerates the precipitation of the silica.

This is especially expedient for low silica bauxites, because in that case the desilication reaction is slow.

Even after the digestion procedure it may be useful to desilicate the aluminate liquor, in order to improve the quality of alumina by decreasing its SiO_2 content. In order to achieve better results as high temperature and retention time should be achieved as possible and the addition of seed may also be useful.

DIGESTION TECHNOLOGY AND EQUIPMENT

Digestion Technology

The digestion technology is determined principally by the chemical composition of bauxite and the mineralogical form of its components; it is also a significant factor whether floury or sandy alumina is going to be produced.

As regards the chemical composition of bauxite the minimum Al_2O_3 content of bauxite to be processed is about 40 %, the maximum Al_2O_3 content practically does not exceed 60 %. The total Al_2O_3 content is the main factor determining specific bauxite consumption.

As regards the mineralogical form of the Al_2O_3 content of bauxite:

From the Al_2O_3 minerals of bauxite the gibbsite, $Al_2O_3 \cdot 3H_2O$; boehmite, $Al_2O_3 \cdot H_2O$ and diaspore, $Al_2O_3 \cdot H_2O$ can be dissolved under adequate technological conditions, while other Al_2O_3 bearing minerals /first of all kaolinite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$/ can not be dissolved, yet in the course of digestion they may cause excessive alumina losses.

The above listed Al_2O_3 bearing minerals can be found in the bauxites in a mixed form. Three main bauxite types are distinguished: gibbsitic, boehmitic and diasporic bauxites.

In gibbsitic bauxites the Al_2O_3 content occurs preddominantly - practically at least in 80 to 90 per cent - in the form of $Al_2O_3 \cdot 3H_2O$. These kinds of bauxites can be easily digested in sodium-aluminate liquors. In the Fria Alumina Plant the Al_2O_3 content of the gibbsitic bauxite is dissolved in open tanks at a temperature of about 105 °C. At the other alumina plants processing gibbsitic bauxite the digesting temperature is 140 to 145 °C, as at a higher temperature gibbsite is transformed into the less soluble boehmite and a significant part of the Al_2O_3 content is separated out in this latter form. Such kinds of bauxites are generally digested by low-concentration digestion liquor, 100-130 g/l Na_2O and the plants usually produce sandy alumina. These are the main features of the "American Bayer process".

The digestion of boehmitic bauxites requires a temperature of 200 °C at least. Owing to practical considerations, however, digestion is performed generally at about 240-250 °C at present. The concentration of the digestion liquor is 180-240 g/l kNa_2O and the plant generally produces floury alumina. These are the characteristics of the "European Bayer process".

When processing mixed gibbsitic-boehmitic bauxites having a gibbsite content of less than 90 per cent, high digestion temperature /240 to 250 °C/ is preferred nowadays even in case of low concentration digestion liquor. In this case other factors of technology correspond to the parameters of the American Bayer process and the product is sandy alumina /e.g. Alpart, Jamaica/.

Diasporic bauxites are digested at 240 to 260 °C, generally with high digestion liquor concentration and utilizing the European Bayer technology. Digestion temperature can be decreased only by using additives.

Differences in the digestion temperature do not necessarily imply similar differences in the steam consumption under the conditions of up-to-date technologies. As it will be seen when discussing the heat-balance of the digestion, the heat recovery connected to the multistage flashing permits to reach a low specific steam consumption even in case of high temperature digestion and the water eliminated by flashing results in savings in the evaporation /92/.

Another technology applied at few plants is to carry out digestion in two stages: gibbsite is digested in the first stage and the residue added to the second stage - boehmite - digestion. The aluminate liquors are combined.

An up-to-date solution of the above "sweetening process" is to add "trihydrate" slurry to one of the flashing stages of the monohydrate digestion. Gibbsite is digested "free of charge" and molar ratio of the boehmite digestion is lowered.

Selection of Digestion Parameters

Volume 6. chapter 3.3 on technological testing of bauxite describes the "characteristic curve of the digestion" and the concept of the "optimal molar ratio". This characteristic curve serves as the basis of the digestion technology. It is principally determined on the basis of preliminary economic calculations whether to use high or low temperature digestion techniques, and these calculations give the first indication of the optimal digestion concentration, too. Finally, the characteristic curve specifies the molar ratio to be chosen as the basis of the digestion. With regard to the inevitable fluctuations in the plant, the suggested molar ratio is generally higher by 2-3 per cent than the optimal one, in order to avoid the occurrence of undigested Al_2O_3 in the mud.

At the same time, it is of principal importance for the selected molar ratio to be as close to the optimum as possible, both in view of reaction kinetics and that of the subsequent processes. A higher molar ratio would unfavourably influence the overall economy of the plant.

Korcsmáros /51/ recommends the following differential equation for describing the digestion process of Al_2O_3 bearing minerals:

$$\frac{dC_A}{dt} = \frac{D}{r} \cdot S \cdot /C_{At} - C_A/ \cdot /C_{Ae} - C_A/ ,$$

where: C_A = Al_2O_3 concentration of the liquid phase, $kmol.m^{-3}$

D = diffusion coefficient, $m^2.s^{-1}$

r = thickness of diffusion layer, m

S = characteristic specific material transfer area of the mineral, $m^2.kmol.^{-1}$

C_{At}= the Al_2O_3 concentration, $kmol.m^{-3}$ in case of total dissolution of the aluminium-oxide content soluble by the given digestion technology

C_{Ae}= equilibrium Al_2O_3 concentration of the liquid phase $kmol.m^{-3}$

The following interesting conclusions justified by tests, too, can be derived from the above formula:

a/ under similar digestion conditions the rate of reaction is greater if the soluble Al_2O_3 content of the bauxite charged into the digestion liquor is more than the amount necessary to achieve the equilibrium Al_2O_3 concentration.

b/ in case the soluble Al_2O_3 content of the bauxite added is less than the amount necessary to achieve the equilibrium Al_2O_3 concentration, the Al_2O_3 concentration of the liquid phase tends towards the maximum value, which was determined by the amount measured in, with a slower rate than under the previous condition.

c/ finally, in case of adding so much bauxite as to reach an Al_2O_3 concentration corresponding to the equilibrium value, the equation will take the following form:

$$\frac{dC_A}{dt} = k\,/C_{Ae} - C_A/^2$$

Behaviour of Contaminants During Digestion /93/

The behaviour of silica during the digestion depends on its chemical form, the temperature and the duration of the digestion. The chemically not bound silica and quartz start to react with the sodium-aluminate liquor only at higher digesting temperatures, generally above 150 °C. Thus, in case of digesting at a low temperature, the part of the total amount of SiO_2 present in the form of quartz migrates into the red mud and can be removed in the form of "sand", separated after the digestion, or together with the red mud, without causing any losses in the alumina and caustic soda.

The chemically bound SiO_2 /principally in kaolinite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ or in other aluminium-silicates/ reacts with the liquor already during the desilication and this results in the formation of the following compound:

$$3/Na_2O \cdot Al_2O_3 \cdot 2SiO_2/ \cdot Na_2X \cdot nH_2O$$

where: X = a two-valent anion /SO_4^{--}; $2Cl^-$; $2AlO_2^-$ etc./

From the formula above it can be calculated that 1 kg of SiO_2 binds about 0.7 kg Na_2O /0.9 kg NaOH/ and /in case X is not an aluminate ion/ 0.85 kg Al_2O_3.

Therefore, when selecting the digestion technology bauxites of high quartz content should be digested as far as possible at low temperatures. More exactly, economic calculations will decide upon whether to choose low digestion temperature, when only Al_2O_3 present in the form of gibbsite can be extracted from the bauxite but the silica bound in the form of quartz will not take part in the reaction, or to choose high digestion temperature, when both the boehmite and the diaspore content will be dissolved, but the silica present in the form of quartz will also take part in the reaction.

An extreme example is, for instance, the gibbsitic bauxite of Madagascar having a reactive SiO_2 content of about 2 per cent and a quartz content of 16-18 per cent. This kind of bauxite can be digested economically only at low temperatures.

It must be noted that silica content of certain bauxites /e.g. Australian ones/ have such a compact crystal structure that sodalite formation takes place rather slowly even at higher temperatures. In case of digesting such kinds of bauxites - if other factors justify higher digestion temperature - retention time of silica at high temperature has to be shortened significantly /e.g.: to 10 minutes/. This can be realized in the so-called two-way digestion system, detailed later in this chapter.

Iron content of bauxites plays no significant role in the digestion process itself. Yet three facts must be pointed out in this field:

- red muds of the bauxites having their iron-oxide content present in form of goethite, have generally unfavourable settling and filtration characteristics. Settlers, washers and filter equipments have to be oversized and this results in excess investment expenditures costs.
- goethite generally has some Al_2O_3 content which builds into the crystal-lattice by isomorphic substitution /alumogoethite/; this can amount to 2 per cent of the total Al_2O_3 content.

- hematite shows favourable characteristics from the point of view of red mud settling and filtration, though it can also contain some Al_2O_3 built-in by isomorphic substitution which may range to 1 per cent.

In order to solve the above problems the digestion technology utilizing additives has been worked out. This is based on the fact that the addition of reactive CaO, certain Na-salts and/or catalysts /e.g.: hydrogranate compounds/ to the slurry digested at high temperature has several favourable effects:

a/ the major part of goethite is converted into hematite and, consequently, red mud settling conditions improve;

b/ Al_2O_3 built into the goethite by isomorphic substitution is released from the crystal-lattice and becomes soluble, thus increasing the amount of total soluble Al_2O_3 and decreasing hereby the specific bauxite and caustic consumption;

c/ CaO may partly substitute Na_2O in sodalite by giving a compound of $3CaO \cdot Al_2O_3 \cdot kSiO_2$-composition and thus can be saved;

d/ in case the additive is choosen properly /NaCl, Na_2SO_4/, its caustic content can partly substitute the Na_2O content of sodalite as well; this practically means that part of the more expensive caustic soda can be substituted by a cheaper sodium-salt.

The two-valent iron-oxide is an unwelcome contaminant of bauxites. Digesting such bauxites brings about a significant decline in red mud settling and in the sedimentation of the floating contamination of the clear zone of the settlers. Siderite, $FeCO_3$, is an essentially detrimental contaminant of bauxites, as it increases the soda content of the liquors, too.

Titanium content of bauxites /anatase, rutile or brookite/ in the form of TiO_2 is transformed into sodium-titanate, $2Na_2O \cdot TiO_2$, during digestion. In the course of red mud settling and washing the sodium-titanate undergoes hydrolysis and various sodium-hydrotitanates may form /e.g.: $Na_2Ti_6O_{13}$ etc./. Finally 1 kg of TiO_2 will bind 0.1 kg Na_2O or even less. On the other hand at higher temperatures and in the presence of lime titanate forms calcium-titanate /$CaTiO_3$/ and though the caustic consumption decreases the calcium-titanate inflicts a relatively hard deposit on the high temperature preheaters, which is difficult to remove /15/.

P_2O_5 is dissolved in the digesting liquor, and, it precipitates in the alumina-hydrate as Na_3PO_4, forming generally a double salt with the NaF or a triple salt with the NaF and Na_3VO_4, which can be removed by washing. In case the bauxite contains lime, or lime is added to it, P_2O_5 is precipitated in the form of calcium-phosphate /$Ca_3/PO_4/_2$/ and apatite $Ca_5/PO_4/_3X^-$, /X being mainly F/ and leaves the system with the red mud.

Major part of the V_2O_5 is dissolved in the course of digestion as sodium-vanadate. It is affected to a smaller extent than P_2O_5 by the presence of lime. V_2O_5 forms a triple salt with the P_2O_5 and the fluorine /F/ present, which crystallizes in form of octaeders.

If there is no P_2O_5 present, the separation of V_2O_5 is more complicated, as the solubility of the double salt formed with NaF is higher. In such cases V_2O_5 is separated from the spent liquor or from the strong liquor by cooling. Either form of the thus separated "V_2O_5-salt" is a by-product of high value as raw material of V-containing products.

The fluorine /F/ content of bauxites also reacts with the liquor and the NaF formed deposits as a hard layer on the walls of the evaporators, but it can be washed off by water. The fluorine-level of the cycle may be decreased by separation of the above mentioned double or triple salts, or - in case of much F and less P_2O_5 and V_2O_5 present in the solution - by separation of an independent "fluorine-salt":

The CO_2 content of bauxite is generally bound in the form of calcite or magnesite /dolomite/. During digestion the CO_2 forms carbonate soda /Na_2CO_3/, a contaminant of the plant liquors that is difficult to remove. In some cases the siderite content of bauxite is the source of CO_2.

The organic material content of bauxite is mainly dissolved during digestion and, though it gets partly degraded to oxalate and soda, both the residual organic matters and soda and oxalate are unwelcome contaminants; their role in the process and the way of their removal will be discussed later.

The gallium content /Ga/ of certain bauxites also dissolves during the digestion process. Gallium metal can be extracted from the strong liquor by electrolysis or other processes.

Heat Balance of the Digestion

Heat balance of the digestion is dealt with in more detial here, because the principles expounded can be used also with two other plant sections, i.e. flash cooling of the aluminate liquor and evaporation.

Bauxite and digestion liquor have to be heated up to the temperature of digestion in preheaters and digesters. For this purpose the heat content of previously heated up slurry is used in counter-current, reducing hereby the required steam consumption. By the multi-stage flashing of the hot slurry and the heating up of the cold slurry by means of vapours released during flashing, considerable heat recovery can be achieved.

Fig. 2.25 gives a schematic flow-sheet of digestion, where: T_i = temperature of input slurry

T_f = temperature of flashed slurry

T_r = temperature of recovery

T_d = temperature of digestion

S_h = heating steam

S_e = flashing vapour

C_h, C_c = condensate waters

Owing to given physical limitations the cold slurry /Tl/ can not be heated up to the temperature of digestion /Td/ by the heat content of the cooling hot slurry, but only to the so-called final temperature of recovery /Tr/. Further heating of the slurry from the temperature of recovery to that of digestion is carried out with live steam /indirectly or directly/.

Let us examinate the counter-current heat recovery in the i-t diagram /Fig. 2.26/. The change of heat content of the slurry cooling down is

$$\Delta i_s = G_s c_s \Delta T$$

where: G_s = mass of the slurry

c_s = specific heat of the slurry

ΔT = temperature difference /Td-Tf/

Let us take a quantity of slurry where $G_s c_s = 1$.

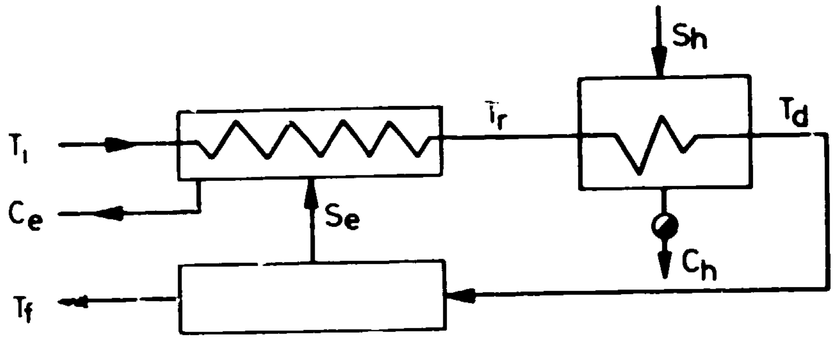


Fig. 2.25

SCHEMATIC FLOW-SHEET OF DIGESTION

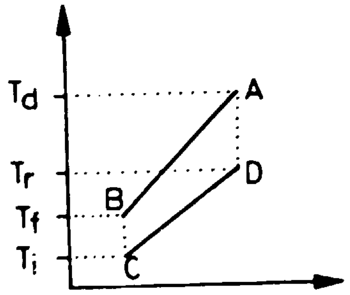


Fig. 2.26

FLOW-SHEET OF DIGESTION IN i-T DIAGRAM

If no heat were lost, the slope of the line $\overline{AB}$ would be 45°. In practice part of the heat is lost, this can be taken into account as an efficiency, η_s

$$\Delta i = \eta_s \cdot \Delta T$$

and the slope of the line $\overline{AB}$ will be greater than 45°.

The cold slurry is heated up from the initial temperature T_i /point C/ to the temperature of recovery T_r /D/ along the straight line $\overline{CD}$. In practice the slope of the straight line $\overline{CD}$ is always smaller than that of $\overline{AB}$ and smaller than 45°. Namely part of the Al_2O_3 is dissolved in the liquor; this endothermic reaction extracts heat from the slurry, and heat is lost, too. The ratio of the slopes of the two lines represents the total thermal efficiency of the recovery.

Special attention has to be drawn to the fact that the heat transferred from the warmer slurry is not available on the same temperature for the colder slurry. The temperatures of the two slurries deviate by a temperature gap from each other in the course of recovery: $\overline{BC}$ and $\overline{AD}$ resp.

This temperature gap is composed of 3 factors:

1. dt_b is the temperature gap resulting from the boiling point rise. Namely the temperature of the flash steam is lower from the outset than that of the slurry, the difference being the boiling point rise which, according to experience, can be considered as constant in the course of flashing.
2. dt_f is the temperature gap resulting from throttling of the flashing vapour and may be reduced by increasing the number of stages.
3. dt_h is the temperature gap due to restricted heating surface area and may be reduced by increasing the latter.

Let us first investigate in more detail the process taking place in the heat-exchangers /Fig. 2.27/.

Steam condensing at temperature t transfers its heat content to the input slurry having temperature T_o and heats it up to the temperature T_1. The temperature difference of $t - T_1$ corresponds to the temperature gap dt_h.
Based on the known relations:

$$KF = G_s \cdot c_s \cdot \ln \frac{t - T_o}{t - T_1} = G_s \cdot c_s \cdot \ln \Delta tm$$

where: K is the heat transfer coefficient, F is the heating surface area of the preheater, $t - T_1$ is the temperature gap due to the limited heating surface areas and $\ln \Delta tm$ is the average logarithmic temperature difference in the course of heating up.

Let us consider the heat balance of the first flashing stage /Fig. 2.28/.

Heat-Exchanger

$$G_s c_s /T_R - T_1/ + q_1 = g_1 \, /i_1'' - i_1'/ = g_1 r_1 ,$$

where: g_1 is the amount of vapour released in the first flash tank, i_1'' the specific heat content of steam, i_1' that of the condensate, and r_1 is the latent heat of the vapour.

Expressing the heat loss g_1 in terms of efficiency, it would read:

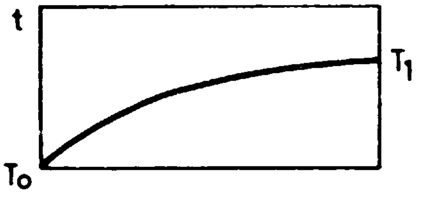


Fig. 2.27

HEAT TRANSFER IN PREHEATERS

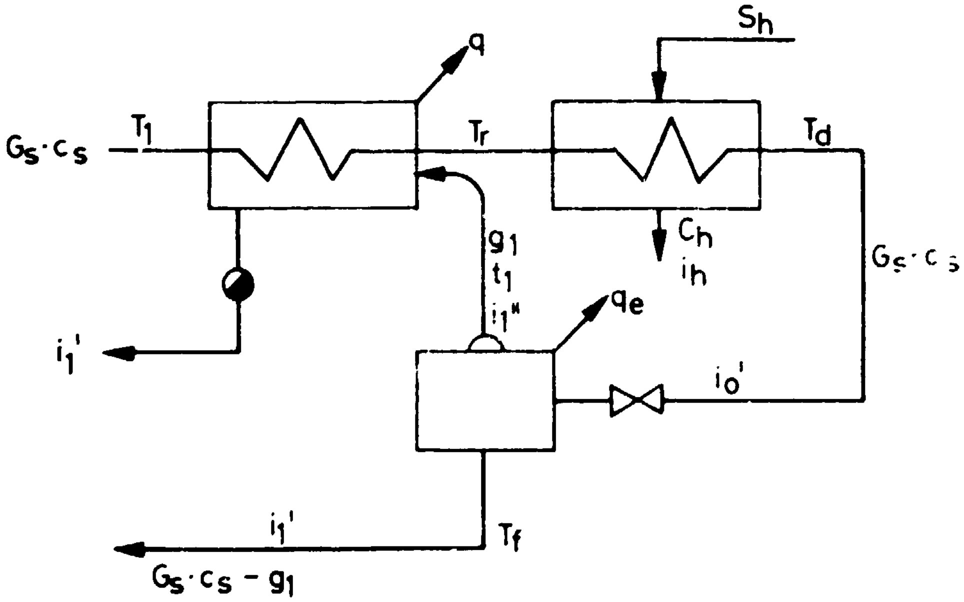


Fig. 2.28

FLOW-SHEET OF FLASHING STAGE

$$G_s c_s \cdot \Delta T_1 = \eta_1 g_1 r_1$$

Flash Tank

$$G_s c_s \cdot i'_0 = g_1 \cdot i''_1 + /G_s c_s - g_1/\ i'_1 + q_e$$

$$G_s c_s\ /i'_0 - i'_1/ = G_s c_s\, \Delta i_1 = g_1\ /i''_1 - i'_1/ + q_e = g_1 r_1 + q_e$$

Expressing the heat loss g_e in terms of efficiency, it would read:

$$G_s c_s \cdot \Delta i_1 = \eta_e g_1 r_1$$

Reducing the two equations and summarizing the efficiency symbols in a single factor, η we shall obtain:

$$\Delta T_1 = \eta i_1$$

A more detailed examination of the individual flashing stages can be made on the basis of Fig. 2.29.

The starting temperature that can be considered for heat-exchange in the course of cooling-down of the hot slurry is $T_d - dt_b$ /point A'/ i.e. the digestion temperature reduced by the boiling point rise. As the warming up slurry enables cool-

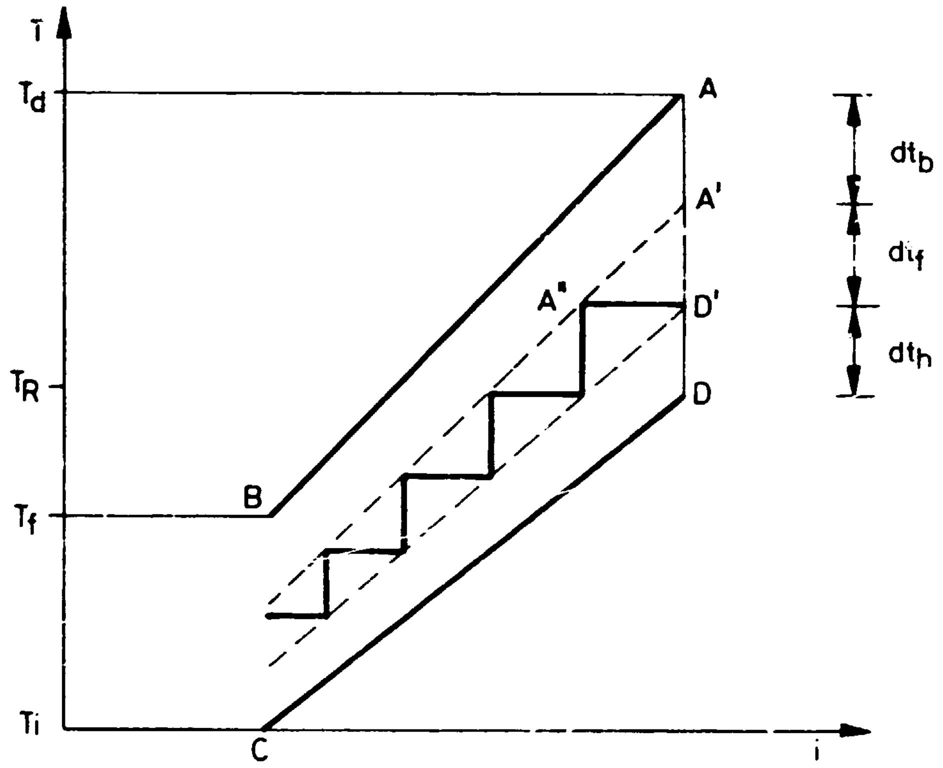


Fig. 2.29

DETAILED DIAGRAM OF THE HEAT RECOVERY

ing down of the flashing slurry only to the point D', the difference $\overline{DD'}$ is maintained by the temperature gap dt_h. This difference could only be reduced by increasing the surface area. Summarizing the above the process is the following:

The slurry can be considered as flashing along the line A'D' /i = constant/, the amount of flashed vapour is g_1, the utilizable condensing heat of which in the heat-exchanger would be D'A'' i.e. $\Delta i_1 = g_1 r_1$.

Heat transfer is terminated at point A" and the slurry enters the subsequent flashing stage where the preceding procedure is repeated.

It can be clearly seen from the figure that the amounts of heat transferred to the warming up slurry are on and on diminishing, even if taking identic preheater surface areas and heat transfer coefficients into consideration, and the cold slurry is heated up to temperature T_r only.

From T_r to T_d the slurry has to be heated up by high-pressure steam. Steam requirement of this operation is:

$$S_h = G_s c_s \cdot \frac{T_d - T_r}{i_h'' - i_h'}$$

where: i_h'', and i_h' resp. represent the enthalpy of the high-pressure steam and its condensate.

Though conditions are more complicated in the plant practice, every factor may be calculated on the basis of known data. Calculations are made by computer and ready programs are available.

It should be noted that the heat of condensate of the vapours flashed from the slurry are used in the recovery system similarly as the heat of the slurry. The two systems had already been combined in the above calculation. The operative solution is the successive flashing of the condensate waters of the flashed vapour into the steam space of the preheaters of the corresponding stage.

The temperature of recovery can raised - thus reducing the high-pressure steam requirement - by raising the temperature of the cold slurry by means of low-pressure steam. Thus high-pressure steam can be replaced by less expensive low-pressure steam.

