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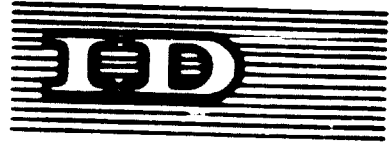
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DEVELOPMENT AND PROSPECTS OF THE BAYER SYSTEM OF ALUMINA PRODUCTION^{1/}

by

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Hungary

^{1/} The views and opinions expressed in this paper are those of the author and do not necessarily reflect the views of the Secretariat of UNIDO.

We regret that some of the pages in the microfiche copy of this report may not be up to the proper legibility standards, even though the best possible copy was used for preparing the master fiche.

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SUMMARY

The Bayer process known for about 80 years, by means of which approximately 95 per cent of alumina produced all over the world is processed, has not changed basically since its introduction. However, in the last 25 years, keeping abreast with advances in techniques, the process has undergone substantial development. The Bayer process lends itself to the processing of good quality bauxites from which, according to their tri- or monohydrate character, two specific variations have been developed, namely European and American. Substantially these differ one from another only in their temperature and concentration conditions; both adapt themselves to an increasing extent to the quality of bauxite processed.

From the metallurgical point of view alumina production may be considered an enrichment characterized by the efficiency of the process, its specific consumption of reagents and energy, as well as the extent of specific capital investment. These factors are determined by the technical level of the realization of the process and by the bauxite composition to be processed. The Bayer process is essentially a solvent circuit, energy consumption from which is determined the extent of temperature difference brought about and the efficiency of counter-current heat recuperation. The latter can be realized with continuously operating equipment only. A further important condition of its rentability is the selection of high-capacity equipment units as well as the realization of a technological optimum. In plants operating with up-to-date technology the effect of the bauxite quality is less sensitive to the efficiency of the process and its technical-economic characteristics in consequence of the notable development of processing techniques; this, however, does not apply to alumina recovery and caustic soda consumption.

Taking into account the ever deeper knowledge of process chemism and the development of investigation methods it may be expected that on the basis of laboratory investigations more and more accurate consequences will be drawn as to the expected technological behaviour of bauxites, and this will pave the way for further improvements of the technological process. The effect of mineral modifications of aluminium hydroxide and of silica and titanium oxide on digestion chemistry may already be considered to be cleared. Iron oxide modifications have first of all an influence on red mud settling, appreciation of which should not be neglected. As regards elimination of other impurities, industrial solutions are already available at present; furthermore recuperation of valuable elements (Fe, V, F, Ga etc.) on an industrial scale is also solved. Decomposition kinetics, which in the recent past was still considered a "difficult art", may be set in equations.

In the course of alumina production large-size equipment serving the exclusive purpose of alumina production has been developed. As a further means of development, introduction of autogenous bauxite milling has also been taken into consideration. Continuous digestion at high temperature ensuring a good heat recuperation has been realized, and in the near future introduction of digestion over 250° C may be expected, perhaps in the form of tube digestion. For the settling of red mud

one-chamber settling tanks of 30 to 36 m ϕ are used and for the filtration of red mud continuously operating drum filters and pressure filters with a large surface (230 m²) are put into service. The pneumatic automatic pressure filters supply adequately transportable storable red mud with a moisture content below 30 per cent.

Development of decomposition technology has resulted in the increase of tanks (2000 to 3000 m³), further in the continuity of operation and the realization of air-lift agitation with low energy consumption. In evaporation the trend of development is likewise an increase in size (up to 1400 m² corpus), usage of mixed or counter-current equipment with a view to decrease scale formation and better heat utilization. For calcination in general furnaces of a length of 75 to 110 m are used and efforts are being made to solve preliminary drying of the hydrate and introduction of dust cyclones.

With the development of the Bayer process the necessity presented itself to elaborate quick automatic analyzers of raw materials, intermediate and final products with continuous operation which from the point of view of automation and optimization of the process appear to be of decisive importance, and thus the alumina plants reached the stage of realizing computer control.

From the technological point of view processing of poorer quality ores and recuperation of useful components (Fe, Ti etc.) merits certain attention. By means of equipment development, automation as well as computer control, energy, working hours and investment costs have decreased considerably; however, development does not stand still and in the near future appreciable results may be expected.

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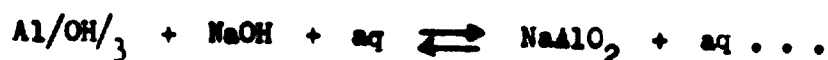
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INTRODUCTION

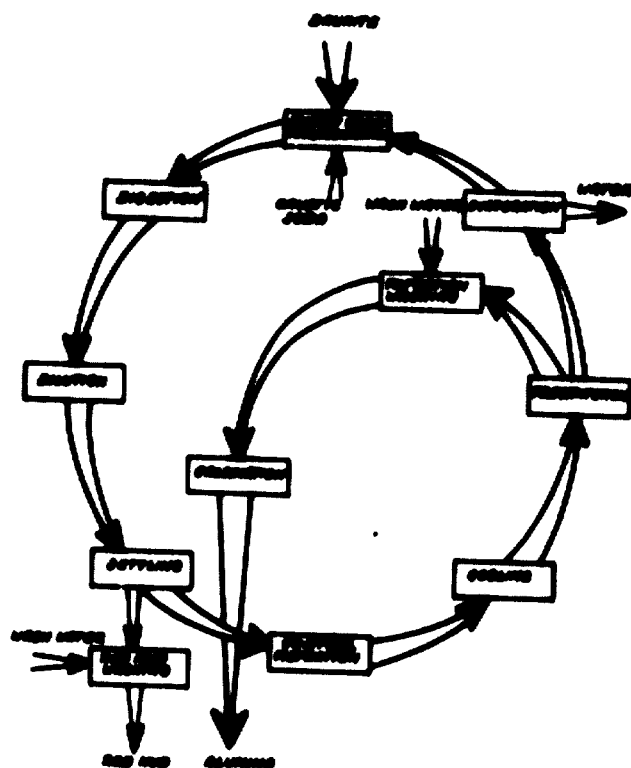
1. At present about 95 per cent of the world's alumina is produced on the basis of the Bayer process known for about 80 years. This process is based on the realisation of K.I. Bayer that the reaction