Instead of the conventional preheaters, digesters may also be used to preheate the slurry. The advantage is less scale formation, easier cleaning. However, the heat transfer coefficient of the digesters is lower, than that of the preheaters, as the entering slurry is mixed with the hotter slurry in the digester, reducing thereby the possibility of favourable heat transfer. The investment cost of the digesters is higher than that of the preheaters and in general, the differences are not counterbalanced by the lower cleaning costs.

Machinery of Digestion

For the industrial realization of digestion the system described in the previous chapter /"Heat balance of digestion"/ is built up in commercial scale. The slurry is heated up in preheaters and/or digesters until it reaches the temperature of recovery and than it is heated further in digesters to the digestion temperature. The digested slurry cools down, while it emits flash steam in the flash tanks and transfers its heat to the cold slurry.

The general scheme of the above system is shown in Fig. 2.30.

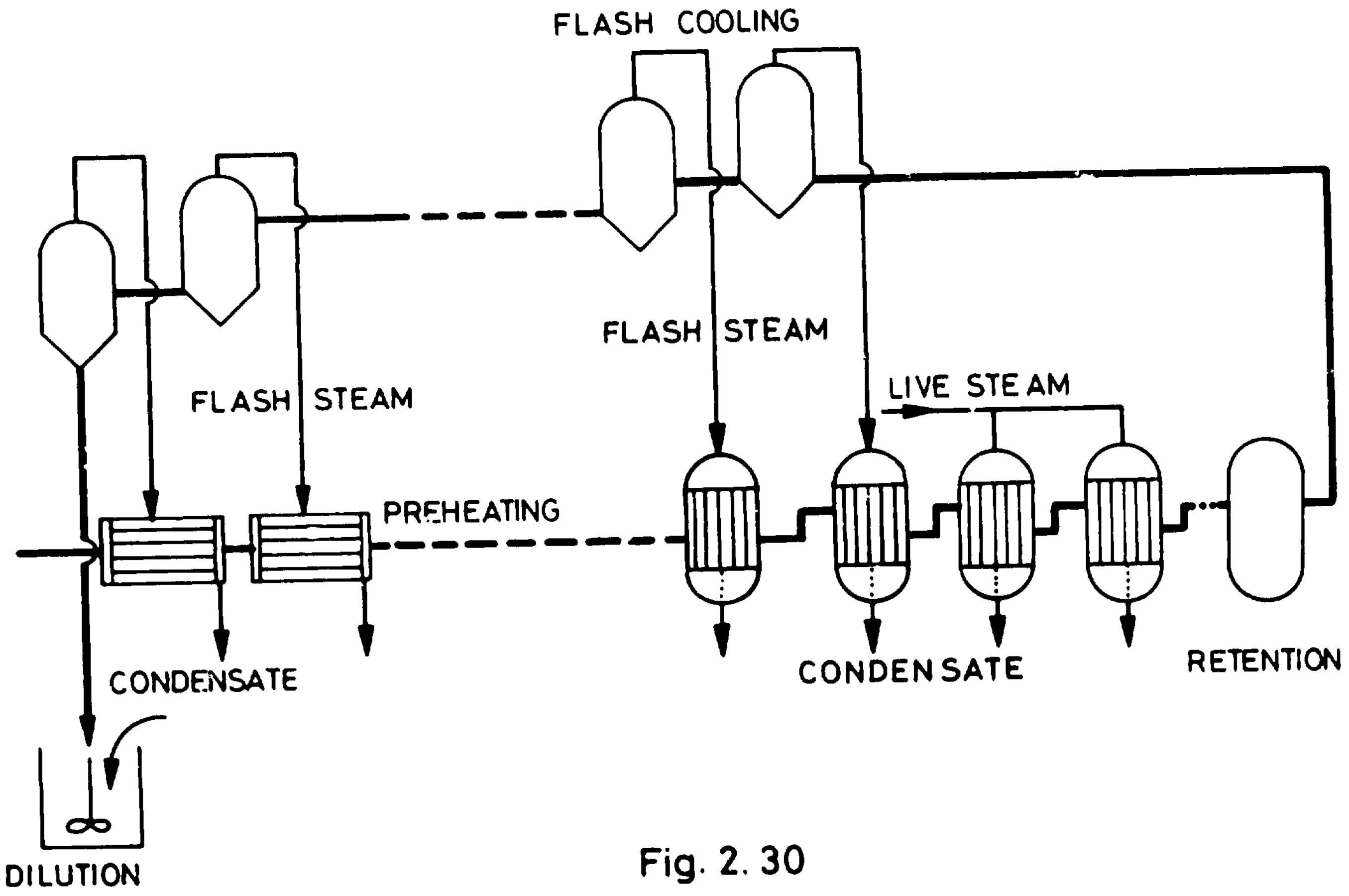


Fig. 2. 30

PREHEATER-DIGESTER SYSTEM

In up-to-date plants three major versions of digestion systems are commonly used:

1. preheater-digester system
2. two-way system
3. tube digestion

1. Preheater-Digester System

In this system the mill slurry is completed with the remaining part of the digestion liquor before or after the desilication and the total amount of slurry is delivered by centrifugal-, piston- or diaphragm pumps to the digestion line consisting of preheaters and digesters.

Feed Pump

Centrifugal pumps are generally used only in case of low digestion temperature because, when transporting slurry of high solids concentration, their performance is low and the control of quantity is inadequate.

Piston pumps are adapted from the oil-industry. There are two problems concerning their application:

- comparatively low performance
- intensive abrasion during operation

The performance limit of the piston pumps is about 200 m^3/h and this requires the installation of 2-3 units for the digester lines generally used at present. As a consequence of abrasion, the maintenance cost of the pumps is high and their operation time is low. The average cycle time between two maintenance periods is 70-250 hours, however, it can be shorter in case of diasporic bauxites.

A significant lenghtening of the cycle time of piston pumps was achieved by the flushing liquid system: Fig. 2.21.

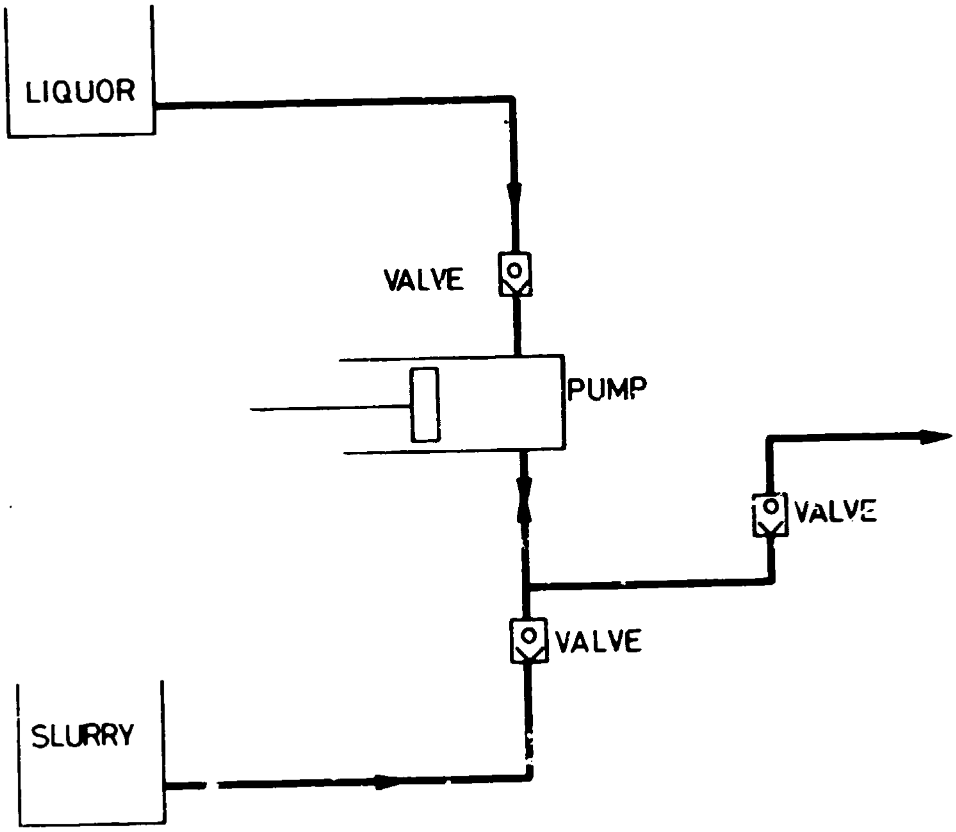


Fig. 2. 31

FLUSHING LIQUID PUMPING SYSTEM

The piston first sucks the liquor in, the slurry-side suction valve opens only later, thus no slurry can enter the operating cylinders. In the pressure-step the liquor in the cylinder pushes the slurry forward into the delivery pipe. The total amount of the flush liquor and slurry is in every case more than that of the original slurry.

Because of the short duration and high maintenance expenses, European producers switched over to the usage of diaphragm pumps /Emmerich, Marep-Pechiney/. As it can be seen from Fig. 2.32. the slurry does not contact the cylinder, the transmitting medium is oil. The operation time of diaphragm pumps ranges between 1000-3000 hours.

Preheaters

The preheaters are generally of multipass tube-bundle type. The diameter of the tubes is 38 to 57 mm, the total heating surface area is 200 to 500 m^2. The advantage of the preheaters is that the investment cost of 1 m^2 heat transfer area is essentially less than in case of digesters.

On the other hand, their disadvantage is that they are more easily clogged than the digesters by mechanical contaminants entering with the bauxite /pieces of wood, wire, smaller fractures of iron etc./. Preheaters are designed for 1.5 to 2 m/sec flow-rate of the slurry, diminishing thus the danger of scaling.

Slurry is generally heated up to 150 to 180 $^{\circ}C$ in the preheaters, as at a higher temperature hard scales /first of all calcium-titanates/ may form. The heat transfer coefficient of the preheaters is 2000 to 4000 W/m^2K; as it decreases in time and the thermal capacity of the line declines, additional heating with low-pressure steam and, finally, cleaning of the preheaters is necessary. The cycle-time of the

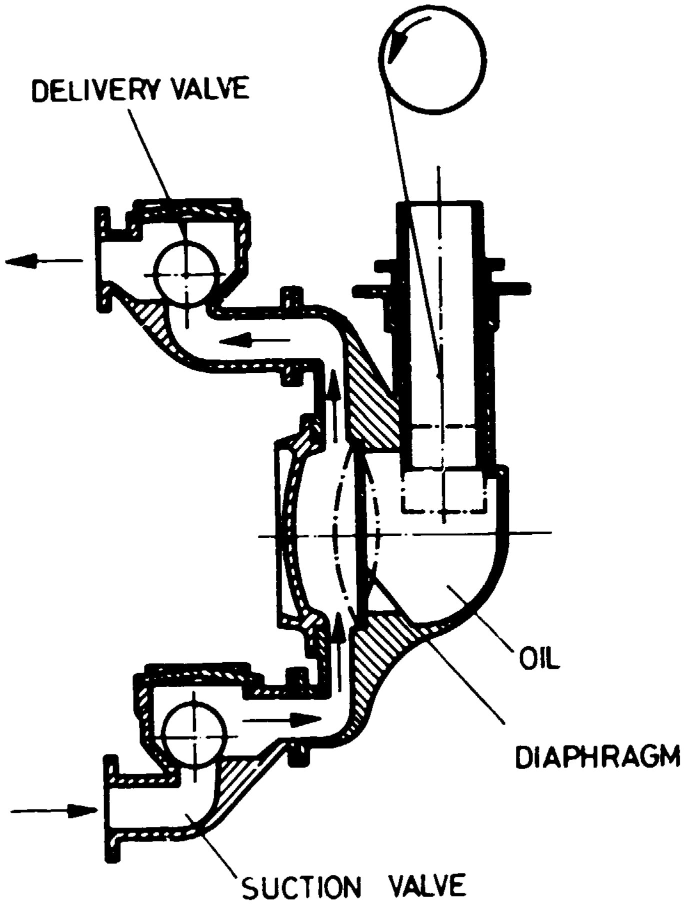


Fig. 2.32

EMMERICH DIAPHRAGM PUMP

preheaters is 3 to 6 months. Cleaning is carried out either mechanically by high-pressure /VOMA/ pumps, or by acid treatment. Spare-preheaters are generally provided to operate during cleaning periods.

Digesters

Digesters are generally applied in the last stage of the digestion series, where heating is performed directly or indirectly by means of high-pressure steam. There are, however, systems /La Barasse, France; Ajka, Hungary/ utilizing digesters instead of the preheaters, too.

The advantage of the digesters lies in the fact that the formation of scales may be minimized in them, especially in case, if proper care is taken to maintain an intensive flow rate of slurry /3 to 4 m/sec/ near the heat transfer tubes by stirring.

The heating surface of digesters heated by flash steams is a pipe, a register or a spiral tube, and of those heated indirectly by high-pressure steam is principally a spiral tube. The cycle time of digesters may exceed even 1 year's time, their cleaning is generally carried out manually.

Depending on technology and capacity of the plant the volume of digesters can vary between 50 and 600 m^3.

Flash Tanks

The dimensions of the flash tanks are determined by the amount of steam released in the different stages. The determination of the dimensions is based on the admissible volumetric and surface loads.

The basis of dimensioning

for volumetric load: $B = X \,.\, P^{-n} \,.\, k^{-m}$

for surface load: $T = Y \,.\, P^{-n} \,.\, k^{-m}$

where: P = pressure in the flash tank
k = density of the slurry /Bé°/
$X = 2100$
$Y = 8000$
value of the exponents:
$n = 0.7$
$m = 0.6$

The level of the flash tank is generally controlled by isotopic detection. The control valves may be substituted by throttling orifices, which car be satisfactorily operated within the ranges of certain capacity limits. Parallelly with the depositing of the line an additional heating with low-pressure steam must be applied.

As it was mentioned already provision should be made in the digestion for collecting the condensate water and flashing it generally to the subsequent stage; a certain number of units may also be coupled together. The alkaline condensate originating from the flash steams is utilized as wash water in the red mud washing.

The pure condensate of digestion is flashed into the low-pressure steam pipeline /the resulting savings are 0.6 to 0.7 t of steam per ton of alumina/, later it is returned to the power plant. Its purity is checked on the basis of conductivity.

2. Two-Way Digestion

The two-way digestion is preferably used in several plants. In this system the mill slurry is not mixed with the remaining part of the digestion liquor, the latter is preheated separately in the preheaters by the flash steam of the total amount of slurry. The mill slurry is pumped into the digesters - directly or after a one-two staged preheating process - where it contacts the preheated liquor; the slurry is heated to the digestion temperature usually by direct steam. This system has several advantages:

As only the liquor passes through the preheaters it can be fed by series-coupled centrifugal pumps. In practice one centrifugal pump is installed after every third preheater. The size of the expensive piston- and diaphragm pumps, delivering the mill slurry only, can be reduced considerably. Preheaters are scaled only after a longer time and their cleaning can be carried out by simple acid handling /H_2SO_4, HCl etc. + inhibitor/.

A further advantage may arise from the fact that the bauxite remains in the digester for a very short period /e.g. for 10 minutes/, and thus, part of the reactive silica content does not react with the liquor. In case of certain bauxites this decreases the caustic soda consumption.

The two-way digestion, however, can not be considered as satisfactory as regards the heat economy, since total steam consumption is higher than in case of the uniflow process.

The centrifugal pumps of this system delivering the liquor are usually operated by steam, the exhaust steam is used for preheating purposes or it is flashed into the low-pressure system.

By direct steam the slurry can be heated up to the temperature corresponding to the saturated steam-pressure or /as a consequence of boiling point rise/ even above that, without any temperature gap. This means that in case of gibbsitic bauxites energy requirement of the system can be provided by the back-pressure steam of turbines, too, giving an extra production of electric power. Of course, the dilution of the slurry must be reckoned with.

Tube Digestion

The up-to-date mechanical digestion system is the tube digestion process. It is proved that increasing the digestion temperature by 10 °C the retention time can be decreased to its half, while the output remains the same. Therefore, at around 280 to 300 °C, digestion requires only a few minutes.

The heating surface is formed by tubes; the amount of steel required for 1 m^2 heating surface area weighs 120 to 140 kg, that is about half the weight of steel required in case of digesters.

Tube digestion became widespread first of all in West Germany; in Stade the whole plant operates on tube digestion, whereas in other plants the old digester lines operate parallelly with the tube digester.

In the West German /VAW/ system a duplex-tube is used as heat-exchanger. The heat content of the slurry is recuperated to 210 °C; the additional heating up to a temperature above 250 °C is performed by salt solution /Fig. 2.33/.

In Hungary there is an experimental tube-digester unit operating at the Magyaróvár Alumina Plant. The unit is equipped with multi-tube one-way preheaters - this gives the opportunity to improve the ratio of tube-diameter to

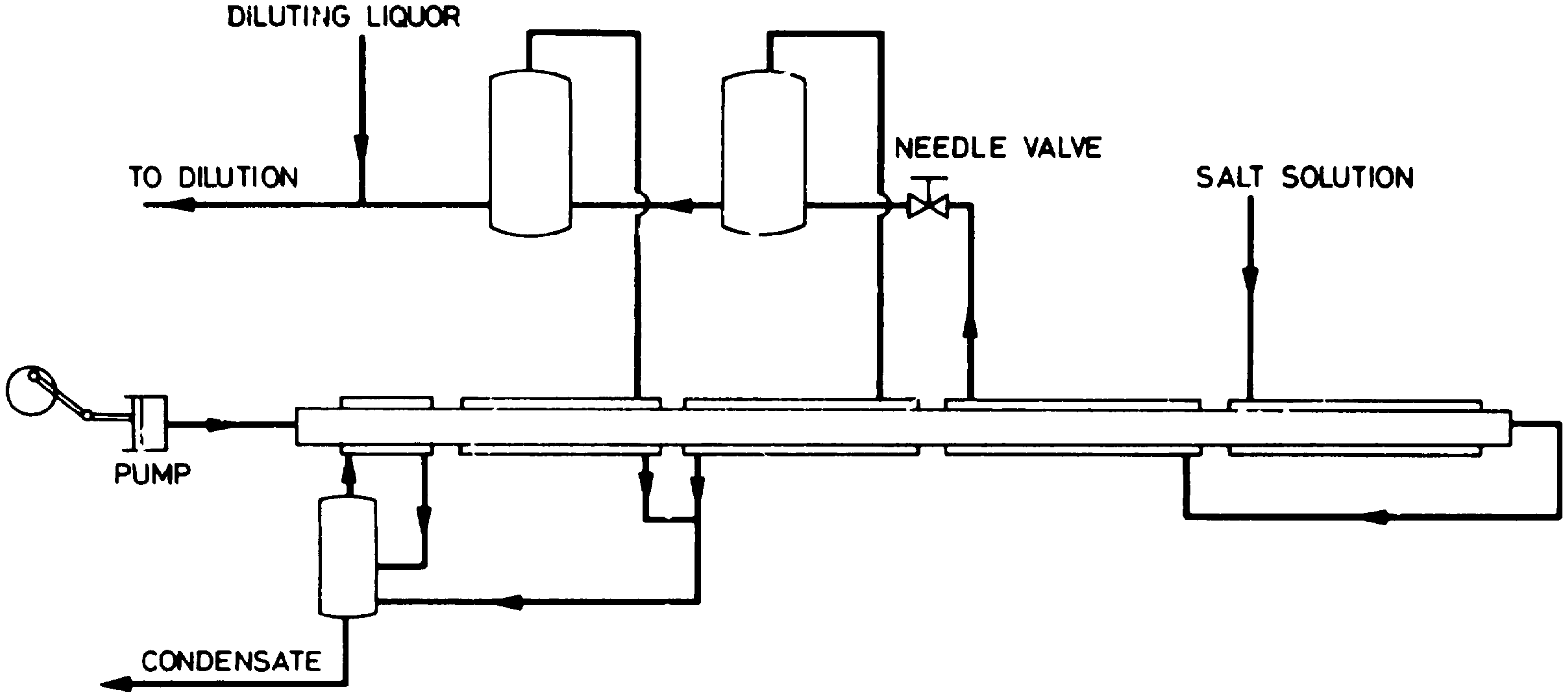


Fig. 2. 33

VAW TUBE DIGESTION

heating surface area. Digestion temperature is 260 to 265 °C. The average heat transfer coefficient during one month's cycle was 1850 W/m^2K. Deposits formed in the temperature interval up to 250 °C can be removed relatively quickly and with a satisfactory efficiency, whereas the removal of deposits formed above 250 °C has not been solved yet properly. On the basis of plant experiences a 120 m^3/h capacity digester unit is being designed /Fig. 2.34/.

The tube-digester is fed by flush liquor pumps with cycle time of about 1000 operating hours.

Significant calorific advantages of the tube-digestion process are the essentially higher heat transfer coefficient and the more favourable recovery and calorific efficiency as compared to the preheater-digester systems.

RED MUD THICKENING, WASHING AND FILTRATION TECHNOLOGY AND EQUIPMENT

The department of red mud settling and washing performs the work of separating the solid red mud residue of the digestion from the aluminate liquor and of washing out the Al_2O_3 and NaOH content of the red mud slurry.

Because of space utilization consideration multi-chamber units were used formerly for red mud settling and washing: the flow conditions in them, however, turned out to be unfavourable and the amount of red mud settled per unit surface area was significantly less than in a single chamber equipment. As a consequence single chamber settlers and washers with great diameter are predominantly in use at present.

Grain-size distribution of red mud suspensions is generally inhomogeneous and the grains are embedded in a solv-

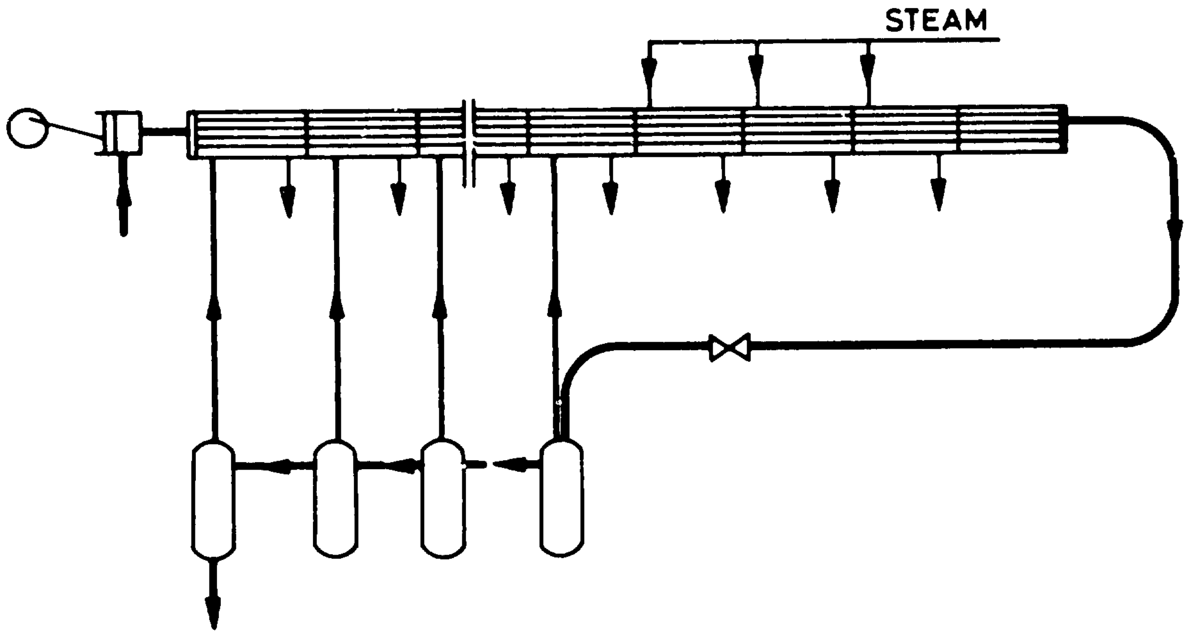


Fig. 2. 34

HUNGARIAN TUBE DIGESTION SYSTEM

ate wrapper. Due to the pressure originating from the upper mud layers, the volume of the latter may vary as a function of the depth; the mud is compressible. Its compressibility is also depending on the type of bauxite, the digestion technology, the settling accelerator additives being used and on the age of mud. Basic design parameters are provided by batch settling experiments.

Theory of Settling

The instantaneous settling velocity of solid grains in the liquor is determined by the equilibrium of gravity and friction forces. Settling velocity can only be calculated exactly in case of laminar motion of a single ball-shaped grain, using Stokes' rule. The size of the balls is a significant factor:

$$U_s = \frac{d^2 /\rho_s - \rho_f/}{18\,\eta}\, g\,, \qquad /1/$$

where: U_s represents the settling velocity of the solid grain; "d" its diameter; ρ_s and ρ_f the density of the grain and of the settling medium resp.; η the viscosity of the settling medium and g the gravity acceleration.

Settling tests of polydisperse suspensions revealed, however, that Stokes' rule is observed only in low solids concentration. In case of higher solids concentration, moreover, in case of adding settling aids, collective settling of different size grains is experienced even in polydisperse suspensions.

Several semi-empiric formulas were elaborated on the relationship of the settling velocity and solids concentration, which are relatively accurate in a narrow interval even if considering compressible suspensions. These formulas can be checked by static settling tests performed in a small-size settling tube. The most widely accepted among these is the Richardson-Zaki formula /6/:

$$U_c = U_{sH} /1 - \alpha c/^n$$

where: U_{sH} is the Stokes-velocity of the hydrated /solvated/ particle; α the volumetric correction factor due to the solvation; c is the volumetric correction factor of the solid material; n is a factor determined empirically, depending on the Reynolds-number; in case of red mud $n \simeq 4.7$.

Dimensioning of Thickeners

Several studies had been worked out aiming at determining plant conditions by utilizing the results of the settling tests carried out after laboratory digestion. In these tests the slurry diluted to the required concentration - after addition of the proper settling aid - was mixed and poured into a 30-50 cm high cylinder and the time dependence of clear zone formation was determined. The straight section of the settling diagram plotted vs. time was taken as basis of the settling rate, and the following simple relationship was used:

$$S = \frac{M}{h}$$

where: S means the required surface area of the settler /m^2/, M the liquor overflow per hour of the settler /m^3/h/ and h the clear zone formed in an hour above the mud in the settling tube /m/h/.

This relationship, however, is not of general validity, it does not give the solids concentration of the underflow, and, especially in case of voluminous muds with unfavourable settling characteristics, provides unreal results. The correct dimensioning of settlers is very important, as:

- the total investment cost of this plant section, especially in case of muds with unfavourable settling characteristics, may exceed 5 per cent of total investment of the alumina plant;
- improper operation of settlers may deteriorate the quality of alumina;
- operating trouble of settlers and washers may considerably increase the Al_2O_3 and NaOH losses at the end of the washing line;
- the muddy overflow may bring about an autoprecipitating process, the precipitated gibbsite has poor settling characteristics and thus it may cause production breakdown.

A method for the safe dimensioning of settlers and washers developed at ALUTERV-FKI will be described in Volume 7.

Principle of Counter-Current Washing

The dense red mud slurry from the underflow of the settler is diluted by the overflow of the second washer and then it is fed into the first washer. The overflow of the first washer is the "diluting liquor", used for diluting the slurry leaving the digester to the required settling /and precipitation/ concentration before feeding it into the settler.

The process continues on the same principle; slurry from the underflow of the first washer is diluted by the overflow of the third washer and the mixture enters the second washer. The underflow of the second washer is diluted by the overflow of the fourth one, it enters the third washer and so on.

Denoting the overflow of an individual washer by Tn, its underflow by Kn and the concentration by Cn, the following equations can be constructed:

Balance of liquor $K_{n-1} + T_{n+1} = T_n + K_n$

Balance of dissolved material $/Na_2O$ or $Al_2O_3/$ $K_{n-1} \cdot C_{n-1} + T_{n+1} \cdot C_{n+1} = /T_n + K_n/ \cdot C_n$

A numerical example is shown in Fig. 2.35: 9 m^3 digested liquor of 234 g/l caustic soda concentration is discharged from the digester per each ton of mud and the task is to have less than 6 kg/t dissolved loss in the underflow of the last washer, while producing 14 m^3 aluminate liquor of 150 g/l concentration. The problem was chosen so that the concentrations would correspond to Na_2O in the European Bayer process, and to Na_2CO_3 in case of the American one.

The amount of liquor discharged through the underflows is uniformly 5 m^3/t, presuming a mud of poor compression characteristics.

It can be seen that six washing stages are necessary in order to achieve a final loss of 6 kg/t. In case the mud gets compressed more intensively and 3 m^3 liquor is discharged in the underflow per each ton of mud, the task can also be solved by four washing stages. This fact illustrates the importance of compression.

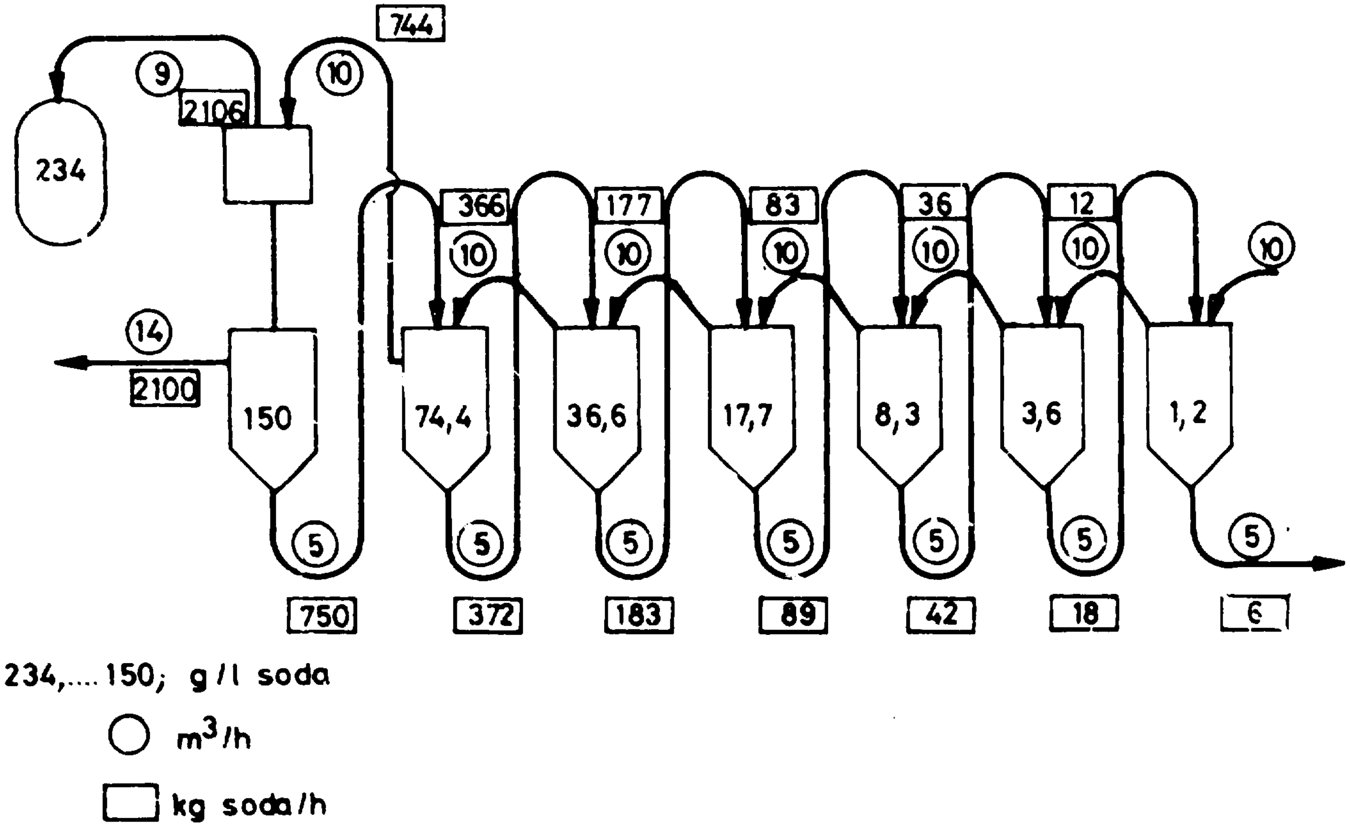


Fig. 2.35

EXAMPLE OF COUNTER-CURRENT WASHING

As it was mentioned previously, the compression may be intensified in case proper care is taken not to leave undigested Al_2O_3 in the red mud. Satisfactory compression may also be promoted by digestion with additives, by keeping the hydrolysis at a minimum value, by selecting adequate settling aids and by proper dimensioning of the settlers and washers.

The above numerical example refers to ideal conditions. The losses arising from the washing are, in fact, always higher than that given from the above simplified calculations. One reason for this lies in the fact that the liquor discharged through the underflow has always a higher soda concentration, than that of the overflow.

One possible explanation for this fact is that the red mud adsorbs part of the soda, which gets partly released in the subsequent stage. E.g. the adsorption of a given red mud had the following relation with the actual concentration:

$$a = 0.43 \frac{c}{1 + 0.25\ c}$$

where: "a" means the adsorbed Na_2O in terms of percentage of mud and "c" the Na_2O_c concentration of the solution in g/l.

Though the above formula is by no means of general validity, it expresses the basic principle that the Na_2O concentration of the individual members of a washing line is, in all cases, higher than that calculated from the material balance.

Instead of assuming adsorption, Scandrett /52 / introduces an E-factor, characterizing the imperfect mixing:

$$E = \frac{C_{n-1} - C_n}{C_{n-1} - C_k}$$

where: C_k represents the actual underflow concentration. The value of E varies between 0.7 and 0.9. The values calculated by the adsorption-formula gives also a result of 0.7–0.9 for E. Consequently, any of the methods can be used as a first approach for designing.

The other reason of deviating from the idealized scheme may be the autoprecipitation itself. On the first hand the precipitated gibbsite increases the amount of mud i.e. the higher washing stages shall be calculated for a higher red mud quantity. On the other hand the gibbsite decreases the compression of the red mud and thus the amount of liquor discharged through the underflow will increase. Both cases result in increasing caustic soda loss.

An accepted method for inhibiting the autoprecipitation is to charge spent liquor to the dilution or to the underflow of the settler increasing by that the molar ratio of the whole counter-current washing system.

An interesting characteristic of the counter-current washing series is that different liquors can be fed into it, without causing any significant increase in the soda loss.

A good illustration for this case is the feeding of spent liquor into the settler. Diluted causticized liquor may also be fed to one of the washers: the overflow of a certain washing stage /second or third/ may be causticized in order to release more considerable amount of Na_2O from Na_2CO_3 and feed it back to the washing line. In case the introduced liquor is fed into a washer with similar concentration the increase in the soda loss at the end of the line is minimal.

The intermediate causticization mentioned earlier should be performed as far as possible with a liquor of low soda concentration /10-40 g/l/, using slaked lime and a temperature above 90 °C.

The method is applied by several alumina plants on operating scale and it is sometimes supplemented by salt separation. The efficiency of lime /amount of active CaO producing causticized soda/ can exceed even 90 per cent /89/.

In the course of design the material balance of the counter-current washing line is calculated by computers with special regard to the technological characteristics of bauxite and red mud determined by laboratory analysis and by the consideration of all the above correction factors.

Filtration of Red Mud

Filtration for separating the red mud from the aluminate liquor is becoming increasingly widespread, simultaneously with the modernization of the filters.

In case of red muds with favourable filtration characteristics, the digester slurry may be filtered directly, however, as the viscosity of the digested slurry is relatively high and its solids content low, this method has not become common in practice.

The number of stages after which filtration is introduced will be determined by experiments and economic calculations. Generally, filtration can supplement economically 3 to 4 washing stages depending on the settling and filtration characteristics of the red mud. These two characteristics are generally in correlation: in case of poorly settling muds the filtration performance will also be low /40-50 kg/m^2h/, whereas with muds of favourable settling characteristics a filtration performance of 200 kg/m^2h can be achieved. The filtration conditions can generally be improved by adding lime or other additives to the bauxite.

An important advantage of filtration is that it closes the washing system and no unfiltered slurry can be delivered to the red mud pond. This prevents the rising of soda and alumina losses to considerably high values especially in times of operating troubles.

The filtered mud contains 40 to 50 per cent of adhered moisture: it is generally pumped to the red mud pond after being repulped by water /to around 200 g/l solids content/. The soda and alumina content is leached out by the water of the pond and can be recharged into the washing line.

The red mud is not always washed on the filters themselves, as relatively small amounts of water pass through the filtering medium. Repulping of red mud by water and its repeated filtration can be advantageous depending on the economic conditions.

It should be noted that part of the extra-fine-grain red mud passes through the filter cloth and returning, it loads the washing line and causes hydrolysis losses.

Equipment of Red Mud Settling, Washing and Filtration

Instead of the multi-chamber settlers generally used previously - requiring less space but having a low specific performance - predominantly single-chamber conical or flat bottomed /Fig. 2.36/ settlers and washers are used at present with central or peripherical drive and with central or side discharge. The diameter of the settlers is commonly between

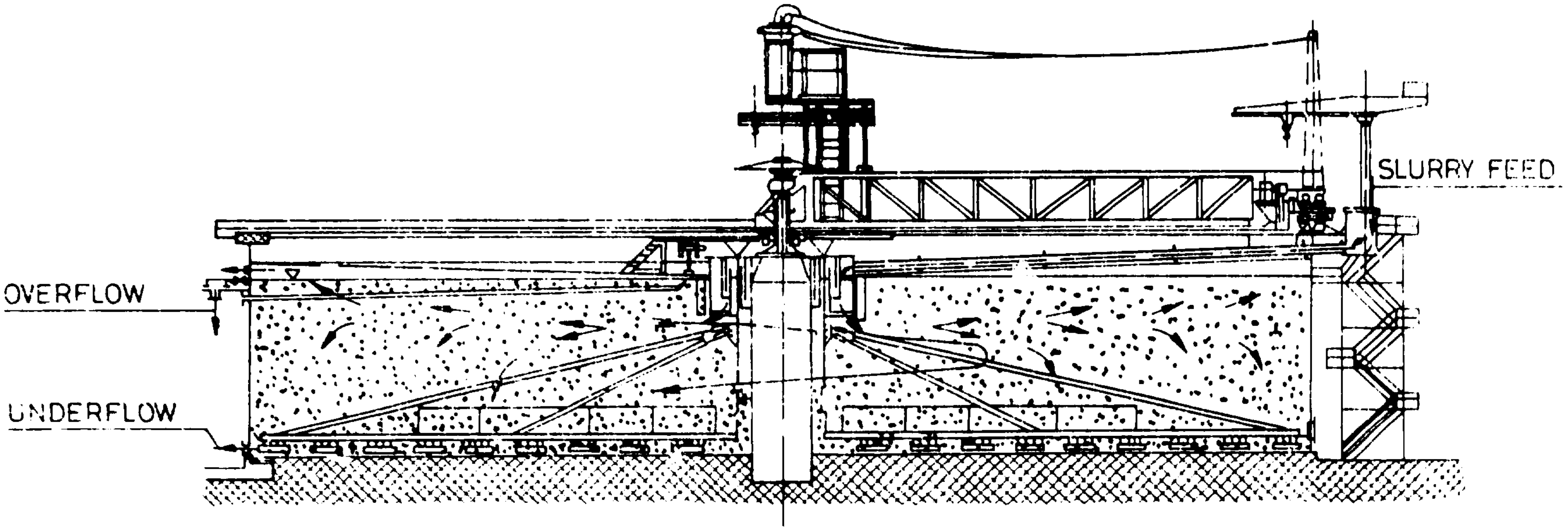


Fig. 2. 36

RED MUD SETTLER

30 to [illegible] m, though there are settlers of 42 m diameter in use, too. The height of the chambers ranges from 3 to 6 meters.

The disadvantage of settlers with central discharge, cone bottom and central drive lies in the fact that a special foundation is required to ensure the easy accesibility; their specific performance is on the other hand higher and they can be equipped with cable-hauled rake arms. They provide automatic torque relief; the hinged arms are lifted when deposit is formed at the bottom. Rigid agitators applied in settlers with flat bottom and side discharge may get distorted, or even broken if clogging occurs, therefore, they are normally provided with an automatic lift-out device, too.

The advantage of settlers with flat bottom and side discharge is, however, that their investment cost is low and they require a more simple foundation. On the other hand, by directing the mud outwards to the peripheries, the thickening conditions for the red mud are worse than in case of settlers with central discharge.

In some plants Kelly filters are applied for red mud filtration. In the Magyaróvár Alumina Plant Dorr-Oliver type roll-discharge drum filters of 50 m^2 surface area are in operation. The thin mud layer forming on the surface of these filters is removed by a separate cylinder and then it is scraped off by blades, thus renewing the filter surface /Fig. 2.37/. These filters are manufactured in Hungary, on the basis of the Dorr-Oliver licence.

Causticization of Red Mud

In plants where the price of caustic soda is high and that of the lime is low /e.g. if the plant burns lime from a nearby situated limestone deposit/, red mud causticization can be advantageous. This is performed by adding lime slurry or burnt

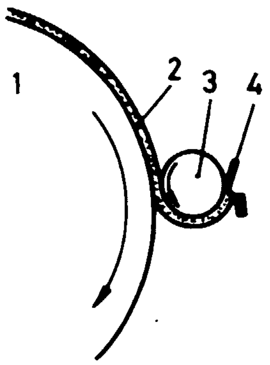


Fig. 2.37

ROLL DISCHARGE OF RED MUD CAKE

1. Filter drum, 2. Cake, 3. Discharge roll, 4. Hair-pin scraper

lime at the highest possible temperature to the underflow of the last washer slurry having low soda concentration. The lime release part of the caustic soda from sodium-aluminium-silicate to form calcium-aluminium-silicate. In order to release 1 kg of Na_2O, 3 to 4 kg of lime are charged to the mud. The efficiency of causticizing can be as high as 30 to 50 per cent. Efficiency can be further improved by a higher retention time. A practical formula of the efficiency is given in the following:

$$\eta = \frac{1.5 \cdot T \cdot /1-e^{-0.534t}/}{/L + 2.5S/ \cdot /70 + 3C/} \cdot 100$$

where: η = efficiency, per cent;
L = lime charged to the mud, in terms of mud percentage /available CaO content min. 72 per cent/;
T = temperature, °C;
t = time, hours;
S = SiO_2 content of the mud, per cent;
C = Na_2O content of the original solution, g/l.

In case of causticizing with 10 per cent of lime, at 90 °C temperature a mud having 6 per cent of SiO_2 in a 10 g/l Na_2O solution, an efficiency of 48 per cent can be expected in 4 hours time.

In the course of causticization, the solution becomes more concentrated and, when recharged to the washing line after filtration, it increases the caustic soda concentration of the washing line. The best way, therefore, is to causticize after 5 to 6 washing stages.

It must also be taken into account, however, that the lime would bind a certain part of the Al_2O_3 content of the solution entering the causticization, thus causing alumina losses and the segregated calcium-aluminate even deteriorates the filtration conditions of the red mud. In order to reduce these unfavourable effects, the time of causticization should not exceed 4 to 5 hours.

Red Mud Disposal

Red mud slurry leaving the last washing stage, or filtered red mud repulped with water is pumped to a red mud pond. Dams for the red mud disposal are made of local material /earth, fly ash, etc./. Red mud is stored normally up to a 10 m layer thickness. Water is recycled from the clear upper zone of the pond to the alumina plant and is introduced into the last washer.

In order to avoid soil contamination the bottom of the red mud lakes has to be sealed. Sealing can be done with plastic foil or with a 0.5 to 0.7 m thick clay layer. Drainage can be used as well to collect water before entering the soil: the costs of investment of this system are very high but the territory may be recultivated.

In the system Giulini - KHD red mud is filtered by roll-discharge filters and, after addition of chemicals, it is pumped without repulping by diaphragm pumps to the disposal. Red mud solidifies in this case and it can be piled up to 20 to 30 m height. After certain time the territory may even be recultivated.

As sea water is neutralizing the soda content of red mud, in cases where deep valleys are available in the bottom of the sea some of the factories pump their red mud into the sea by pipeline or discharge it from ships into these valleys.

PRECIPITATION TECHNOLOGY AND EQUIPMENT

Theory of Precipitation

The basic principles of precipitation were already recorded in the first Bayer-patent of 1887, in which he stated that the sodium-aluminate solution commences to decompose if previously precipitated aluminium-oxide-hydrate is added to the solution kept in motion. The above basic principles are still valid today, though despite almost 100 years of research work the theoretical establishment of the precipitation mechanism is not yet completed.

In practice the sodium-aluminate liquor of the settler overflow filtered in order to remove its floating contaminants, then cooled to increase its supersaturation is seeded and agitated in large tanks.

Two tasks must be solved in the course of precipitation: the first one is to achieve the highest amount of precipitated Al_2O_3 out of 1 m^3 solution, i.e. to achieve the highest possible efficiency, thus ensuring the high efficiency of the circuit itself and, correspondingly, the decrease in the material flow, steam consumption and investment costs. The other task is to produce alumina hydrate of the required physical characteristics. Principally the grain-distribution is meant here under the physical characteristics, which is significant as regards metallurgical considerations, and, at the same time, it can not be considerably influenced during calcining. Other physical characteristics can be formed mainly by the calcination process.

Two basic types of alumina hydrate produced by precipitation are distinguished:

1. Fine grain-size alumina hydrate of the European technology giving floury alumina by intensive calcination.
2. Coarse grain-size, compact hydrate of the American technology giving sandy alumina by moderate calcination.

A comparison between the approximative grain-size distribution of the two hydrate-types is described as follows:

Grain-Size Distribution of Sandy and Floury Type Hydrate

Table 2.9

Grain-size	floury	sandy
+ 150 micrometer	2-4 %	2-6 %
+ 74 micrometer	18-20 %	55-60 %
+ 44 micrometer	55-58 %	88-94 %
- 44 micrometer	42-45 %	6-12 %

Four principal mechanisms are distinguished in the course of precipitation: nucleation, crystal growth, agglomeration and breakdown. The numerous data compiled in the relevant literature can not be utilized for the elaboration of general relations, as the kinetic constant of the process may significantly be influenced by the contaminants of plant liquors and, to a certain extent, by the mode of agitation. The plant precipitation technology is based generally on self-made prescriptions, which do not correspond always to the theoretical optimum.

The importance of the four mechanisms in the two technologies is summarized in the followings:

1. Nucleation: in the European /floury/ technology the aluminate liquor is cooled to 50-56 °C in order to

achieve the highest possible efficiency by decreasing the equilibrium Al_2O_3 concentration. The low temperature at the same time provides favourable conditions for spontaneous grain formation: however, the "secondary" nucleation - due to the effect of the seed - has much greater importance in this technology, the seed charged is 3 to 5 times the amount of the production. The effect of the secondary nucleation, therefore, practically damps the effect of the primary nucleation. The small sized grains formed by the primary nucleation get partly into the final product, as generally there is no proper classification in the European technology and partly increase in size, though their growth is rather limited.

Precipitation in the American technology starts at high temperature, when no primary nucleation or only a rather limited one takes place.

Adequate theoretical relationship for the primary nucleation can not be found in the relevant literature, just because of its smaller importance. Halfon and Kalliaguine /53/ assume that the rate of nucleation is proportional to a certain power of the oversaturation. According to their opinion at the same time, secondary nucleation is the significant mechanism in the process.

2. Growth of Crystals: the growth of crystals in both technologies can be described by nearly similar relationships.

Adamson, Bloore and Carr /34/ give the following formula for the discontinuous precipitation process:

$$\frac{-\,dZ}{dt} = k'F_tZ_t^2 \quad ,$$

where: $Z = X-X_e$, that is the difference between the actual and the equilibrium concentration; F = the active surface area of the seed and K' = a constant, depending on the temperature.

The equation can be integrated giving:

$$1/Z_t = 1/Z_o + K'F_tt$$

where: $Z_o = X_o - X_e \;\; /X_o$ is the starting Al_2O_3 concentration/.

In practice the European technology utilizes series connected precipitator tanks, whereas in the American technology batch precipitators are favourized. The advantage of the series connected tanks lies in the smooth and uniform technological running and simple handling, but one of their disadvantage is that in every subsequent tank the aluminate liquor is mixed with a solution of higher molar ratio, and this causes the slow-down of the precipitation process.

In case of continuous precipitation the Shimosato formula is applied in the Hungarian technology:

$$-\frac{dA}{dt} = K\;/C_1 + r/\;/A - A_c/\;.\;\frac{/A - A_e/^2}{A_e^2} + K'\;\frac{A - A_e}{A_e}$$

where: A represents the actual, A_0 the starting, A_e the equilibrium Al_2O_3 concentration; t is the time; C_1 the seed concentration; r the activity coefficient of the seed, K and K' are constants depending on the temperature and the caustic soda concentration. The constants were determined on the basis of actual plant data.

In case the problem is investigated from the crystal growth's aspect, the crystal growth rate G can be divided in two parts, one depending on the supersaturation and the other on the grain-size.

$$G = g/c/ . D/r/$$

The expression g/c/ follows the quadratic rule described above.

On the basis of the McCabe-rule /D/r/ = 1, that is, the growth rate of all crystals is equal in the first approximation, independently from their sizes. The alumina hydrate precipitated disperses among the existing nuclei and seed grains in proportion of their surface areas and the total growth of a crystal comes to 1-2 µm-s in a cycle.

It can be mentioned here that the surface activity is significantly influenced by the contaminants, principally the organic matters and especially oxalate, Fe and Ca ions, etc.

3. Agglomeration: While the agglomeration has no practical importance in the European technology, in the American practice the alumina hydrate precipitated under adequate conditions sticks together the seed

grains to form large compact alumina-hydrate grains. The agglomeration is principally dependent on the number of impacts of the grains, but it is also influenced by the cohesion between the grains.

Halfon and Kalliaguine came to the conclusion that the rate of agglomeration is proportional with the fourth power of the difference between the starting and the final concentration.

Instead of a detailed description of the agglomeration relationships let us describe a practical method based on an article of Sakamoto and his collaborators /54/, which helps the estimation of the expectable occurrence of agglomeration.

In their view agglomeration largely depends on the balance of the gibbsite precipitation rate A as binding agent, and the amount of gibbsite B required for holding strongly the flocculated particles.

A factor P was determined as the "driving force of agglomeration"

$$P = \frac{A}{B} = \frac{Ku^2 /G_o + G_e/}{G_o + G_e \cdot /1 - u/}$$

where: u is proportional with the difference of the actual and equilibrium concentration at a given temperature, G_o is the amount of seed at the beginning of precipitation, G_e the amount of precipitated gibbsite in case of equilibrium, K is a constant, depending on the surface area of the seed, supersaturation and temperature.

The value of P draws near to 0.1 in case of effective agglomeration. By the use of the above formula the value of P can be calculated for different concentrations, molar ratios and seed surface values, moreover, conditions for the possibility of agglomeration can be determined.

The value of P on the figure annexed is illustrated as a function of concentration and molar ratio, at a temperature of 70 °C /Fig. 2.38/. It is apparent from the figure that the optimum of agglomeration ranges between 90-100 g/l Na_2O concentration.

In case of the above low concentrations P-value is adequate even at a molar ratio of 1.6, whereas in case of European concentrations, adequate agglomeration would be ensured only at a molar ratio below 1.4.

Plant conditions /presence of soda, oxalate, other organic substances an contaminants/ can naturally cause significant shift in the numerical figures, the trend remaining the same.

In practice the concentration of 110 g/l and the molar ratio of 1.5 are the upper limits of efficient agglomeration.

In case of contaminated liquors the molar ratio is often reduced to below 1.4 in order to achieve effective agglomeration e.g. by the "sweetening process", though in such a case the increase of autoprecipitation during thickening and washing can not be avoided.

4. Breakdown: The breakdown, contrary to the above, is solely a mechanical phenomenon, as it is the conse-

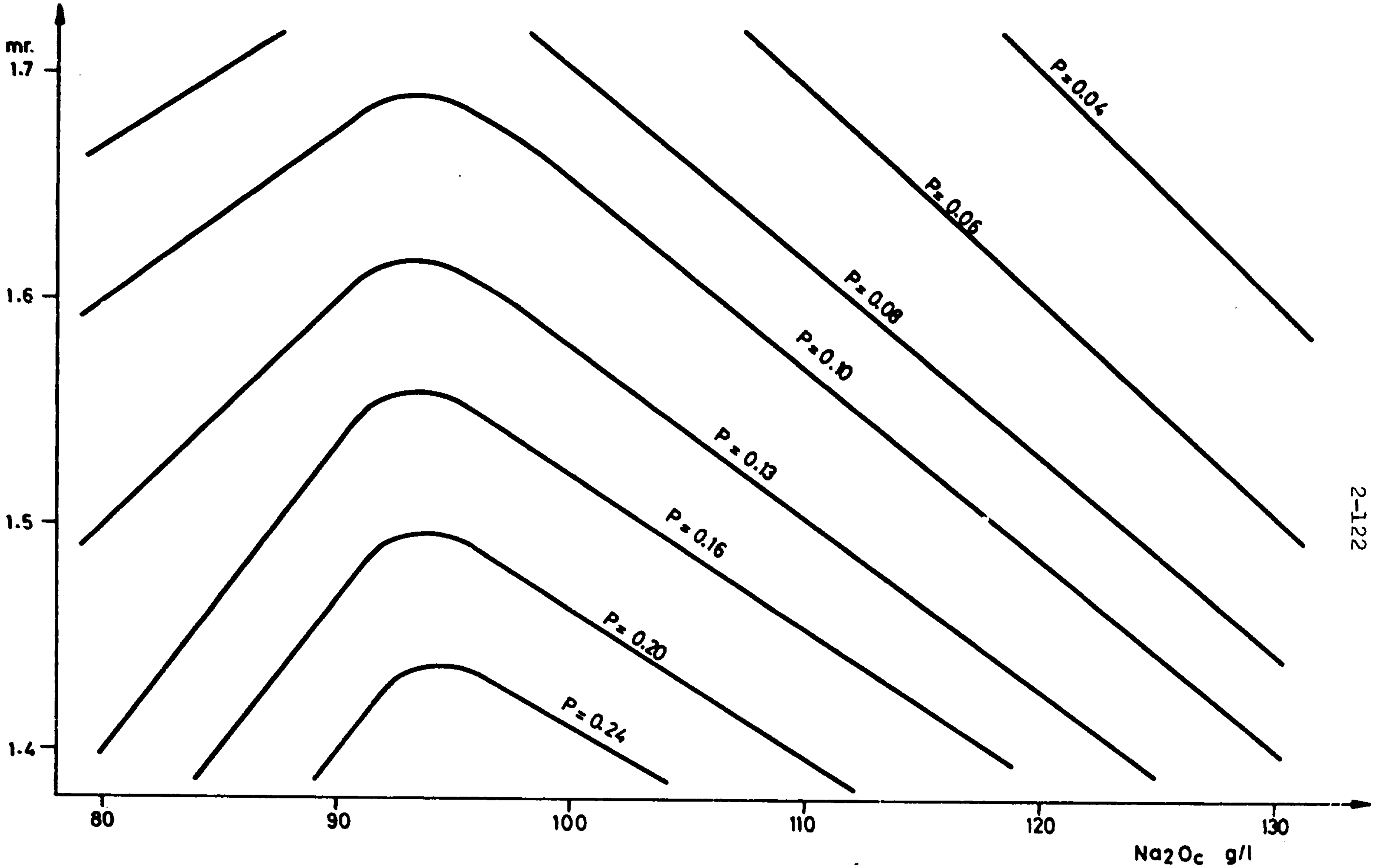


Fig. 2.38

AGGLOMERATION DRIVING FORCE vs. CONCENTRATION AND MOLAR RATIO quence of collision between the particles themselves and between the particles and the wall /or agitator/: the phenomenon can be described by the function of probability density. In case of up-to-date agitation systems /air lift and Ekato stirrer/ it has no great importance, and is practically negligible.

Precipitation Systems

Floury Alumina Production

Precipitator tanks of plants producing floury alumina are generally series-connected, 10-15 tanks in one line. Seed is filtered, repulped by the filtered and cooled aluminate liquor and is added into the first /sometimes partly in the second/ tank of the series.

As it was already mentioned, classification of alumina hydrate in plants producing floury alumina is of no importance. In case of high seed ratio and concentration the hydroseparator would have minimal classification ability - the difference between the general grain-sizes of the underflow and the overflow would be only a few micrometers - in the practice, therefore, the total quantity of seed is filtered and tray thickeners are only applied for thickening the finest grains passing through the filter cloth of the hydrate filters. The thickened slurry is then fed back to the seed filters.

This thickening stage can be ever left out of the process as it is, for example, in the New Ajka Alumina Plant. In plants producing floury alumina, consequently, the seed is practically the same, as the product hydrate.

Sandy Alumina Production

Batch Precipitation

In plants applying batch technology precipitation with the fine and coarse seeds is performed separately in the so-called special and normal tanks. The optimum conditions of agglomeration taking place in the special tanks deviate significantly from the necessary conditions of satisfactory efficiency of precipitation, consequently the smallest possible volume /20-40 per cent/ of aluminate liquor is precipitated in the special tanks in the presence of fine seeds, and the rest in normal tanks to achieve a better circuit efficiency. The total precipitation volume is generally divided approximately in 2:1 proportion between the special and normal tanks.

In order to promote agglomeration, the special tanks are generally - but not exclusively - fed with aluminate liquor of 4-5 °C higher temperature than the normal ones. The lower temperature applied in the normal tanks promotes precipitation efficiency.

Classification of precipitated hydrate is performed in steep-cone hydroseparators /thickeners/. The low solids content due to little seed charge, the high temperature at the end of precipitation and the low liquor concentration ensure favourable classifying conditions for the classification. The solids concentration of the underflow rises to above 1000 g/l, it has hardly more moisture content than the filtered hydrate. Consequently, neither the coarse nor the fine seed have to be filtered, unless oxalate destruction is necessary.

The technological scheme of batch precipitation is illustrated in Fig. 2.39. The hydrate slurry is fed to the primary thickener /PT/ the underflow contains the product hydrate and is filtered. The overflow is fed to the second-

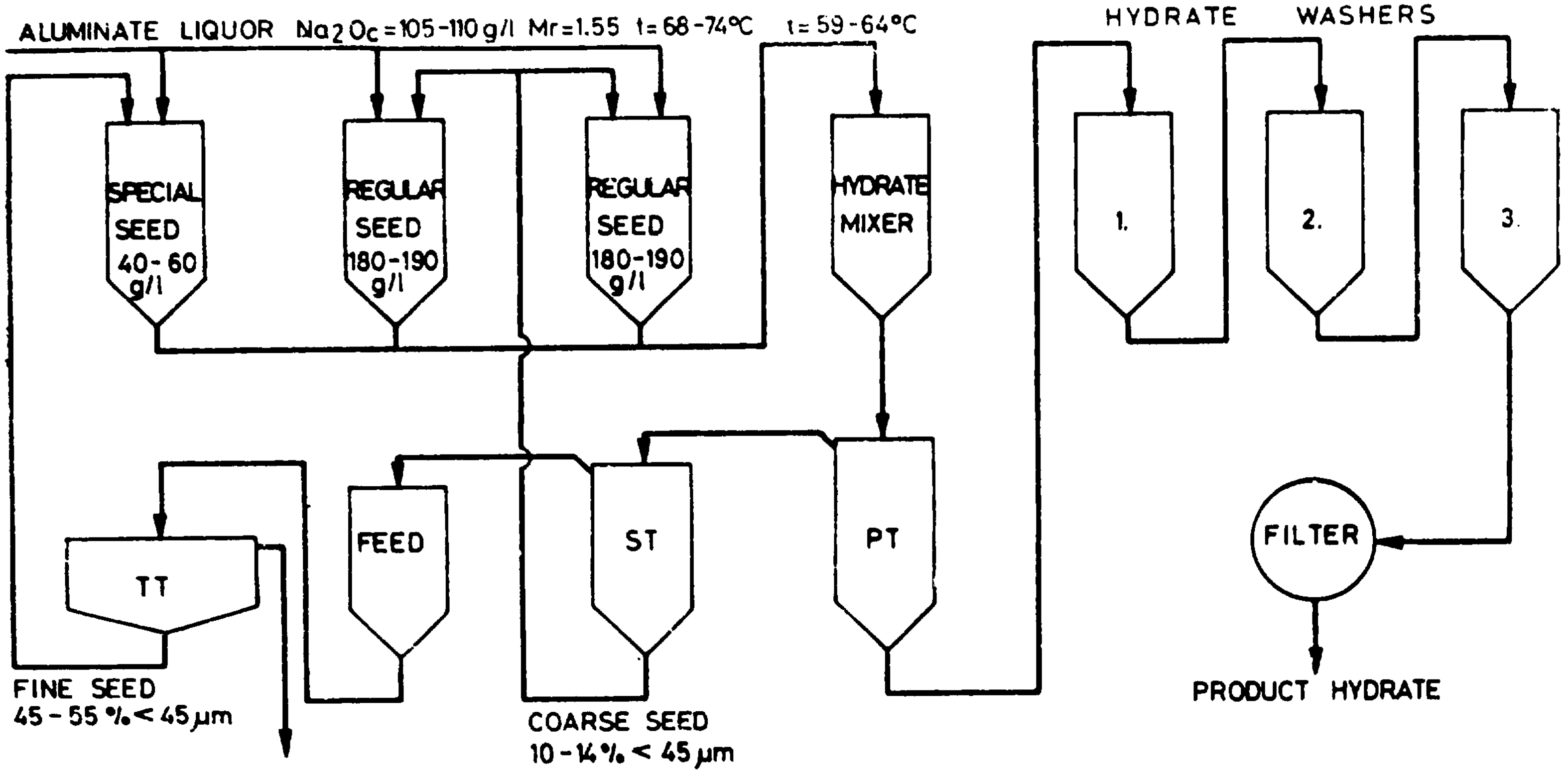


Fig. 2.39
FLOW-SHEET OF BATCH PRECIPITATION

ary thickener /ST/. The underflow of ST is the coarse seed, the overflow is fed to the tertiary thickener /TT/. The underflow of TT is the fine side, the overflow is the spent liquor.

Continuous precipitation has not yet become as familiar in plants producing sandy alumina as the batch technology. Many of the plants applying continuous precipitation returned to the batch system, as the results did not prove to be satisfactory. In case of continuous precipitation, in fact, the first tank - where the fine seed is charged in - contains already slurry of higher molar ratio since the velocity of precipitation is high, consequently the low starting molar ratio necessary to the agglomeration is not ensured. The hydrate separated in the first tank - its amount nearing to that of the fine seed charged in - also increases the starting seed ratio and affects adversely the agglomeration. The above disadvantages can be moderated by reducing the molar ratio of the aluminate liquor.

At the same time, due to the mixing of slurries with always higher molar ratios from tank to tank in the continuous precipitation, the decomposition rate is slower as compared to the batch precipitation. This has a further unfavourable effect on the precipitation efficiency and, associated with the high precipitation temperature necessary for the production of coarse hydrate, brings about a decline in the economy of production, too.

The conceptual schemes of continuous precipitation systems are illustrated in Fig. 2.40 /55/. In the simplest system the fine and coarse seed are introduced together into the first tank /a/. In other plants they are fed separately, the fine seed advantageous for the agglomeration enters the first tank and the coarse seed the 3rd or 4th tank, where the agglomeration has practically come to an end already /b/; or both the fine and the coarse seed are charged into separate lines. In an other version coarse seed is added into the line former-

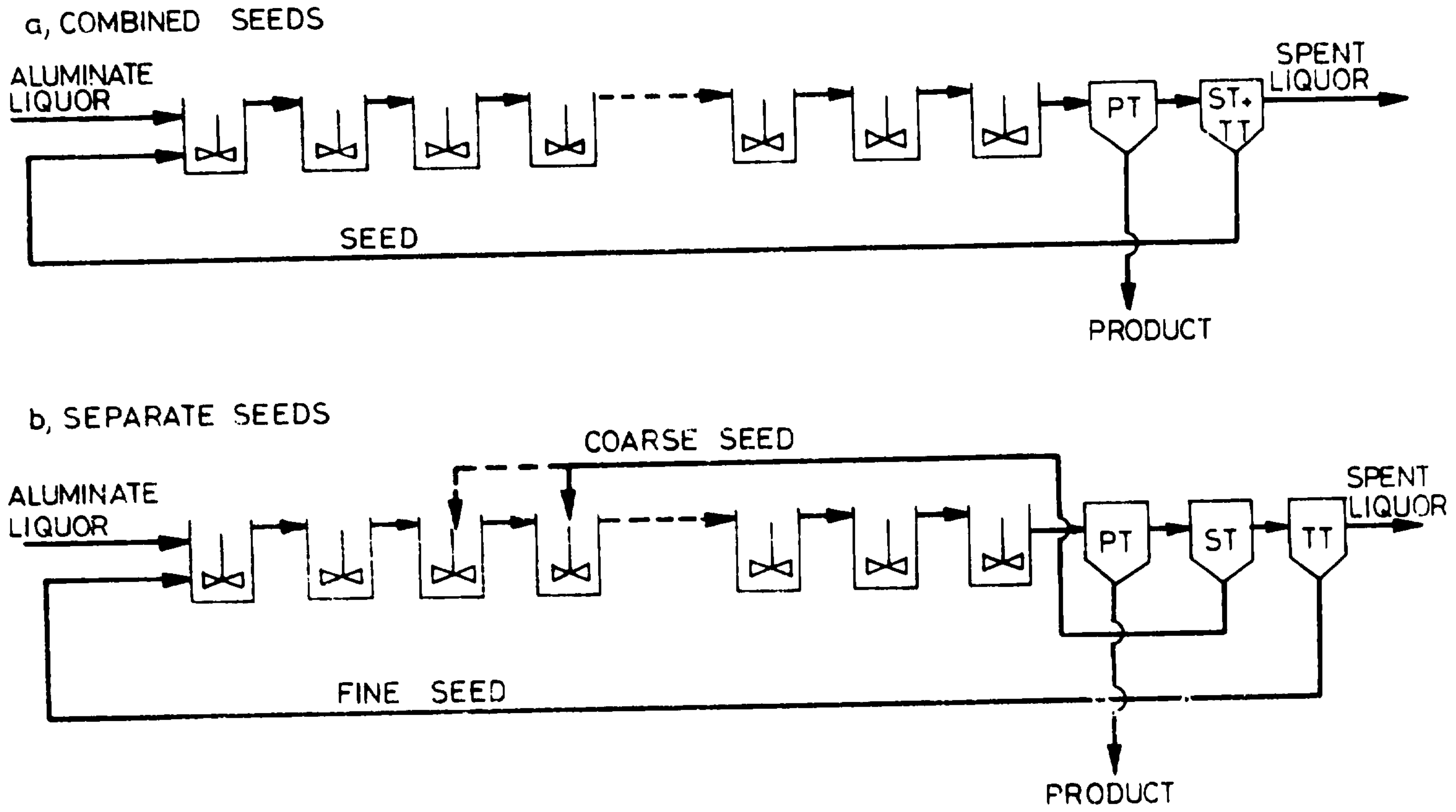


Fig. 2.40
CONTINUOUS PRECIPITATION SYSTEMS

ly treated by fine seed after the agglomeration stage, with the aim to improve the precipitation efficiency.

A very important operation in the course of continuous precipitation is the intermediate cooling. This makes possible to apply the highest advantageous temperature for the agglomeration at the beginning of the precipitator line, and to cool down the slurry after the agglomeration stage in order to reach the final temperature necessary to increase the final molar ratio. Intermediate cooling is introduced at that point of precipitation, where the molar ratio comes near to 2.0. Coarse hydrate is charged after intermediate cooling.

Equipment of Precipitation, Classification and Hydrate Filtration

Control Filtration

Control filtration of aluminate liquor is performed almost solely by Kelly pressure filters. Dorr-Oliver type filters up to 400 m^2 filtering surface area are generally used. Filtration is performed through a filtering aid, generally lime hydrate. A disadvantage of the Kelly filters is that the filtering aid can be removed only after opening the filter.

In Hungary the LVAZS filter is used, a practical equipment available also in automated version. Its advantage is that the filtering aid is removed at the end of the cycle time by washing off with water and the filter need not to be opened. Its disadvantage is, however, that the size of the largest unit is only 125 m^2.

The performance of pressure filters is 0.8 to 1.5 m^3/m^2h, in case a suitable filtering aid is used.

Cooling of the Aluminate Liquor

For cooling the aluminate liquor plate heat exchangers become increasingly widespread. There are heat exchangers constructed abroad considerably exceeding already 380-420 m^2 the size of units generally used in Hungary at present. The cooling medium is spent liquor. Due to the excellent heat transfer coefficients - about 2000 W/m^2K - the temperature of the spent liquor draws near to that of the aluminate liquor. No special treatment is required for the filters, they can be cleaned without dismantling, by the change of flow directions.

In plants producing sandy alumina flash cooling system is used generally, releasing significant amount of water from the voluminous aluminate liquor. Cooling is generally applied in 3 stages, and the steams /and gases/ are sucked off by vacuum from the last stage. The heat transfer /flash steam to spent liquor/ is less efficient than in the plate heat exchangers and even the temperature gap is greater because the increase of boiling point must also be reckoned with.

The system operates practically the same way as the digestion heat recovery, consequently it will not be detailed in this chapter.

The intermediate cooling mentioned in the chapter on continuous precipitation is generally solved by flash cooling in one stage applying vacuum suction.

Precipitation, Classification, Filtration

Precipitation was originally performed in mechanically agitated, flat-bottom tanks. Later on air-lift agitation was developed, too. At present, the greatest tanks in Hungary are of 2100 m^3, air agitated and the bottom is shaped in a special form to prevent scaling Fig. 2.41. As the investment cost of tanks with conical bottom is more expensice, new plants have, in the meantime, returned to erecting mechanically agitated, flat-bottom tanks.

There are two widespread agitation methods: the draft-tube propeller system in the cone bottomed tanks, where the slurry is either lifted in the central tube by the propeller stirrer or it is pushed down from upwards, and the MIG-system stirrer of the flat-bottom tanks /Fig. 2.42/.

Slurry transfer introduces some problems. In the Ajka Alumina Plant an overflow channel was installed which solved the level control problem, too. In other plants the tanks are located in cascade-system or have subsequently decreasing dimensions.

The bottom cone-angle of the steep coned thickeners is 60°: their diameter is determined by the throughput. Tray thickeners are of 30-40 m diameter and 2 meters high units with central discharge, the slope of the cone is about 4 per cent.

In case of floury technology disc filters are used for the seed hydrate filtration having maximum surface area of 240 m^2. The seed is generally not washed /Fig. 2.43/.

The discs have individual discharges, the filtered hydrate is separated by blowing high-pressure air into the discs covered by filter cloth.

Several plants apply vacuum drum filters for the filtration of product hydrate which can have 0.8-2.0 t/m^2h performance in case of 10-12 per cent adhered moisture.

In order to achieve better washing performance the hydrate on the filters is washed by water and several filters are con-

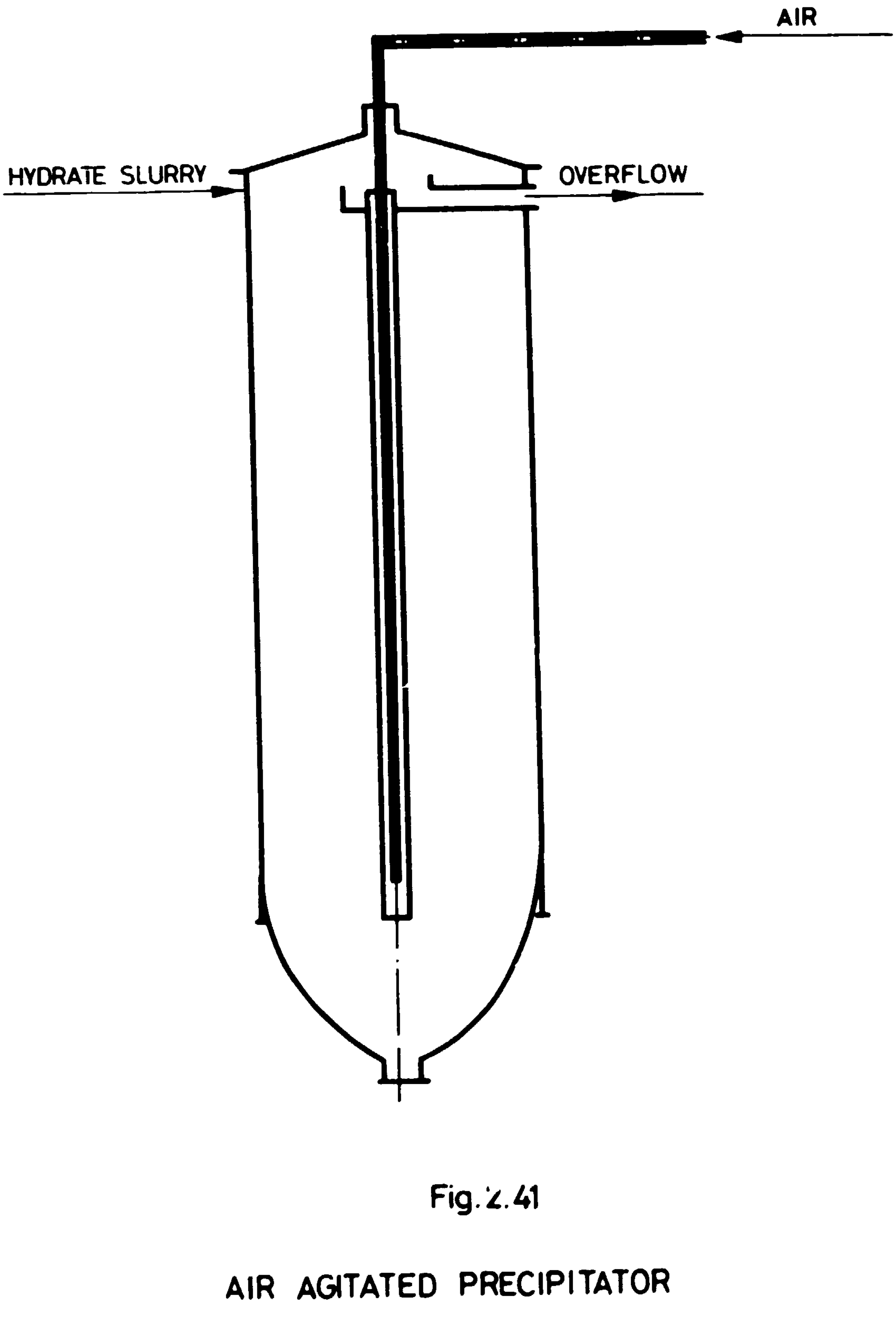


Fig. 2.41

AIR AGITATED PRECIPITATOR

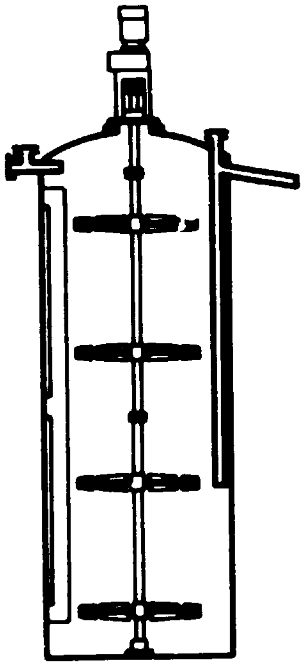


Fig. 2.42

PRECIPITATOR WITH EKATO STIRRER

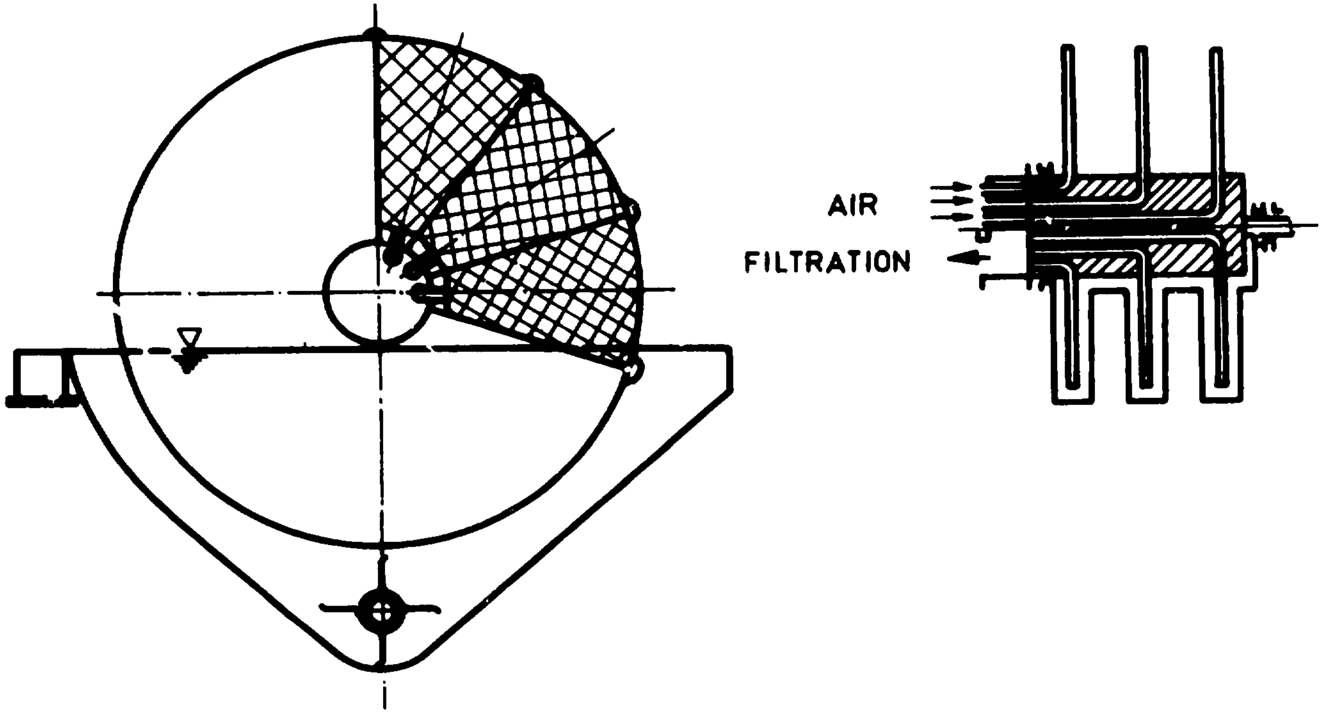


Fig. 2. 43

DISC FILTER

nected in counter-current: the filtered hydrate is repulped by water, then it is filtered on a second filter and washed, whereas part of the wash water is utilized to wash the primary filter.

In case of sandy alumina production disc filters are also used, though rotary table filters /pan-filters/ are the most widespread. The pan-filter consists of filter plates on a horizontal disc, the wash water passes through in counter-current flow and washed-off hydrate is removed by tilting the plates.

The amount of water used for aluminate hydrate washing figures 0.2-1 m^3/t alumina depending on the technology applied.

CALCINATION TECHNOLOGY AND EQUIPMENT

Technology of Calcination

The aim of the calcination is to remove the adhered moisture and bound water content of the alumina hydrate at a high temperature, thus producing alumina consisting of a mixture of alpha- and gamma aluminium-oxide.

The subsequent processes taking place in the course of the calcination of the alumina hydrate are discussed under chapter 2. of the present volume. However, the importance of the different phases /etha, theta, chi, kappa and delta/ found by constant recrystallizations in the course of calcination is practically negligible. Above 1000 °C - i.e. the minimum temperature of the calcination - solely alpha- and gamma aluminium-oxides exist. From practical point of view gamma aluminium-oxide is readily adsorbing water and this has to be taken into account when storing and transporting it.

The chemical impurities of alumina are practically the same as those of the hydrate. However, the SiO_2 content as a consequence of the erosion of the kiln lining, and the Fe_2O_3 content due to wearing of the steel structure rise to a higher level than it is expected from the composition of the hydrate. Part of the Na_2O content, at the same time, volatilizes in form of a sodium-salt at higher temperature. Excess S and V_2O_5 content may get into the alumina from the fuel oil, and this has to be taken seriously into consideration when selecting the type of fuel.

The physical characteristics of the alumina depend partly on those of the alumina hydrate. It is principally the grain distribution of the hydrate which undergoes the most minor change in the course of calcination: in case of adequate calcining parameters the desintegration - characterized by the increase of grain fraction below 44 μ - amounts to 2 to 3 per cent.

On the basis of physical characteristics, in fact, two fundamental alumina variants are distinguished:

Floury alumina, principally produced in Europe and fed to Söderberg-type cells.

Sandy alumina, produced in plants operating by the American technology, and processed in cells with prebaked anodes.

The comparison of the most significant physical characteristics between the two alumina qualities is illustrated in the table below:

Physical Characteristics of Floury and Sandy Aluminas

Table 2.10

Physical characteristic	floury	sandy
	alumina	
loss on ignition	0.3 %	0.9-1.2 %
specific surface area	5-10 m^2/g	40-45 m^2/g
alpha alumina content	60-70 %	20-30 %
bulk density	0.95-1 t/m^3	0.88 t/m^3
angle of repose	$40-45^0$	$28-32^0$
+ 100 mesh	0.1 %	2-8 %
- 325 mesh	50-55 %	6-10 %

It should be noted that the physical characteristics are generally interconnected: in case of lower calcination temperature, specific surface area, and loss on ignition are higher angle of repose and alpha content are lower, and vice versa.

Equipment of Calcination

The conventional alumina calcining equipment is the rotary kiln with refractory brick lining: its diameter is 2-4 m, the length is 50-120 m and the slope of the kiln is 2-3 per cent. The alumina hydrate is fed into its upper side, whereas firing is performed at its lower end and the final product also leaves through this end.

In the Pfeiffer kilns alumina falls through the apertures at the end of the kiln into planetary coolers provided with snakes for heat recovery and the cold air passing through the coolers is warmed up in counter-current, entering after that the combustion chamber as secondary air.

Firing of the calcining kilns is performed by fuel oil or by natural gas: the former is atomized by steam or mechanically by high pressure. The conventional rotary kilns operate at 5000-6000 KJ/kg of alumina specific heat consumption.

The first rotary kiln combined with preheater cyclones was built within the frames of the expansion work of the Almásfüzitő Plant /Fig. 2.44/.

The hydrate is preheated approximately to 600 °C in a 3-stage cyclone system and the final calcination occurs in the rotary kiln itself. Alumina is cooled in the recuperator tubes and in the additionally coupled fluidizing coolers, and preheated air is utilized within the system. The actual specific consumption achieved by this system at the Almásfüzitő Plant approximates a value of 3800 KJ/kg.

The KHD-system installed in the New Ajka Alumina Plant recuperates the heat content of the alumina in a system using cyclones and recuperators.

In the course of developing the cyclone-kilns the fluid bed calcining proved to be the most effective. This is principally utilized for the production of sandy alumina of even grain distribution in which the proportion of grains below the size of 5 μ is negligible. Calcining is performed in a fluid layer of great volume operating at 1100-1200°C for a mean period of 30 to 60 minutes, using return cyclones and a dust trap /Fig. 2.45/.

Alumina hydrate is charged by a duplex screw conveyor system into the Venturi-tube type fluidizing feeder. At this stage the adhered moisture content of the hydrate is eliminated. Dry and mildly dehydrated hydrate is carried by the combustion gases into two series-connected cyclones, where its major part is separated, then it enters the Venturi-tube fluid bed preheater above the return cyclone of the calcining kiln. Combustion gases are cooled as a consequence of the heat exchange with the hydrate and the latter is heated up to 310-370 °C. The corres-

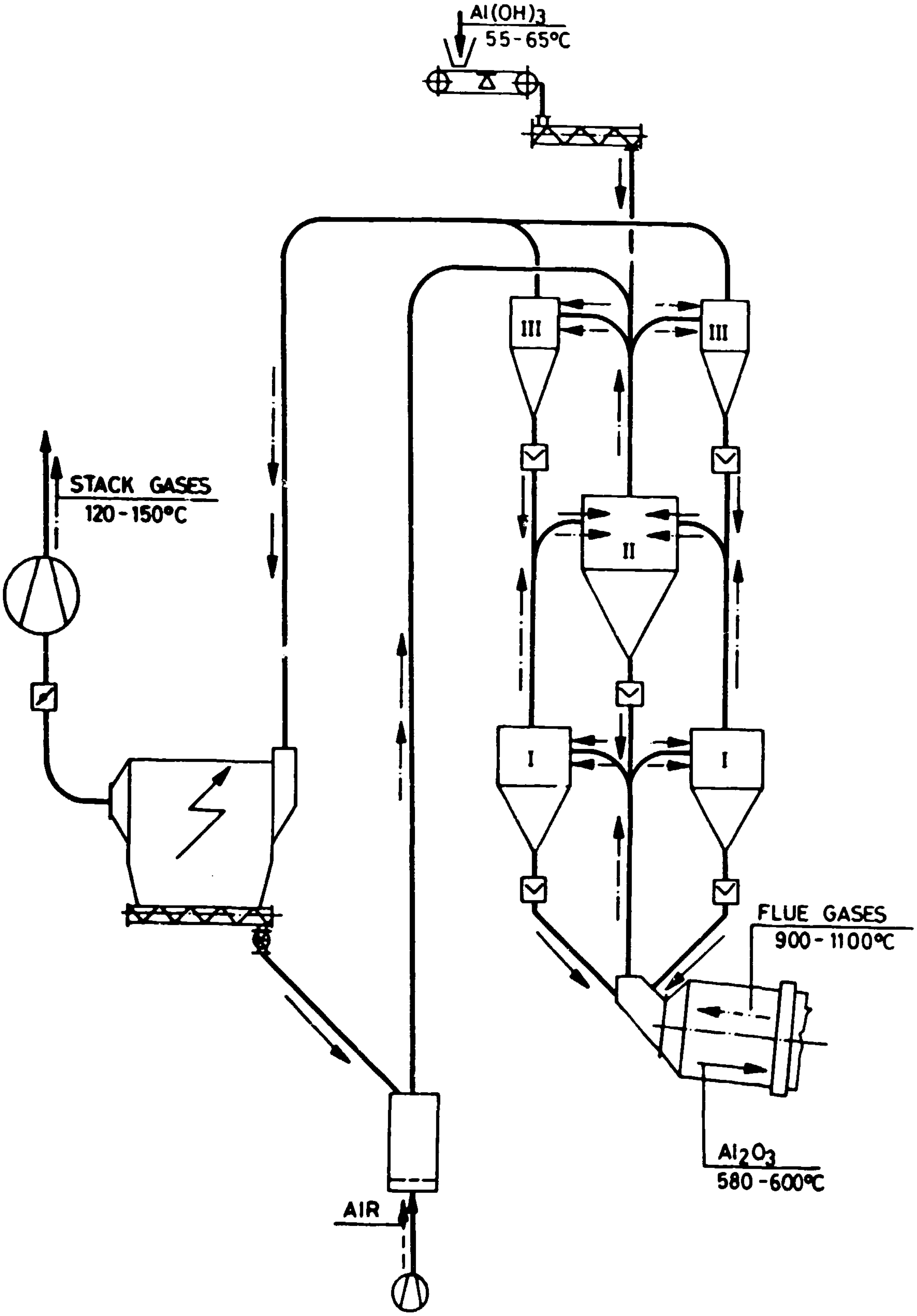


Fig. 2.44
CYCLONE PREHEATING SYSTEM·

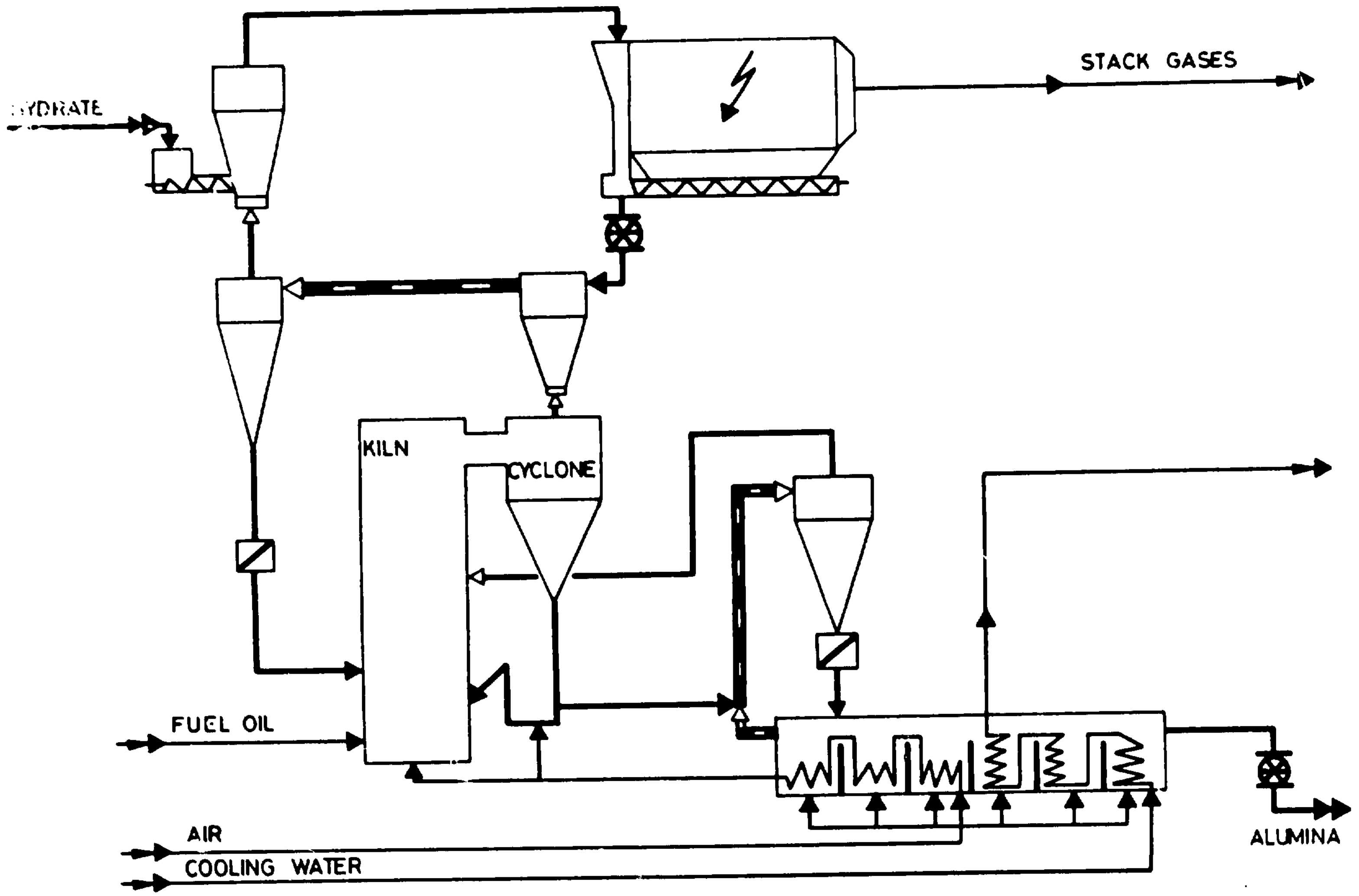


Fig. 2. 45
FLUID BED CALCINING KILN

ponding figure of L.O.I. is about 5 %. Hydrate is separated in a cyclone then it enters the fluid bed calcining kiln where it is heated up to 1100 °C.

TECHNOLOGY AND EQUIPMENT OF EVAPORATION

Water-Balance of the Alumina Plant

Water enters the circuit of the alumina plant at several stages and later on it must be removed keeping in view the equilibrium of the circuit. At the same time the aluminate liquor is diluted at several stages also inside the circuit and this must be compensated by the removal of water at some other points of the circuit; as it will be seen later, the major part of this water will enter the circuit again. The removal of the water is the task of the evaporation, which is inserted into the technological process between precipitation and digestion.

Two circuit-balances will be described in the following for the purpose of illustration: one for processing gibbsitic bauxite and producing sandy alumina, and the other for processing boehmitic bauxite and producing floury alumina. The balances refer to the production of 1 ton alumina.

1. Processing low Al_2O_3 and SiO_2 content gibbsitic bauxite for sandy alumina production

Input:	
Bauxite adh.moisture	0.30 t
Bauxite bound water	0.65 t
Liquid caustic soda	0.07 t
Direct steam heating	0.69 t
Hydrate wash water	0.54 t
Red mud wash water	4.11 t
Sand wash water	0.33 t
Oxalate wash water	0.40 t
Lime slaking water	0.06 t
False water	0.50 t
Total:	7.65 t

Output:	
Flashing at digestion	0.92 t
Red mud liquid phase	1.84 t
Red mud solid phase	0.09 t
Sand	0.05 t
Hydrate adh.moisture	0.19 t
Hydrate bound water	0.53 t
Oxalate slurry	0.03 t
Evaporation	4.00 t
Total:	7.65 t

In case of selecting only those items from the above balance, which enter the circuit from outside, or which leave it finally, the following balance results:

Input:	
Bauxite	0.95 t
Liquid caustic soda	0.07 t
Direct steam	0.69 t
Make-up water, red mud washing	1.12 t
False waters	0.50 t
Total:	3.33 t

Output:	
Red mud	1.93 t
Sand	0.05 t
Hydrate	0.72 t
Oxalate slurry	0.03 t
Evaporator condenser	0.60 t
Total:	3.33 t

2. Processing average quality boehmitic bauxite for floury alumina production

Input:		Output:	
Bauxite adh.moisture	0.49 t	Digestion flashing	2.43 t
Bauxite bound water	0.32 t	Red mud liquid phase	2.82 t
Liquid caustic	0.22 t	Red mud bound water	0.11 t
Red mud wash water	5.91 t	Hydrate adh.moisture	0.22 t
Causticization of soda	0.72 t	Hydrate bound water	0.53 t
Hydrate wash water	1.02 t	Evaporation	3.07 t
False waters	0.50 t		
Total:	9.18 t	Total:	9.18 t

Items entering the process from outside or leaving it finally:

Input:		Output:	
Bauxite	0.81 t	Red mud	2.93 t
Liquid caustic	0.22 t	Hydrate	0.75 t
Make-up water, red mud washing	2.60 t	Evaporation condenser	0.45 t
False water	0.50 t		
Total:	4.13 t	Total:	4.13 t

Consequently the actual evaporation requirements - 3 to 4 tons of water for 1 ton of alumina - are significant in both technological processes and the steam consumption, operational costs, investment and capital costs constitute important factors in the costs of the alumina.

Theory of Evaporation

In case a liquid or a solution is heated through a heat-transferring wall by steam the liquid, or the solvent of the solution - water in case of alumina production - is transformed into vapour as soon as the temperature along the wall increases to a value corresponding to the vaporization pressure, p_v + Hg; where p_v is the pressure of vapour space above the fluid level, H is the distance of liquid particles from the surface of the fluid and g the density of the liquid. The liquid is transformed into vapour in the form of bubbles which move upward, carrying a liquid flow with them. When ascending the warm liquid flow reaches a level of lower pressure, thus bubbles will form also inside it. Reaching the surface the liquid becomes free of bubbles and its relevant part is evaporated. The evaporation absorbes heat, consequently the liquid cools down and flows downwards again.

Surface area formation of steam bubbles requires work, consequently the liquid has to be overheated in order to be evaporated. In case of evaporating a solution, having always lower vapour pressure than the clear solvent has, the necessary degree of overheating is even higher. The boiling point rise, corresponding the decrease of vapour pressure, is between 10 and 20 °C in the alumina plant's practice, and it increases parallelly with the concentration of the liquid.

With regards to the fact that the heating steam condenses on the heating surface, a heating steam of higher saturation temperature has to be applied than the evaporation temperature of the overheated liquor.

As the temperature of the more concentrated solution increases, the difference between this temperature and that of the heating steam /regarded as the motive force of heat transfer/ decreases: consequently the heat transferred through the wall and the amount of the evaporated liquid will decrease, too. The temperature of the heating steam can naturally be increased in order to intensify the evaporation performance, though – as it will be seen later – the contaminants of the aluminate liquor and the advantages of utilizing back pressure steam of turbines for the heating set certain limits to this.

Lower temperature heating steam can be utilized if the evaporation area is under vacuum. In this case gases contained in the condensating steam /including air/ can be removed, too.

Obviously, the vapour of the evaporated solvent has to be removed, too. This vapour is utilized for heating up a further unit, where the liquor partly evaporated previously is also introduced, or – in case its temperature is low – it is flashed into condensers.

Heat Engineering Considerations

Calculation of Heating Surface Area

The following general formula can be used for calculating the heating surface area:

$$Q = F \cdot K \cdot \Delta t \qquad /1/$$

where: Δt represents the average difference between the saturation temperature of the heating steam and that of the liquor, K is the heat transfer coefficient, and F the heating surface area.

The K factor depends on the difference of temperatures and this has to be taken highly into consideration in the course of designing evaporator units.

Steam consumption of the evaporation can be calculated on the basis of the laws of conservation of matter and energy:

For the area of evaporation

$$Q + G_o'i_o' = G_o''i_o'' + G_s i_s ,$$

where: Q represents the heat transferred through the wall; G_o' is the mass of the solution to be evaporated, G_o'' is the mass of the evaporated solution, whereas G_s represents the mass of the evaporated water; i_o', i_o'' and i_s are the corresponding heat contents. The values enumerated are relating to unit time.

Keeping in view that

$$G_o' = G_o'' + G_s$$

the above equation may be converted as follows:

$$Q = G_o' /i_o'' - i_o'/ + G_s /i_s - i_o''/ \qquad /2/$$

Relating to the heating surface area, the thermal balance of the input and output heat quantities are demonstrated in the equation below:

$$G_h i_h = G_h i_c + Q$$

out of this

$$G_h = \frac{Q}{i_h - i_c} \qquad /3/$$

where: G_h is the mass of the heating steam; i_h its heat content and i_c the heat content of the condensate.

Using the equations 1, 2 and 3, first the value of Q, then G_h, i.e. the quantity of the required heating steam and finally F, the necessary surface area can be calculated.

Theoretically, 1 kg of heating steam is necessary for evaporating 1 kg of water. The actual steam consumption is generally higher as

- the heat of evaporation is lower in the higher pressure heating area than in the lower pressure evaporation area;
- the heating steam requirement is also increased by the heat losses;
- finally, the temperature of the solution entering the evaporator is generally lower, than that of the evaporation area. In practice, therefore, preheated solution is fed into the evaporator.

Multiple Evaporation

As it was mentioned formerly, the vapour generated in an evaporator can be again utilized as heating steam in a further evaporator body. In such a case only the first body must be heated with live steam and all others with the vapour of the previous bodies. The vapour of the last body is condensed.

Using triple-, quadruple- or quintuple effect evaporators subsequently 0.5, 0.37 and 0.3 kg heating steam, resp. are required in order to evaporate 1 kg of water. An additional advantage of this system lies in the fact that only 0.5 to 0.3 kg or even less steam enters the condenser, the cooling water consumption of which will decrease proportionally.

In practice the multiple evaporation is performed by providing each unit with the same heating surface area aiming at establishing an even distribution of temperature differences. Each further unit of the evaporator line will naturally involve excess investment and operation costs. The number of stages required for the evaporation process is consequently determined by economic calculations. When making the economic calculations the production cost of steam, the operation cost and capital costs of the units, moreover, the economy of the total alumina plant under given evaporation must be taken into consideration. A real advantage arises from the fact that back-pressure steam leaving the turbines which has already produced electric energy can be utilized for heating the evaporator units.

It must be mentioned that originally uniflow equipment had been used in the alumina plant practice, where the steam and the liquor advanced in the same direction from one unit into the other one. Keeping in mind, however, the facts described in the chapter on desilication the system shows disadvantages: The spent liquor has a high temperature when entering the unit and, consequently, significant silica deposition is experienced principally in the first unit and in the second one, too, which necessitates the acid treatment of the unit at times. At the same time, at low temperature both in the last unit and in the last but one carbonate soda is deposited out of the concentrated solution and this necessitates frequent stoppages of the equipment in order to eliminate the scaling by washing.

Therefore, modern equipments are working in counter-current system: spent liquor enters the circuit at the last unit from the steam-side and is transferred into the last but one unit by pump, and so on. The concentrated solution is directed to a flashing line finally, where it is further concentrated. The danger of silica deposition decreases in this system to such an extent that a single acid treatment per year is sufficient. The soda scaling is also less, thus a weekly water treatment would satisfactorily remove it both from the first and second body.

Tapped steam can also be obtained from the individual evaporator bodies and the closer the tapped unit steam is situated to the end of the line, the smaller will be the amount of excess live steam /back-pressure steam/ consumed by the first body. Similarly, the closer the unit is to the beginning of the line from where this steam is tapped, the higher will be its temperature. Consequently, steam of the proper temperature can be tapped from the evaporator set preheating both the spent liquor and other alumina plant liquors, thus decreasing the boiler steam consumption.

The steam economy can also be improved by rational utilization of condensate waters. The condensate water of live steam is returned to the power plant under pressure, at as a high temperature as possible /its amount may exceed even 90 per cent/, and this results in savings in the boiler steam consumption. The so-called alkaline condensate, originating from the vapours of the evaporator bodies, can also be utilized partly for preheating the spent liquor to be evaporated, but its major part is returned to the circuit as make-up water. It is principally utilized as hydrate wash water, as it is significantly purer than the alkaline condensate water of the digestion, and the balance is added to the red mud washing. Calculation of the necessary number of stages and heating surfaces is made nowadays exclusively with the aid of computers.

Mechanical Equipment of Evaporation

On the basis of the principles envisaged in the above, evaporation is performed at present in high capacity multiple stage sets evaporating 100-200 t of water per one hour.

It must be taken into consideration when designing the evaporator units that the required heating surface area should be located in the smallest possible unit, optimum circulation conditions must be established, no carry-over of drips from the vapour area is allowed into the condensate water and care should be taken for the continuous removal of condensate water from the equipment.

In the oldest type evaporators of the Robert-system, the heating- and vapour area were located in the same unit. These equipments, however, did not allow the satisfactory agitation of the liquor.

Inclined tube evaporators have been installed in all three plants of Hungary, where more intensive circulation conditions for the solution are maintained /Vogelbusch/.

In the New Ajka Alumina Plant Kestner evaporators were installed combining several up-to-date theories /Fig. 2.46/. The units operate by the falling film-type mechanism: the liquor is pumped into the upper section of the vertical tube-bundle in such a volume that the tubes are not filled up and the evaporation takes place by evaporating the water from the liquor film flowing downwards on the inner-side wall of the tube. As this liquor film is very thin, the evaporation can be performed with favourable efficiency.

Flash condensers are used between the preheaters for utilizing the vapours: the heat transfer, therefore, takes place directly. Though the liquor is diluted by the flashed

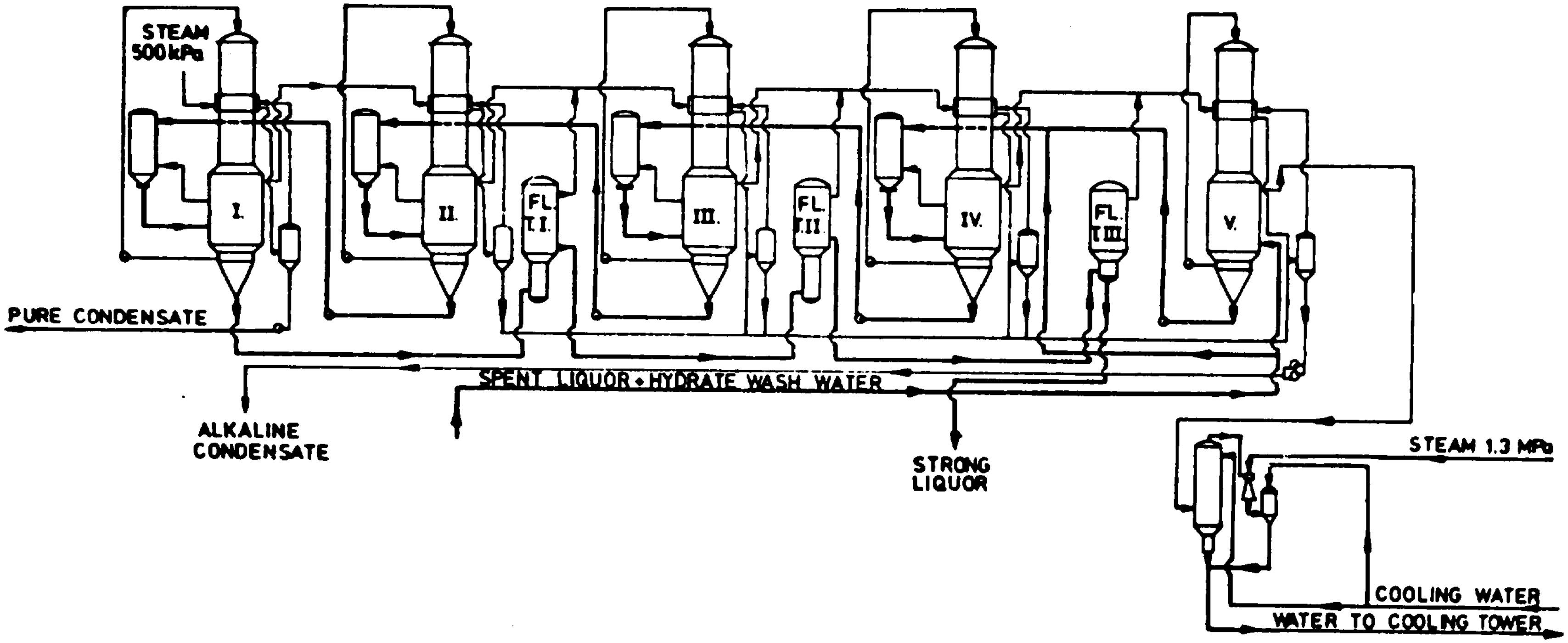


Fig. 2.46

KESTNER TYPE EVAPORATOR

vapour in this method, the temperature of the liquor entering the subsequent unit is significantly higher than that in the other type equipment, and it draws near to the evaporation temperature.

The hot, evaporated solution leaving the last liquor-side unit - i.e. the first steam-side one - is flashed in 3-4 stages and the vapours released in the flash tanks are also fed back to the preheater located between the units.

The vacuum required for the equipment is generated by steam-jet ejectors operating at 1.3 MPa in Ajka and by airpumps in other plants.

Vapour from the last stage is fed into flash condensers where cold cooling water is fed, too. In case if no sufficient amount of cooling water is available the warmed-up water from the condenser is fed into a cooling tower.

Cooling cells with forced cooling by means of fan are up-to-date units with essentially less space requirement and investment cost than those of the cooling towers.

Flash Evaporation

Another up-to-date system of evaporating the spent liquor is the multi-stage flash evaporation. This system is based on the same principle as the counter-current heat recovery digestion, or the flash cooling of alumina liquor.

Spent liquor is heated up to about 130 °C in a series of multi-stage preheaters and then it is flashed in 8 to 10 stages: flash vapours of the first 6 to 8 stages are used to preheat partly the spent liquor and partly the produced strong liquor, while the vapours of the last two flashing stages are condensed in a partitioned condenser.

An example is given in Fig. 2.47. Spent liquor is charged into the evaporator between the 6th and 7th preheater stages corresponding to its temperature, from there it passes towards the first preheater unit, then it is flashed in 10 stages. Strong liquor is cooled down in the 10th flashing stage /X./ below the temperature of the spent liquor, then it is again heated up to about 70 °C by the flash steam of the 8th and 9th stages /VIII. and IX./. Part of the strong liquor can be fed back into the evaporator together with the spent liquor adjusting thus the concentration of strong liquor to the optimum level and decreasing the danger of silica scaling.

The evaporator is heated by the counter pressure steam of 300 to 500 KPa of the turbine. Pure condensate water is fed back to the power plant.

Alkaline condensate water of the first preheater is flashed into the steam spaces of the subsequent preheater units and it is transferred from the last one to make-up wash water.

Flash evaporation is principally applied in the sandy technology requiring relatively minor evaporation of diluted solutions. Due to silica scalings spare preheater units are applied in the higher temperature stages.

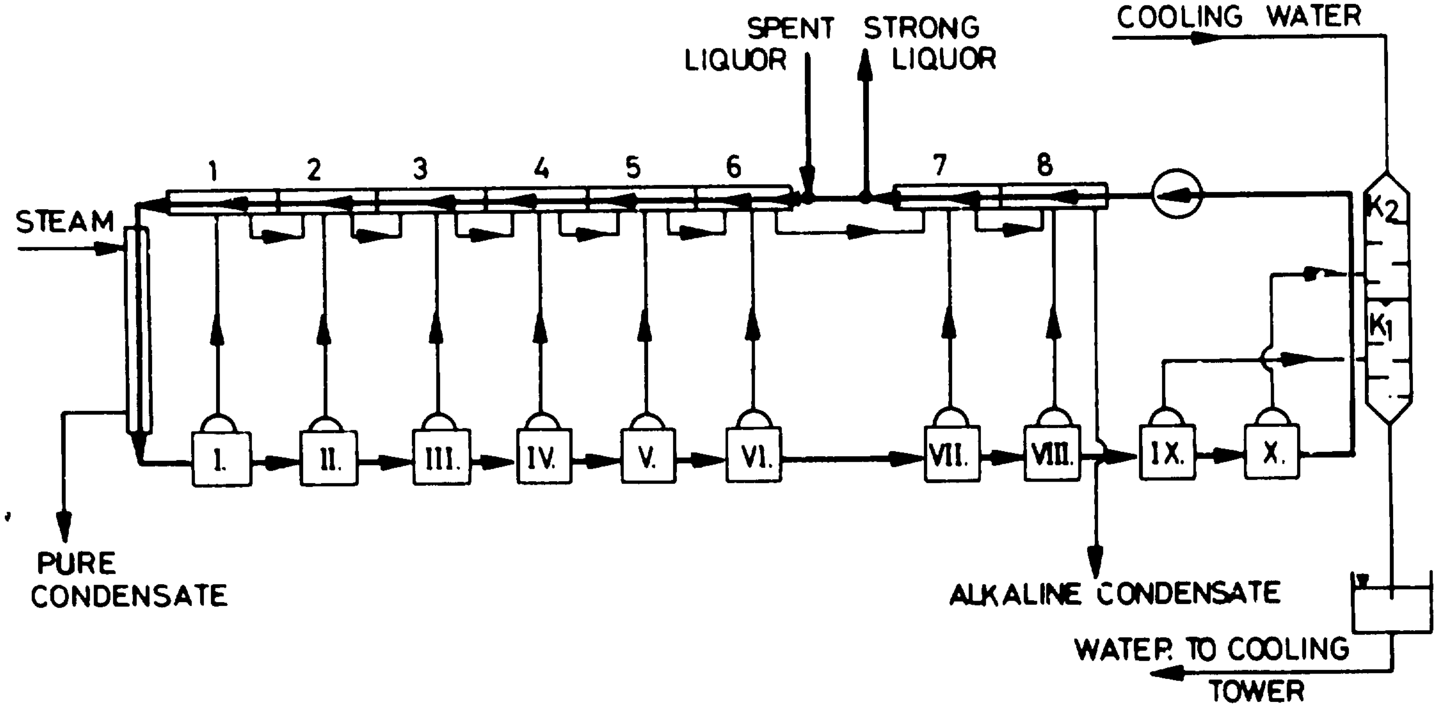


Fig. 2.47

FLASH TYPE EVAPORATOR

CONTAMINANTS OF SODIUM-ALUMINATE SOLUTIONS

Minerals contaminating the bauxite have disadvantageous effects on the Bayer technology not only by forming phases which increase the NaOH and Al_2O_3 losses and decrease the separability of red mud, but by dissolving and accumulating in the digestion liquor, too.

Most important contaminants soluble in the digestion liquor are SiO_2, carbonates, sulphur-compounds, organic material, moreover, phosphore and zinc. Vanadium and gallium content also soluble in the liquor, however, not only contaminate the liquor but, being separated from the circuit liquor of the alumina plant, they constitute the basis of large scale industrial production of valuable by-products.

The role of minerals containing silica was already dealt with in detail, therefore, we only refer now to the fact that an important part of the SiO_2 content of the aluminate liquor entering the precipitation separates on the aluminium hydrate and contaminates the alumina. Consequently, due care must be taken to decrease the SiO_2 content of the liquor.

P_2O_5 content of bauxites is generally 0.1-0.3 per cent, and this dissolves easily in the digestion liquor by simultaneous Na_3PO_4 formation. In certain bauxites, however, the P_2O_5 contained in form of apatite $/Ca_5/F, Cl, OH/ /PO_4/_3$ and crandallite $CaAl_3H/OH/_6 /PO_4/_2$ amounts even to some per cents. In case the P_2O_5 content of the aluminate liquor exceeds the value of 0.6-0.7 g/l, it must be separated by cooling the evaporated strong liquor to 20-30 °C and by simultaneous separation of soda or V-containing salt. If the bauxite is digested by CaO addition, $Ca_3/PO_4/_2$ is formed ensuring the low P_2O_5 level of the circuit and low P content of the alumina.

Bauxites are generally contaminated by zinc, which dissolves in the digestion liquor in the form of $Na_2Zn/OH/_4$. According to the data of some Hungarian experts, one-third of the bauxite's Zn content gets dissolved and this amount precipitates completely during decomposition /56/. Removal of zinc from the solution can be realized by Na_2S-addition, which precipitates it in the form of sphalerite /57/:

$$Na_2Zn/OH_4/ + Na_2S \rightleftharpoons \underset{\downarrow}{\underline{ZnS}} + 4NaOH$$

The most important contaminating sulphuric compounds of bauxite are different sulphides and sulphates, and pyrite and alunite as minerals. Solubility of sulphides in the liquor depends considerably on their mineral modification. The presence of sulphides in the aluminate solutions increases the solubility of iron and, consequently, the iron content of the alumina, too. The reaction of pyrite with the aluminate solutions can be described by the following equations:

$$3FeS_2 + 9NaOH + 4H_2O = Fe_3O_4 + 3NaHS + 3Na_2SO_3 + 7H_2$$

$$3FeS_2 + 9NaOH + 7H_2O = Fe_3O_4 + 3NaHS + 3Na_2SO_4 + 10H_2$$

Sulphates form Na_2SO_4 which, in case it accumulates, must regularly be removed from the circuit. However, the SO_4^{2-} is built in even at relatively low concentrations into the Na-Al-hydrosilicates, and its equilibrium concentration in the liquor will not exceed 1-2 g/l. Considerable Na_2SO_4 concentration /10-20 g/l/, must, however, be reckoned with in case great surplus of Na_2S is added for the Zn-removal, as the former gets gradually oxided.

Constant contaminants of the sodium-aluminate solution are NaCl and NaF. The former enters the circuit mainly as the contaminant of NaOH /especially in case NaCl was electrolysed in diaphragm cell/, whereas NaF enters into it from the bauxite.

In the followings major concern is given to the two most important contaminants of the aluminate solution: Na_2CO_3 and organic material.

Carbonate Soda Content of Aluminate Solutions and its Regeneration

Calcite, dolomite and siderite contaminating the bauxite desintegrate with an efficiency depending on the digestion parameters and on the stability /degree of crystallization/ of the given mineral according to the following general reaction:

$$MeCO_3 + 2NaOH = Na_2CO_3 + Me/OH/_2$$

Consequently, carbonates have highly disadvantageous effect by forming carbonate soda from NaOH. An additional disadvantageous effect of dolomite is that it causes aluminium losses, too, and forms phases causing significant froth formation in the counter-current washing series.

On the basis of data collected from FKI /Research Institute for Non-Ferrous Metals/, the solubility of Na_2CO_3 in synthetic aluminate liquor is illustrated as a function of the caustic Na_2O concentration and the temperature, in Figs. 2.48 and 2.49. The figures show that the solubility of caustic soda decreases significantly as the caustic Na_2O concnetration increases, but it depends only slightly on the temperature. Solubility of caustic soda in higher temperature ranges is displayed in Fig. 2.50, on the basis of Eremin's data /58/.

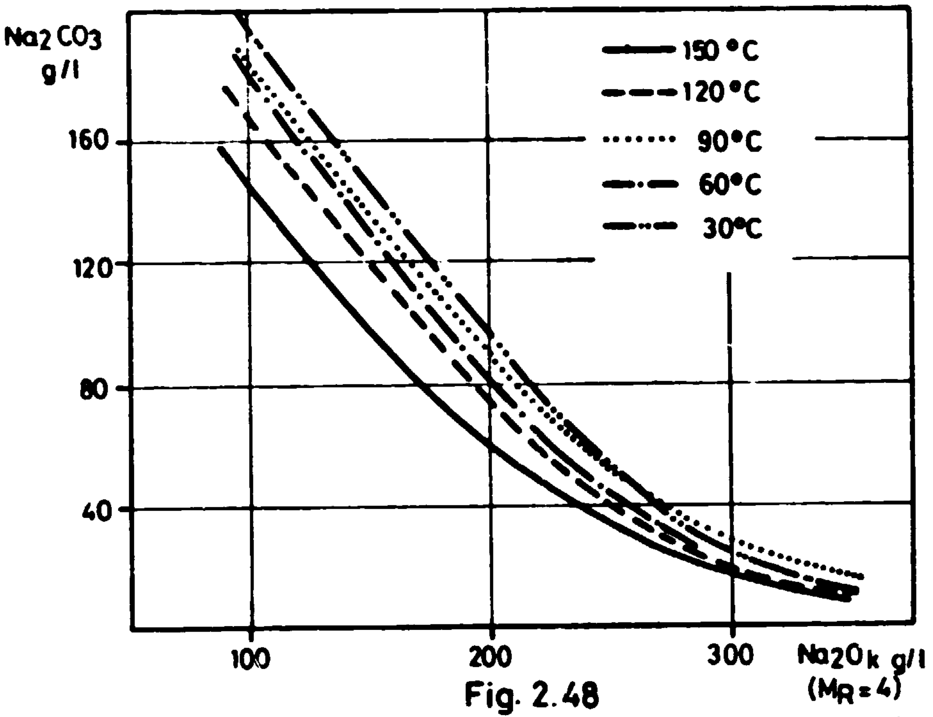


Fig. 2.48

SOLUBILITY OF Na_2CO_3 IN SYNTHETIC ALUMINATE LIQUOR

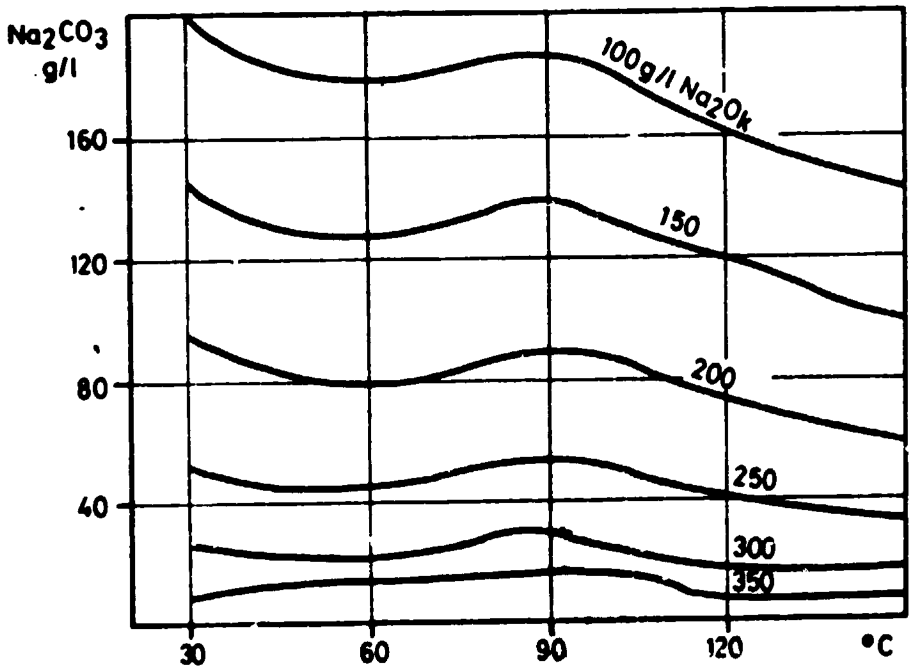


Fig. 2.49

SOLUBILITY OF Na_2CO_3 IN SYNTHETIC ALUMINATE LIQUOR

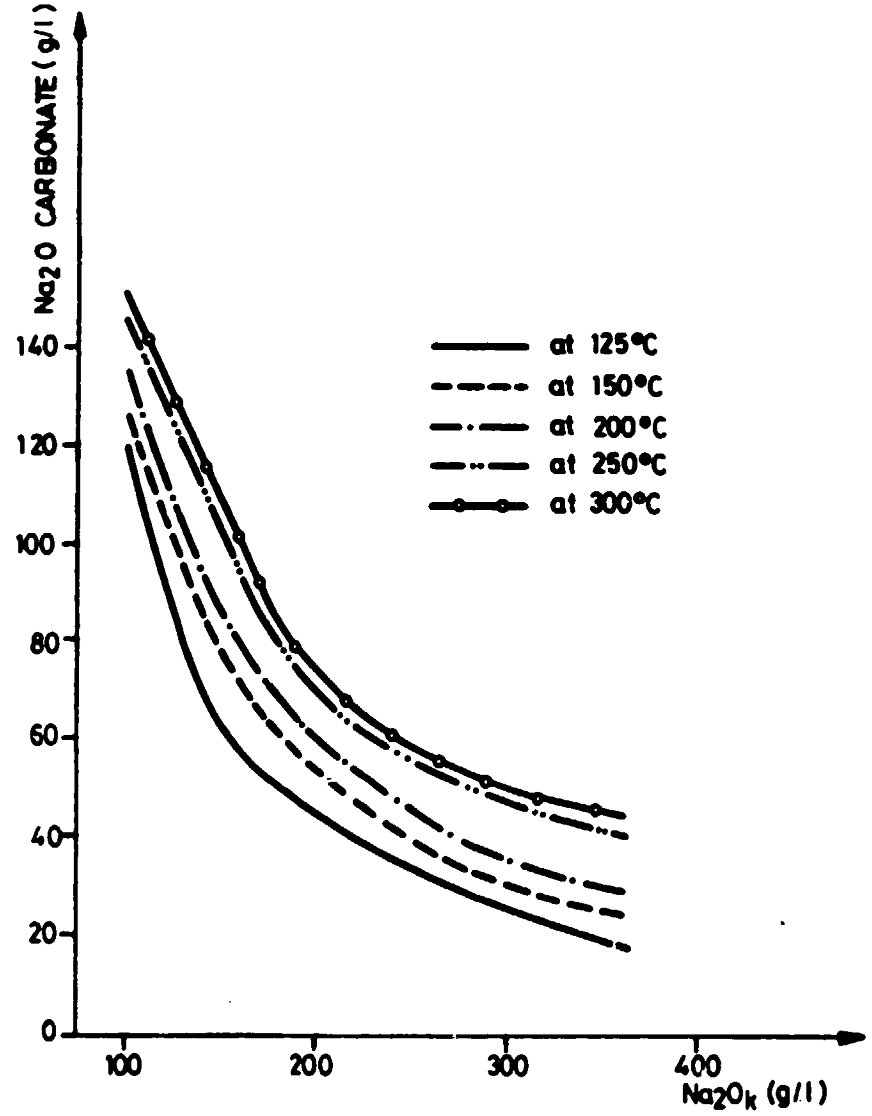


Fig. 2.50

EQUILIBRIUM ISOTHERMS OF Na_2CO_3 AS A FUNCTION OF CAUSTIC CONCENTRATION AND TEMPERATURE AT A MOLAR RATIO OF 3.6

The figures apparently show that the carbonate level of the circuit can favourably be affected by making use of the fact, that the increasing of the caustic Na_2O concentration reduces the solubility of the carbonate soda in strong liquor, and thus the soda can be eliminated. Figure 2.51 illustrates the shaping of the circuit salt level in the Ajka Alumina Plant /Hungary/, as related to the CaO + MgO content of bauxite /59/.

As regards the soda salt separation, the effect of the organic material on increasing the solubility of carbonate and on decreasing the filterability of the separated soda salt can generally be eliminated by heat-treatment of the evaporated strong liquor. The filtered salt is regenerated in order to decrease the NaOH losses by the well-known causticizing reaction,

$$Na_2CO_3 + Ca/OH/_2 \rightleftharpoons 2NaOH + CaCO_3$$

An up-to-date method of soda regeneration is the side stream causticization in the washing series, a version of which is illustrated in Fig. 2.52 /89/. The essence of the method is that /generally/ the overflow of the 3rd stage of the red mud washing series is causticized by lime slurry. It is of basic importance that the concentration of the solution going to causticization should not exceed 40 g/l Na_2O_{caust}. According to the Hungarian plant practice, in case 0.5 mol $Ca/OH/_2$ is added per 1 mol Na_2CO_3, the optimum efficiency is at a temperature of 90 °C and a reaction time of 2 hours. This way 40 per cent causticizing efficiency can be realized.

In case a relatively higher carbonate soda level is admitted in the circuit, this can be maintained often without soda salt separation, simply by side-stream causticization. On the other hand, if the bauxite has high carbonate contamination or if about 10 per cent carbonate soda level is required to be

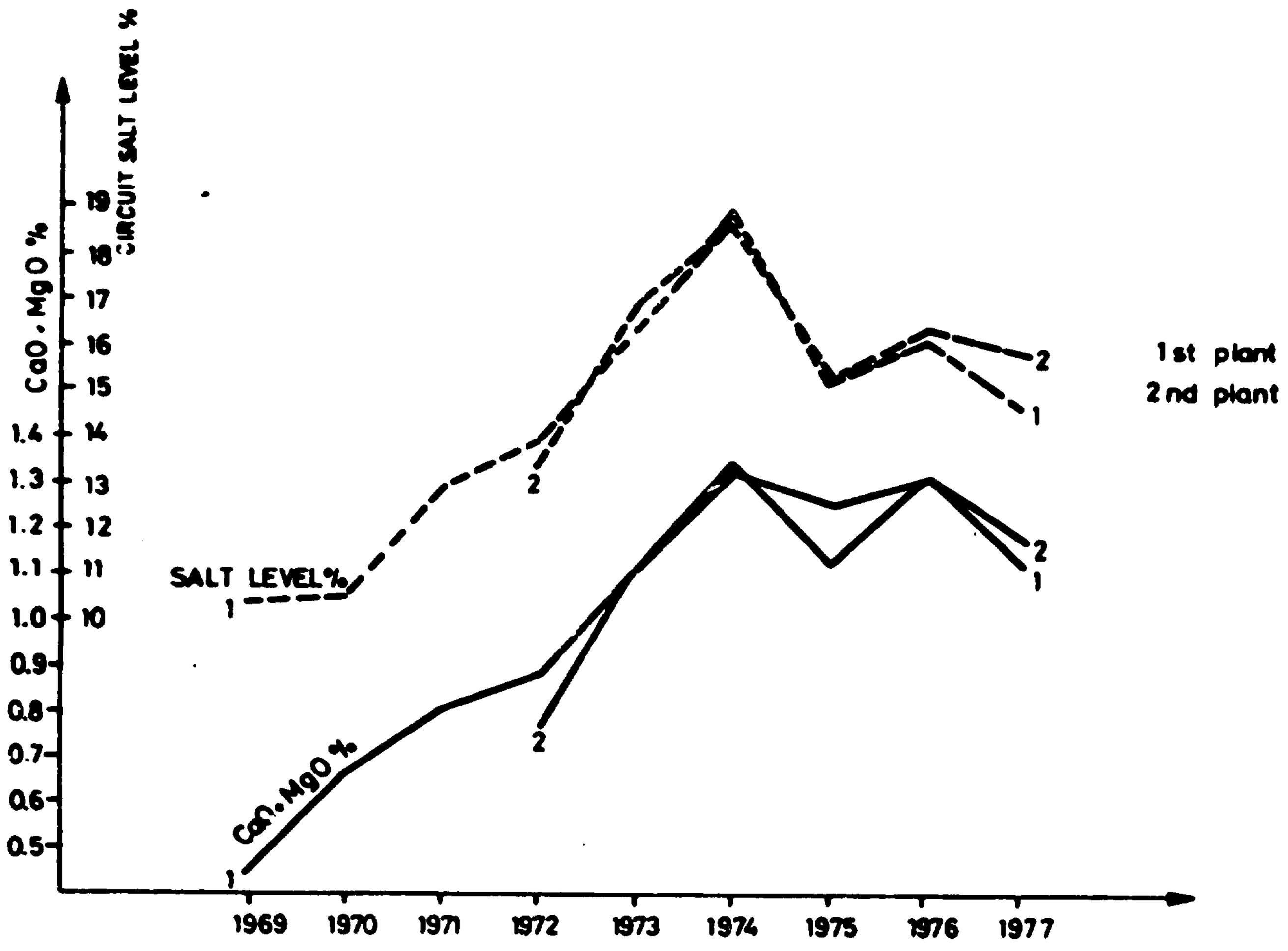


Fig. 2.51
SHAPING OF SALT LEVEL vs. CaO+MgO CONTENT OF BAUXITE IN THE AJKA ALUMINA PLANT

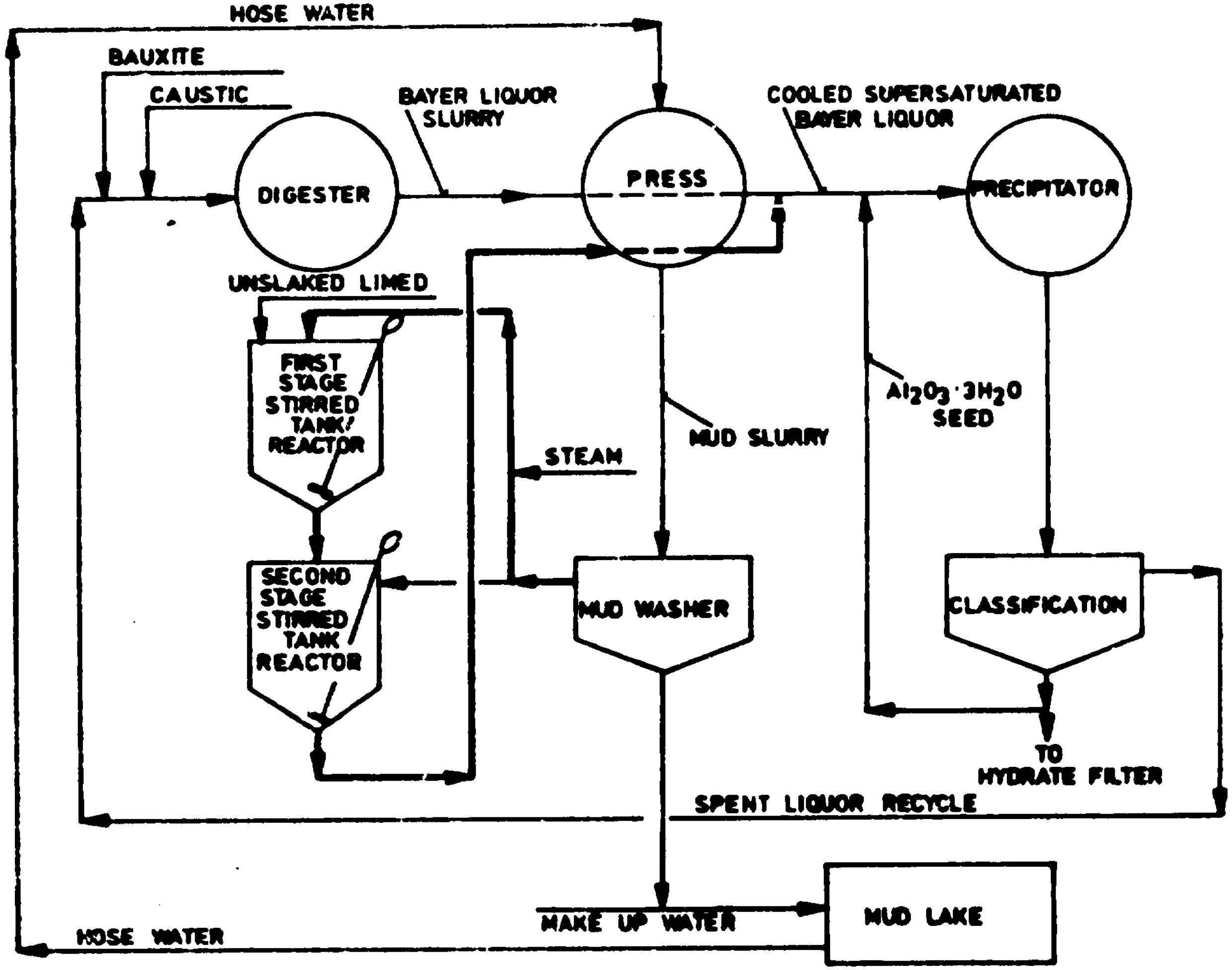


Fig. 2.52

ORMET CAUSTICIZATION CIRCUIT

maintained in the plant, soda salt separation is necessary, too. In such cases the up-to-date method is to causticize the selected salt by dissolving it in the overflow of the given washer, because the equilibrium of the causticizing process does not depend on the starting caustic concentration but on the equilibrium solubility of $CaCO_3$ and $3CaO.Al_2O_3.6H_2O$ of the solution. Unified flow-sheet diagram of soda salt separation by heat treatment and of the side-stream causticization is illustrated in Fig. 2.53 /60/.

ALCAN has elaborated a new method recently for the separation of Na_2CO_3 from the Bayer solutions, which is based on the phenomenon that the solubility of caustic soda in the liquor decreases to its one-eights or -tenth if it is cooled down from + 10 °C to - 10 °C. The Na_2SO_4 concentration decreases in similar proportion, too. The plant techniques introduced in 1974 in the Arvida Alumina Plant resulted in an increase of causticity of the solution from 70 to 90 per cent /61/.

Pechiney recommended recently barium-aluminate treatment for purification of Bayer solutions, which is adequate to remove, besides the carbonate chloride and organic matter, principally oxalate, too. They state that the process is economic if barium-aluminate is continuously regenerated. Caustic content of the solutions can, in all cases, be reduced to below 6 per cent, the chloride will decrease to below 1 per cent and the C_{org} content to below 1.5 per cent of the total Na_2O. Oxalate content of the filtered hydrate decreases to its one-third - one-fourth. Efficiency of precipitation increases by 8-10 kg Al_2O_3/m^3 /62/.

Role of Organic Matter in the Alumina Plant Solutions

Bauxites generally contain 0.05-0.3 per cent organic matter. This amount is usually considerably less in karstic bauxites /0.05-0.15 per cent/ than in latherite bauxites /0.2-0.3 per cent/.

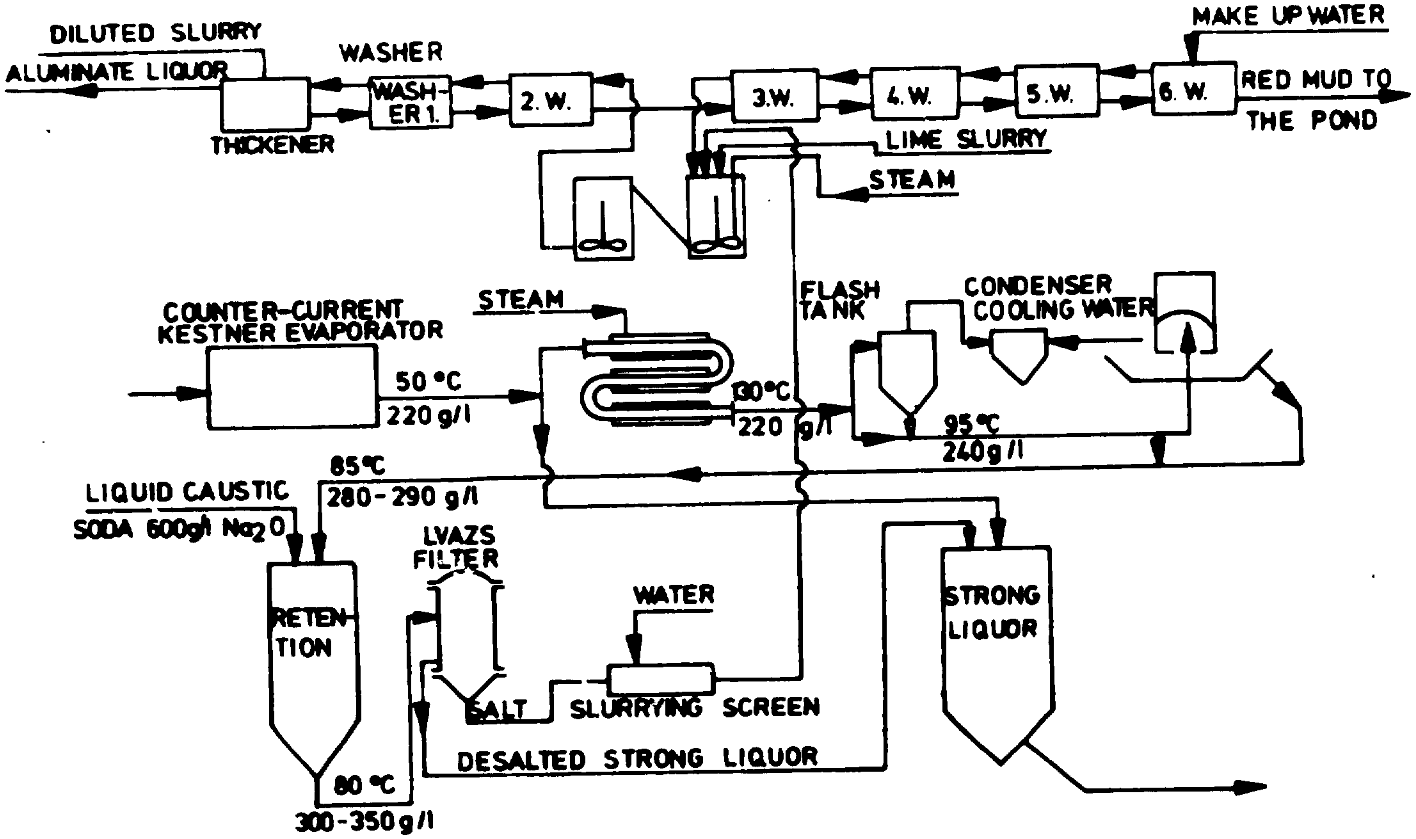


Fig. 2.53

UNIFIED FLOW-SHEET DIAGRAM OF SODA SALT SEPARATION AND SIDE STEAM CAUSTICIZATION

Organic matter content of bauxites partly dissolves in the liquor during digestion and it is enriched to equilibrium level. Apart from the bauxite, considerable organic contamination of the Bayer circuit comes from the desintegration of starch /flour/ charged for promoting the red mud settling, too.

Accumulation of organic matter in the Bayer circuit has unfavourable effects on nearly all the process stages. In spite of this, the problem has not got a final solution yet. In the following, first the role of organic matter in the Bayer technology, than the problems arising from its quantitative and qualitative determination, and finally the elimination possibilities of technological difficulties related to the effects of organic matter will be discussed.

Effect of Organic Matter on Technology

Development of the organic matter equilibrium in the Bayer circuit is illustrated in Fig. 2.54, by the organic matter balance of the Almásfüzitő Alumina Plant /Hungary/ recorded in 1962. The figure shows that about 30 per cent of the organic matter came from the flour charged as settling aid and that not only the quantity separated by hydrate, but also that separated by carbonate salt has a significant role in the formation of the equilibrium /63/.

In the course of analysing certain operations of the Bayer technology, the technical literature deals especially with the problem of precipitation /64, 65/. As regards organic matter fractions, especially sodium-oxalate is considered to be disadvantageous, as adsorbed on the surface of the hydrate significantly decreases its seeding effect, and the efficiency of precipitation, too. Fig. 2.55 illustrates the precipitation data gained from the permanent processing of Weipa bauxites. It can be well observed that the organic matter content increased from 4.6 g/l to 6.9 g/l, and due to triplication of sodium-

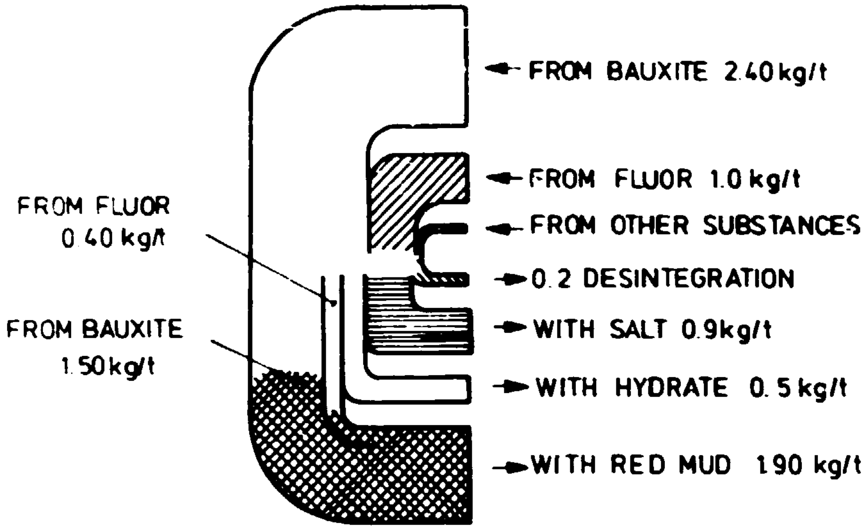
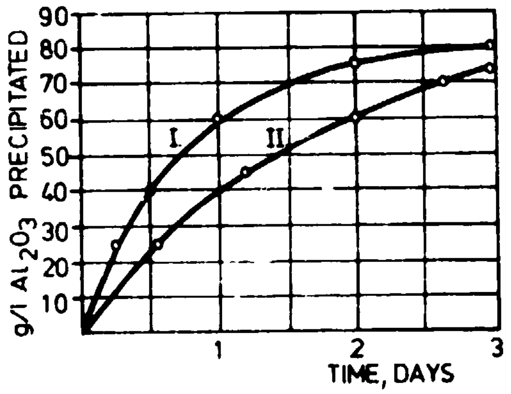


Fig. 2. 54

ORGANIC MATTER BALANCE IN THE ALMÁSFÜZITÖ ALUMINA PLANT IN 1962



I AFTER HAVING PROCESSED EUROPEAN BAUXITE FOR A LONG TIME
II AFTER HAVING PROCESSED WEIPA BAUXITE FOR 5 MONTHS

Fig. 2.55

DECOMPOSITION CURVES (EUROPEAN AND WEIPA BAUXITES)

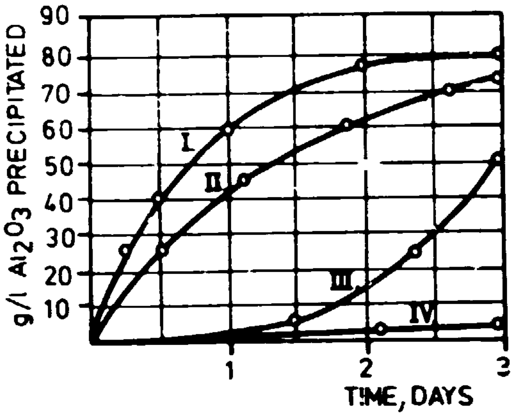
PREGNANT LIQUOR 150 g/l Na_2O, 150 g/l Al_2O_3, MOLAR RATIO 1.645

humanite the precipitation efficiency decreased considerably. At the same time, the fraction below 30 μm of $Al/OH/_3$ increased from 15 to 35 per cent. The study /65/ points also at the fact that the disadvantageous effect of sodium-humanites on the precipitation efficiency as compared to sodium-oxalate is greater by one order of magnitude as it is shown in Fig. 2.56 and 2.57.

According to Bell's tests /66/, 70 per cent of the starch is bound very hard on the surface of the red mud; 10-15 per cent is desorbed in the settlers and about 5 per cent in the washers. Other organic matters occurring in the plant liquors have generally a smaller effect on the adsorption of the starch.

According to Hermann's and Jung's tests /67/, when processing Gove and Weipa bauxites 61.7 per cent of the organic matter entering the circuit leaves with the red mud and 25.6 per cent is transformed into sodium-oxalate. As the solubility of sodium-oxalate depends on the Na_2O concentration, the $Na_2C_2O_4$ accumulates in the hydrate wash water.

The organic matter contributes significantly to the oversaturation of aluminate solutions by soda. This causes technological difficulties and surplus expenses in soda salt separation and evaporation. On the other hand, high soda concentration decreases significantly the efficiency of precipitation and promotes scaling. The effect of organic matters /humic acids/ on the solubility of carbonate soda is shown in Fig. 2.58. The figure clearly shows that, due to the unfavourable filterability of the poorly crystallized soda, the soda content of the solution after filtration is about two-fold of the solution with no organic matter.

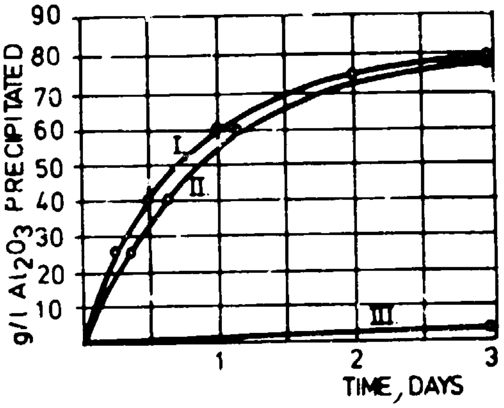


I. WITHOUT ADDITIVE
II. 0,1 g/l Na-HUMINATE
III 5 g/l Na-HUMINATE
IV. 10 g/l Na-HUMINATE

Fig. 2.56

LABORATORY DECOMPOSITION CURVES IN THE PRESENCE OF SODIUM HUMINATE

PREGNANT LIQUOR: 150 g/l Na_2O; 150 g/l Al_2O_3; MOLAR RATIO 1.645



I. WITHOUT ADDITIVE
II 40 g/l Na OXALATE
III. 40 g/l Na HUMINATE

Fig. 2.57

LABORATORY DECOMPOSITION CURVES IN THE PRESENCE OF SODIUM OXALATE AND SODIUM HUMINATE

PREGNANT LIQUOR: 150 g/l Na_2O; 150 g/l Al_2O_3; MOLAR RATIO 1.645

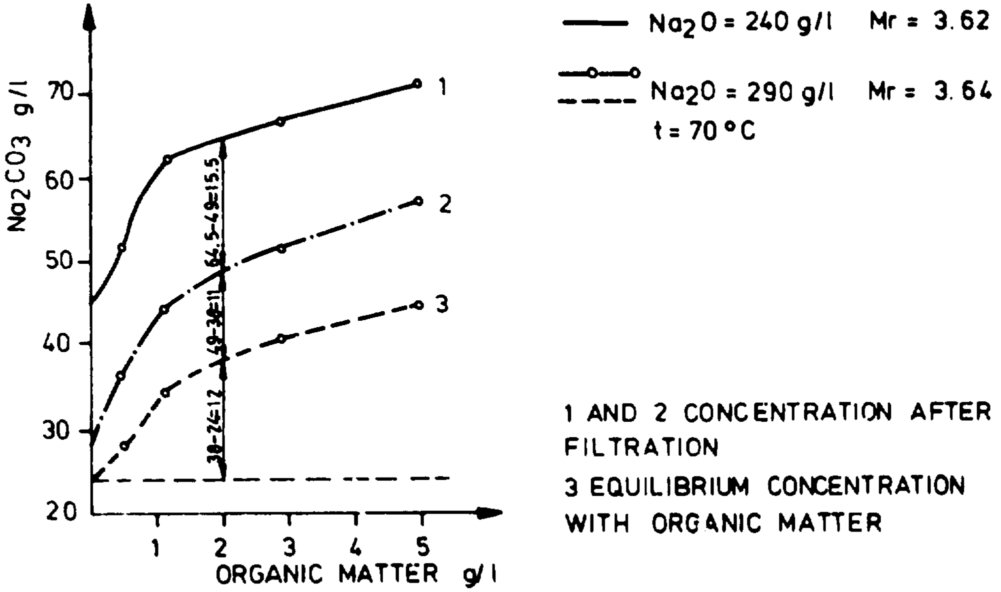


Fig. 2.58

EFFECT OF ORGANIC MATTER ON THE SOLUBILITY OF SODA IN SYNTHETIC STRONG LIQUOR

Identification of Organic Matter of the Solutions

An indispensable condition of revealing and resolving the organic matter problem is to identify not only the total organic material content, but also its different fractions as regards both quality and quantity.

A reliable measuring method of the total organic matter content is based on peroxi-disulphate oxidization /68/. Elaboration of detailed fraction analysis has been solved recently by Hungarian and Canadian researchers /36, 69/. For the illustration of the compositions of different aluminate solutions Table 2.11 based on the tests of Hungarian researchers, is presented /36/.

Lever /69/ classified the organic matters of the Bayer circuit into three groups:

- humic acids, starting degradation product of which has a molecular weight of above 500
- intermediate degradation products forming "building blocks" of the great humin molecules, such as benzine-carboxilic acids and phenolic acids
- low molecular weight degradation products, such as formic acid, acetic acid and oxalic acid etc.

Lever examined liquor samples of two plants processing Jamaican bauxites. He found 8.5 g/l C_{org} content in the liquor of of the plant operating at 135 °C digestion, and 15 g/l C_{org} in that operating at 240 °C digestion. The proportion of the humic acid in both liquors was 25 per cent, whereas that of the intermediate degradation product was 22 per cent. He found, however, characteristic deviations in the group of intermediate degradation products, in the amount of certain fractions.

Distribution of Organic Components in Aluminate Solutions

Table 2.11

Sample	Total amount of organic carbon g/l; g/100 g	Components expressed in organic carbon /in the % of the total amount of org.carbon/						
		C_1-C_5 Fatty acids	Aliphatic dicarboxilic acids	Aromatic poly-carboxilic acids	Humic acids	Amino acids	Fulvic acids	Non-amino acids containing N
Model aluminate solutions								
1.	0.539	22.9	15.6	28.2	1.2	3.3	28.8	not measured
2.	0.435	13.0	29.5	8.1	14.5	4.9	22.1	8.5
3.	4.81	23.1	56.5	0.0	0.0	13.5	3.1	1.9
Plant products								
Plant liquor of Almásfüzitő	6.62	52.8	10.9	11.5	3.4	3.3	13.3	4.4
Alumina hydrate of Almásfüzitő	0.032	43.7	50.8	1.3	5.1	not measured		
Plant liquor of Giulini	16.1	28.5	12.0	27.5	1.0	0.6	26.8	3.6

Reduction of the Unfavourable Effect of Organic Matter

At present, principally in plants processing tropical bauxites, regular separation of oxalate content is performed, utilizing the fact that the solubility of sodium-oxalate is depending on the Na_2O concentration. In Hungary, oxidization of amino acids by sodium-hypochlorites is applied on plant level, to uphold the equilibrium. Successful tests were performed with different adsorbents, too, but the overall spreading of this method has up to now been restricted by the relatively high cost of the adsorbents and by the problem related to their regeneration.

In the European alumina plants organic matter is removed even presently with soda salt. In such cases, however. care must be taken not to return the organic matter into the system after causticization. To solve this problem, soda salt is roasted at some places, or utilized in other chemical plants or purified from the major part of the organic material by crystallization.

For oxalate removal, separate evaporation of hydrate wash water can be taken into consideration.

In the course of processing, certain degradation of the organic matter takes place spontaneously. This phenomenon serves as the basis for researches on the oxidative destruction.

VANADIUM AND GALLIUM RECOVERY AS BY-PRODUCTS

Among the trace elements of bauxites, gallium and vanadium are of special importance as they accumulate in the Bayer circuit to such an extent which makes possible their industrial recovery. Most important raw materials of gallium production at present are the bauxite and the alumina plant liquors, respectively, all over the world, and they can also be regarded in several countries as not quite exclusive but the most important raw material sources of V-production, too.

Vanadium Recovery

Hungarian researchers /70/ established by means of electron-micro probes that the dispersion of vanadium in bauxites is statistically even, that is, neither separate V-mineral nor local accumulation can be detected. Based on dissolution tests the amount of dissolved V is considered to be proportional to the hematite content of bauxites, and the partial dissolution is attributed to the portion built into the goethite lattice as an isomorph contaminant, which can not be dissolved by the traditional technology.

Under usual digestion conditions 30-40 per cent of the bauxites' V-content can be dissolved in the digestion liquor in the form of Na_3VO_4.

The degree of dissolution deviates in case of different bauxite types. Roasting of bauxite increases the amount of dissolved vanadium, due to decomposition of the goethite lattice.

As regards V-equilibrium, not only the Na_3VO_4 content of plant liquors has to be taken into account, but their Na_2PO_4 . . NaF and Na_3AsO_4 content, too, as these form octahedron crystals of the composition

$$2Na_3VO_4 \cdot NaF \cdot 19H_2O$$

$$2Na_3PO_4 \cdot NaF \cdot 19H_2O$$

$$2Na_3AsO_4 \cdot NaF \cdot 19H_2O$$

which can substitute each other isomorphically.

Solubility of the V_2O_5-P_2O_5-F salt system, in function of the temperature, in a liquor of 130 g/l Na_2O_c and a molar ratio of 4 is illustrated in Fig. 2.59, which shows that the solubility of V_2O_5 decreases significantly by cooling-down of the solution /71/. This phenomenon provides the basis of vanadium salt separation.

Equilibrium concentration of V_2O_5 is affected by the amount of calcite or dolomite impurities fed with the bauxite, CaO added to the bauxite in order to intensify digestion, or utilized in side stream causticization in the washing lines.

V_2O_5 dissolution in function of the V_2O_5 concentration of the digestion liquor is illustrated in Fig. 2.60, whereas Fig. 2.61 shows the changes of V_2O_5, P_2O_5 and F content, in function of CaO content of the red mud /71/.

V-salt separation from the alumina plant liquors is generally performed at present by cooling down the evaporated liquor /strong liquor/ to a relatively low temperature. This way a salt with rich V content can be crystallized even from liquors of considerably low P_2O_5 content. This is shown by the curves of Fig. 2.62, where the equilibrium V_2O_5 concentration is illustrated in the function of crystallization period, when cooling liquors with different P_2O_5 content /71/.

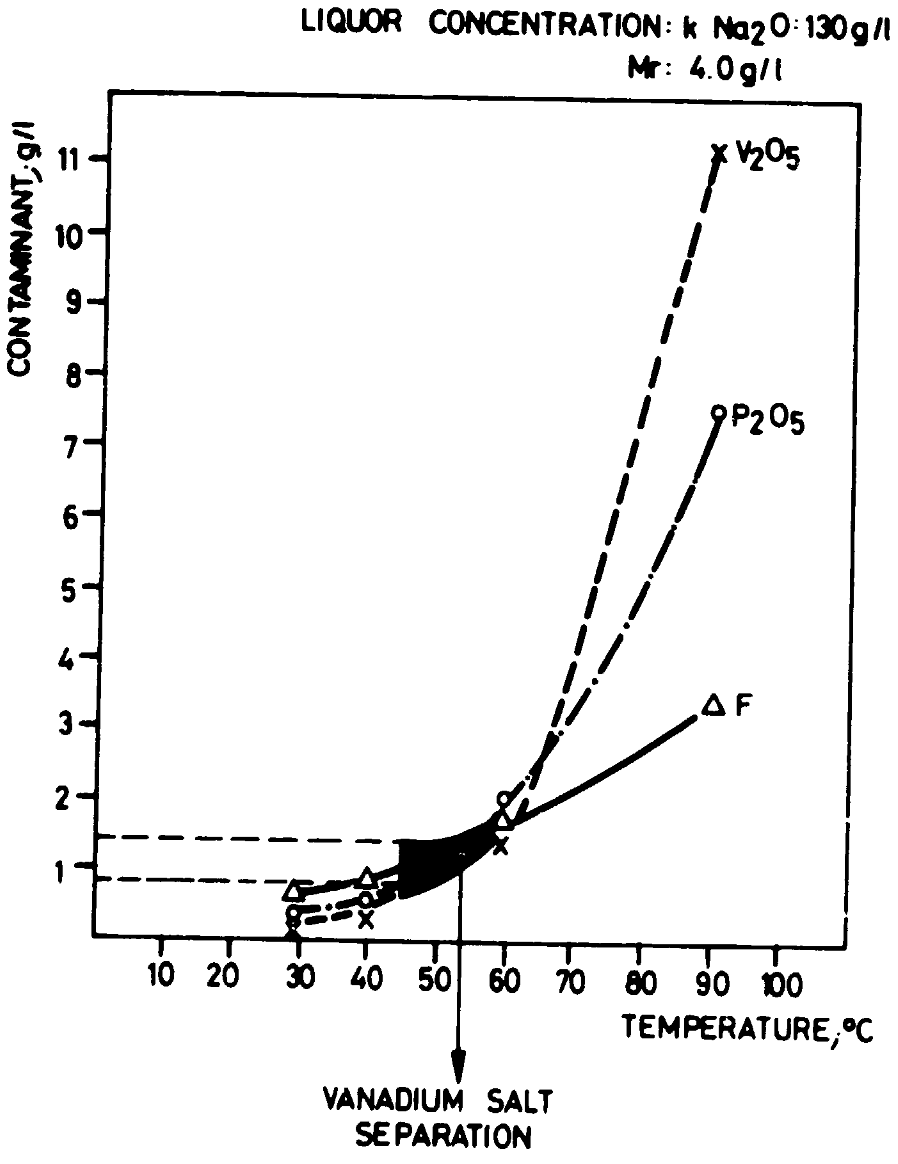


Fig. 2.59

CHANGE OF SOLUBILITY OF VANADIUM-PHOSPHORUS-FLUOR SALT SYSTEM vs. TEMPERATURE

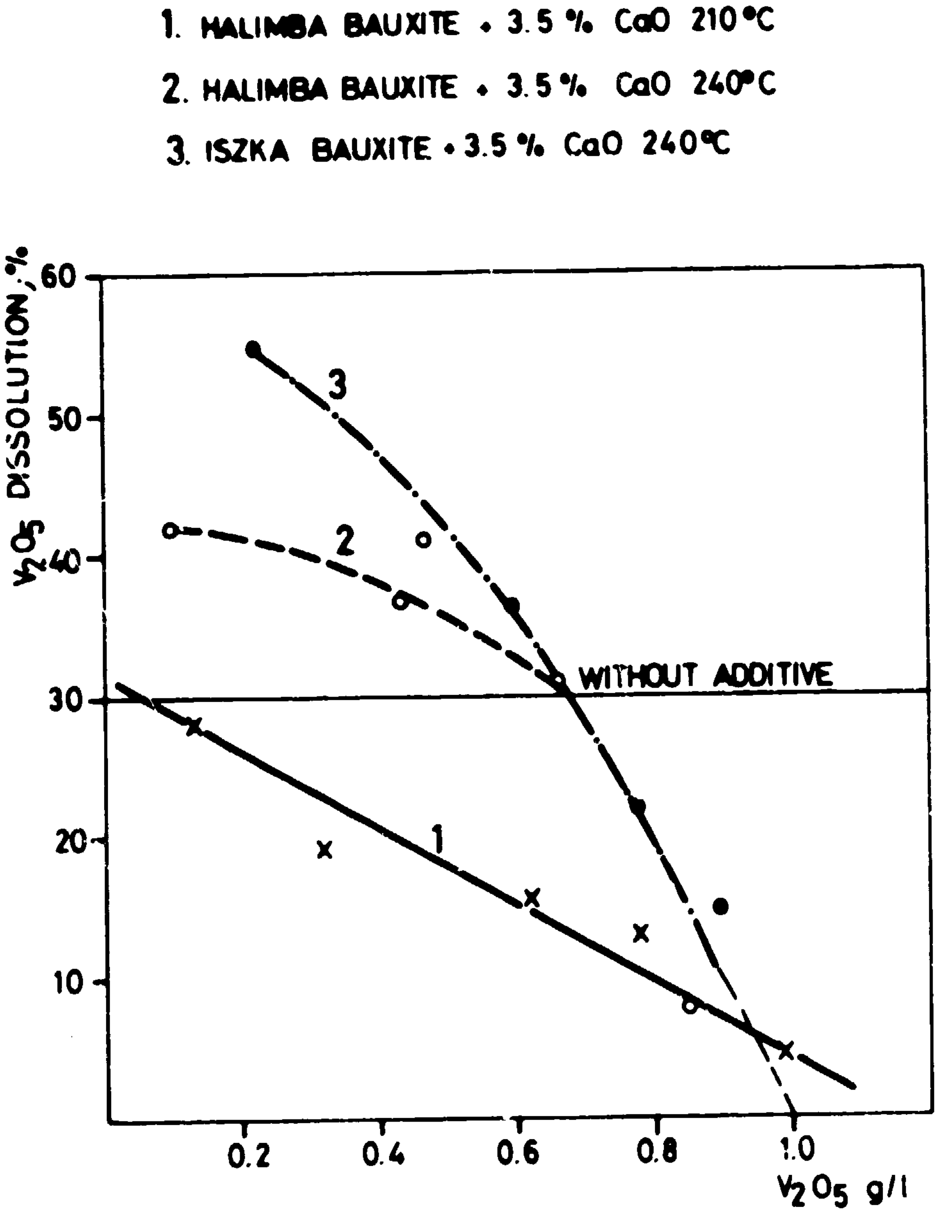


Fig. 2.60

V_2O_5 DISSOLUTION vs. V_2O_5 CONCENTRATION IN THE LIQUOR IN CASE OF DIGESTION WITHOUT ADDITIVES AND WITH 3.5 PER CENT OF CaO, RESP.

DIGESTION LIQUOR (PLANT): k Na_2O : 234.6 g/l
Al_2O_3 : 121.6 g/l
V_2O_5 : 0.84 g/l
P_2O_5 : 0.60 g/l
F : 1.00 g/l

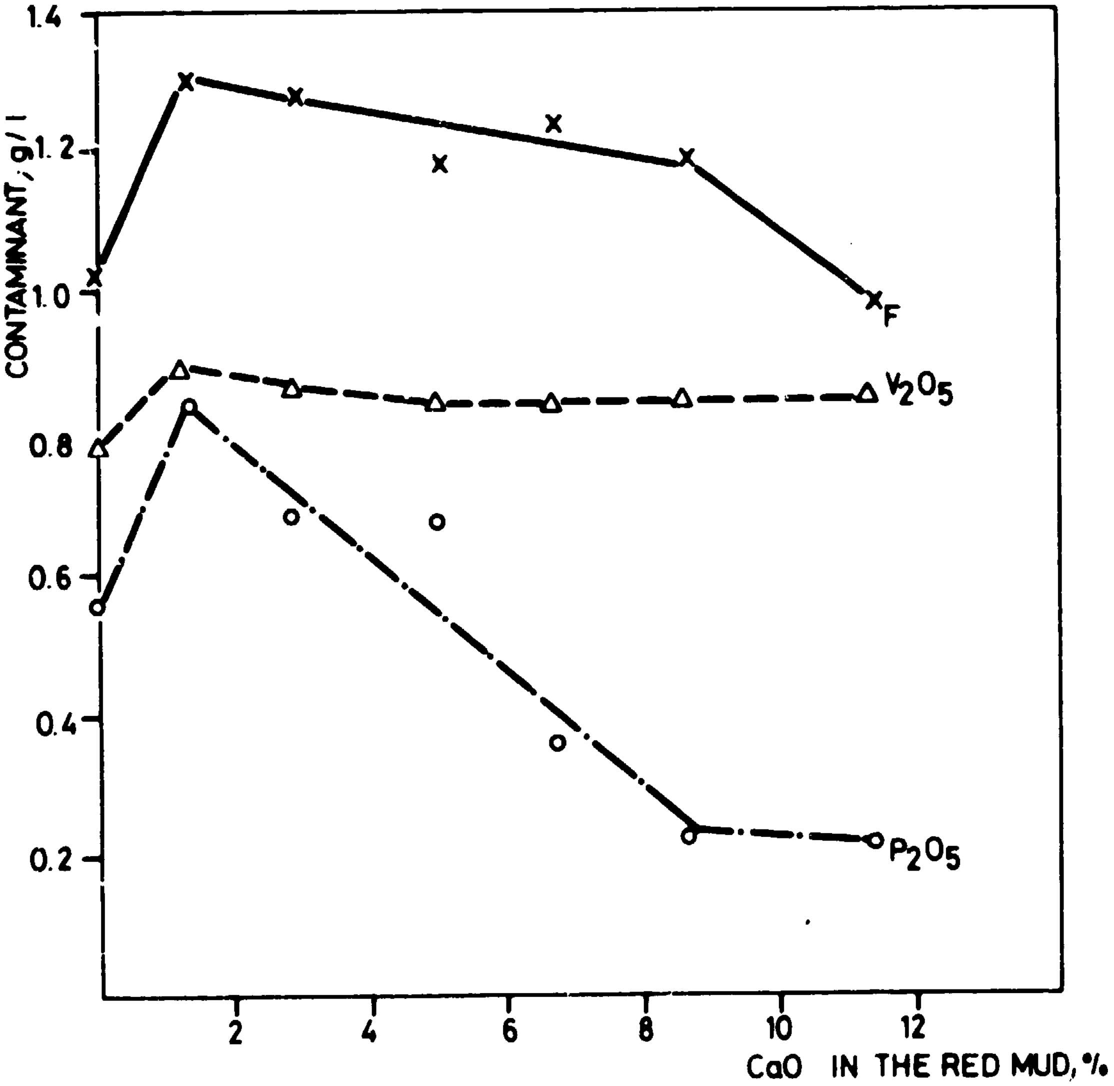


Fig. 2.61

CHANGE OF V_2O_5, P_2O_5 AND F CONTENT OF ALUMINATE LIQUOR IN CASE OF DIGESTION WITH INCREASING AMOUNT OF CaO ADDITIVE (HALIMBA BAUXITE)

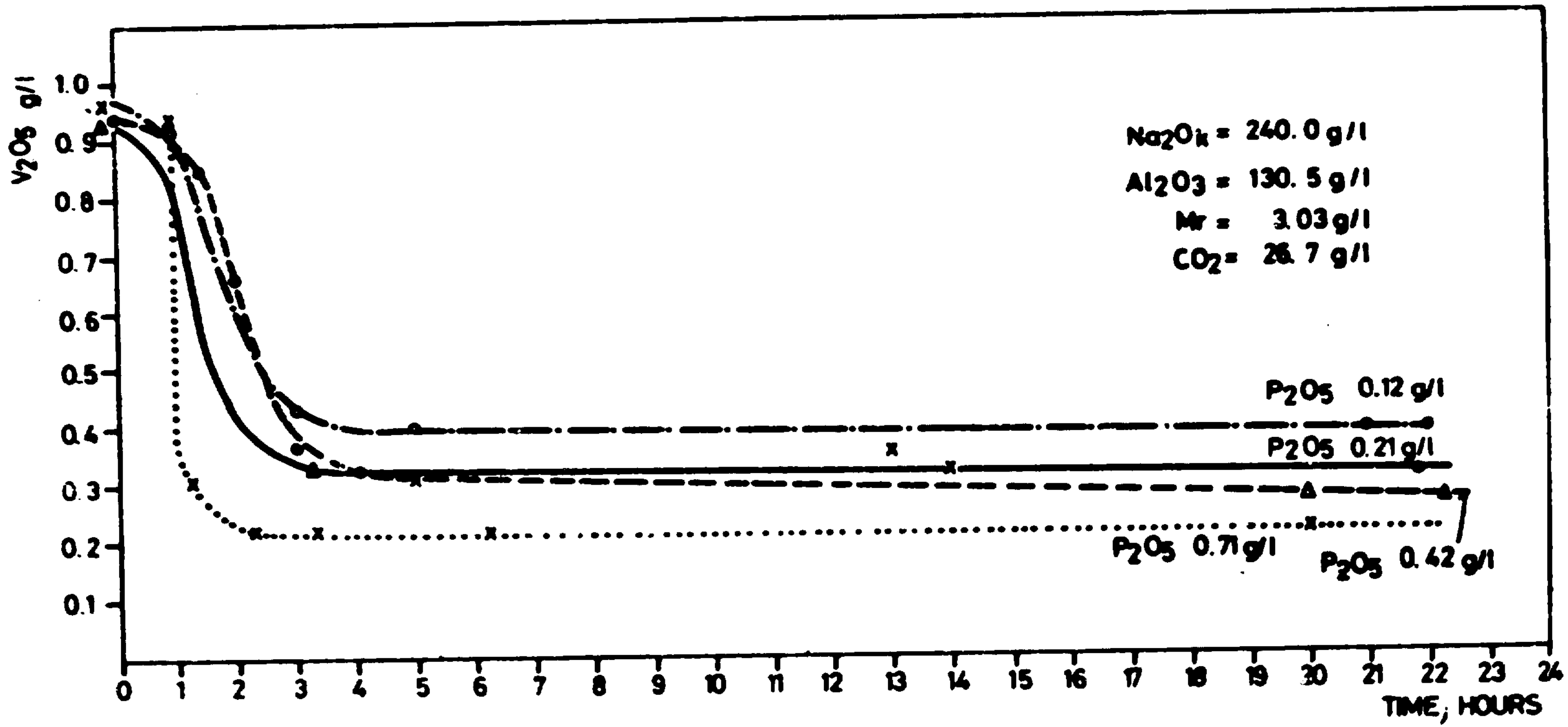


Fig. 2.62

VANADIUM EQUILIBRIUMS AT DIFFERENT P_2O_5 CONTENTS OF THE STRONG LIQUOR

It is expedient to separate first a soda salt with low V_2O_5 content at a higher temperature, and to produce crystals of rich V content by further cooling of the filtrate. For the sake of illustration Table 2.12 displays some data with respect to the composition of V-salts of Hungarian alumina plants /72/.

Composition of V-Salts

Table 2.12

Components	Almásfüzitő	Ajka	Magyaróvár
Adherent moisture	34.6 %	37.2 %	44.7 %
F	3.4	3.2	3.8
V_2O_5	12.5	6.5	13.0
P_2O_5	13.5	16.9	16.5
Na_2CO_3	1.4	5.9	3.2
Na_2[illegible]	1.0	1.4	4.2
Alumina hydrate	27.2	30.5	17.0

V-salt is generally processed into V_2O_5 containing products of various purity, or into ferrovanadium. Most of the V_2O_5 production processes can be characterized by the following process stages /73/:

1. Beneficiation, i.e. generally a fractionized crystallization.
2. Dissolution of the crystal, production of vanadate solution.
3. Purification of vanadate solution, a determining factor as regards the purity of the final product. This process can be performed by different methods, based on:

a/ removal of impurities /crystallization or bounding of the impurities/ /74/

b/ bounding of V/methods applying line or ammonium salts//75/

c/ ion-exchanging /with liquid ion exchangers or with synthetic resins/ /76, 77/

d/ electrochemical separation of V_2O_5 /78/.

Fig. 2.63 illustrates the scheme of V_2O_5 production applied in Hungary.

Gallium Recovery

Ga is a highly significant rare metal of present times. Its production on industrial scale which, in the given case, involves some tons/year order of magnitude, dates back to a few decades only /79/. Ga content of bauxites is generally between 0.002-0.006 per cent. During digestion 60-70 per cent of this amount is dissolved in the sodium-aluminate solution and accumulates to 0.15 to 0.25 g/l.

The first Ga-producing methods were based on the fact that Ga-hydroxide has more acidic characteristics than the aluminium hydroxide does. Beja /80/ and Farary /81/ extracted Ga from Ga- and Al-hydroxide mixtures. The sudden development of Ga-production is attributed to Pierre de la Breteque's /82/ invention, who discovered that the gallium can directly be electrolysed from the plant aluminate solutions on a continuously purified Hg-cathode. Further development of this invention was the application of Na-amalgam cathode and the recognition of amalgam reduction, which led to the developing of different construction intensive cells /83/.

Process flow pattern of the amalgam cathode process is illustrated in Fig. 2.64 /84/.

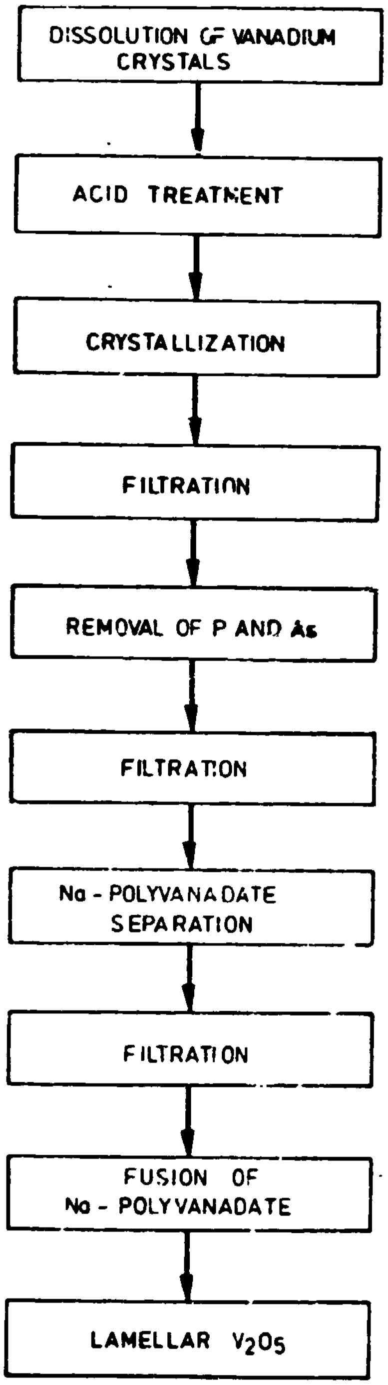


Fig. 2.63

TECHNOLOGICAL FLOW-SHEET OF PRODUCTION OF LAMELLAR V_2O_5

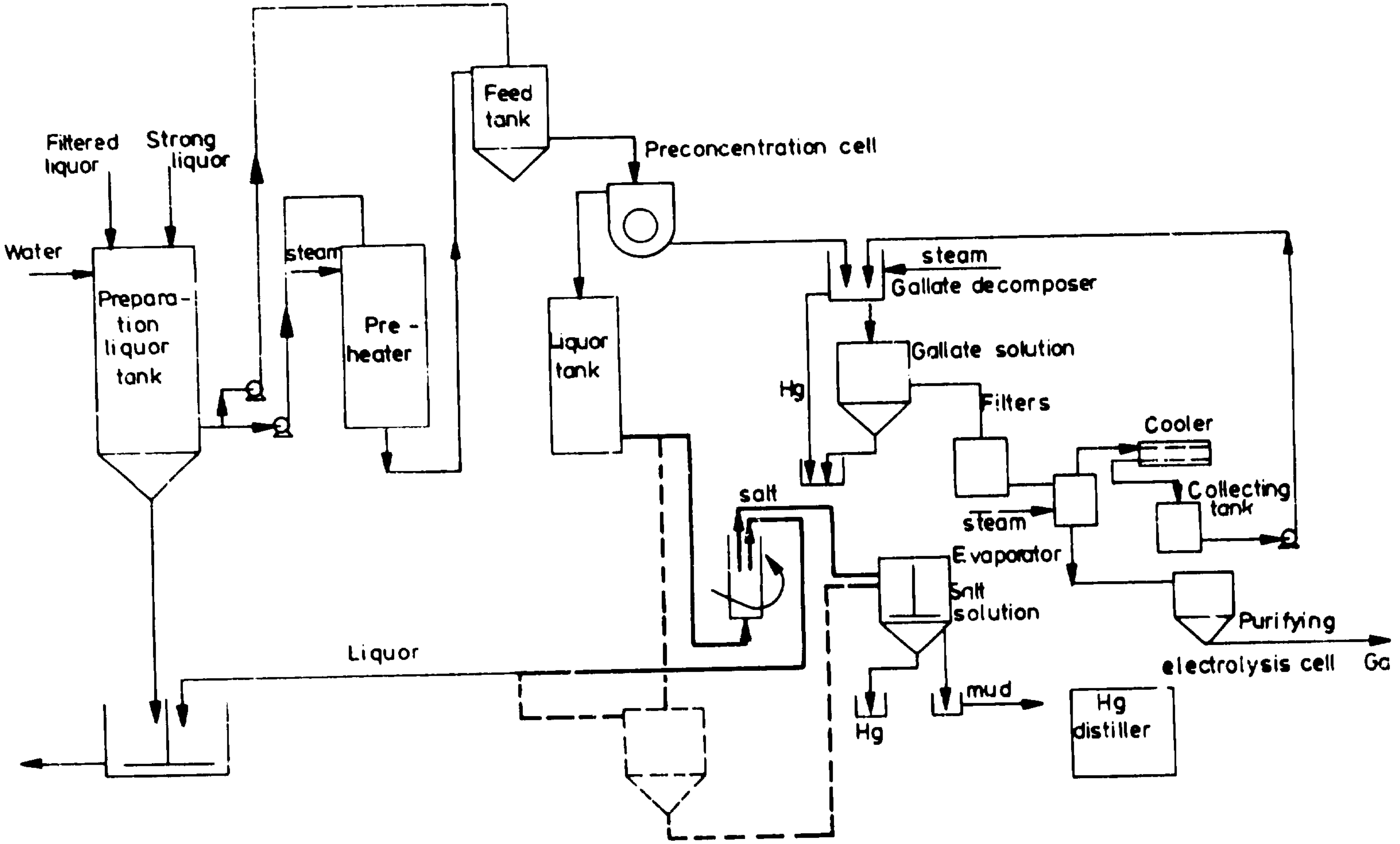


Fig. 2. 64

FLOW - SHEET DIAGRAM OF GALLIUM PRODUCTION

The complex technology of the Ajka Alumina Plant for Ga-production of 6N purity consists of the following main stages:

1. Purification of liquor before electrolysis.
2. Beneficiation electrolysis, separation of Ga in an amalgam cathode electrolysis cell.
3. Desintegration of Ga-amalgam by producing Na-gallate, and filtration of the solution.
4. Fine electrolysis and preliminary acid purification, producing 4N purity metal.
5. Electrolytic refining, in more stages if required, up to even 6N purity.
6. Zone smelting.

High purity Ga_2O_3 production has to be mentioned also which can be realized starting from Na-gallate solution or Ga metal.

In spite of the relatively high production and up-to-date methods, a worldwide intention has been experienced to avoid application of Hg which is an environmental contaminant, harmful to health, and to extract Ga on a solid cathode. It is well known from the technical literature that principally the V_2O_5 and organic content of the plant liquors sets limits to this process /85, 86/. In the recent years several solutions have been suggested to non-Hg cathode recovery of Ga from alumina plant liquors, by preliminary intensive purification of the liquor.

Two main trends can be mentioned:

- recovery on solid cathode or on Ga-Al liquid cathode,
- extraction from alkaline medium /87, 88/.

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