is reversible. The dissolution reaction is endothermal (11-12 Mcal/mol Al_2O_3). By means of temperature and NaOH-concentration variation the reaction can be lead in one direction or another. The basic principles elaborated by Bayer have not changed substantially, but the process itself, in keeping with the general advance of techniques, underwent considerable development, especially in the last 25 years. This paper endeavours to summarize the experiences characterising the present technical level of the process, first of all the chemism of the individual procedures, characteristic phases of technology, development of the most important equipment and the possibility of automation. Reference is made to the trend of further development of some presently accepted solutions.

2. The Bayer process lends itself to the processing of high quality bauxites. However, if combined with additional technological elements, processing of bauxite with high silica content and some other alumina-containing ores may be taken into consideration by this method. According to the trihydratic ($\text{Al}(\text{OH})_3$) or monohydratic ($\text{AlO}(\text{OH})$) character of the processed bauxite, two characteristic variants of the process are known: one is often called the American process and the other the European. Technological flow-sheets of these two processes are practically identical (figure 1), and only temperatures and concentration-ratios are substantially different. Within the two characteristic variants several solutions have been developed regarding individual technological procedures, taking into consideration the raw material situation, price conditions, technical level and other circumstances given. Thus for instance, caustic soda losses are made up by using NaOH or both Na_2CO_3 and lime.

Figure 1
General flowchart of the Bayer process



I. GENERAL CHARACTERISTICS OF THE PROCESS

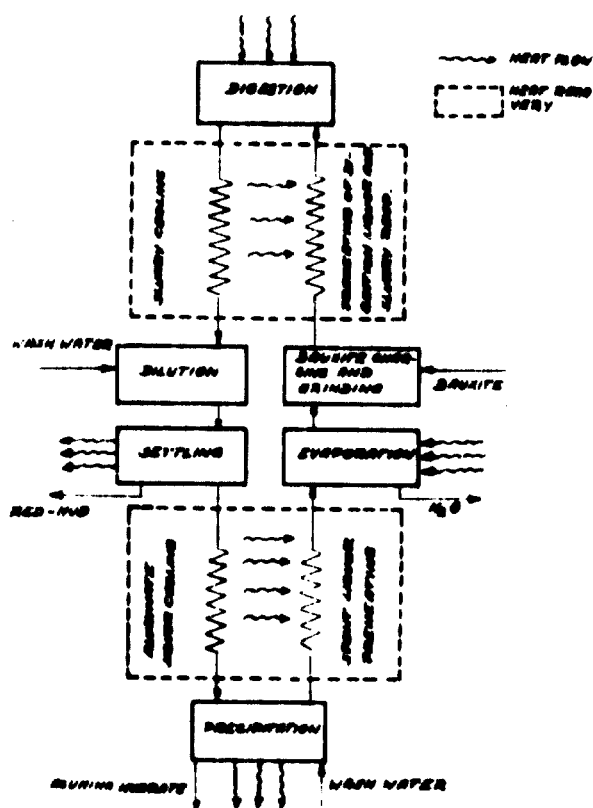
3. The production of alumina from the point of view of the manufacture of aluminium as a metallurgical process may be considered to be a chemical enrichment, its object being to eliminate accompanying contaminations from Al_2O_3 in the bauxite and to render it suitable for metallurgical processing. As an enriching process it may first of all be characterized by its efficiency (Al_2O_3 recovery), further by the specific use of reagents and energy required for the process as well as the extent of specific capital investment. Efficiency of the process and specific utilisation of reagents as well as the extent of the necessary first investment is determined by the composition of bauxite to be processed, that is its

silica content and to a certain extent its iron-oxide content. The technical level of the realization of the process and energy consumption determined by the latter are also determining factors.

4. Essentially the Bayer process is a solvent-circulating circuit, energy consumption of which is determined by the extent of temperature differences produced and the efficiency of counter-current heat-recovery (figure 2). However, counter-current heat-recovery can be effectively realized by the use of continuously operating equipment only. This is the reason for endeavouring to render some of the operations of the process continuous which has proved to be highly successful in the recent past. Another important condition to render the process economic is the choice of high-capacity equipment units as well as a better approach and conservation of the technological optimum which is efficiently backed by automation and quite recently by the use of computers.

Figure 2

Bayer process



5. In the course of recent years the recovery as well as reagent-and-heat-consumption values characterizing the process have shown considerable improvement. This applies especially to plants where modern technology has been introduced, in spite of the fact that the bauxite quality in Europe has gradually deteriorated parallel with the decrease of stocks. It may be observed that the effect of bauxite quality on the efficiency of the process and its technical-economic characteristics is steadily decreasing; this, however, does not apply to specific consumption of bauxite and caustic soda. This tendency may be ascribed to the considerable development of the process and its gradual "accommodation" to the quality of bauxite. At present, predominantly in Europe, processing of such bauxite qualities is considered to be economic by the Bayer process which previously appeared to be utilisable only by applying the sinter or combined processes. The development of the process is characterized by the following values: (32)^{1/}

Table 1

Bayer process - specific consumption

Specific consumptions applying to 1 t of Al_2O_3

	SiO_2 content %	Bauxite (dry) t	Caustic soda NaOH kg	Steam t	Current kWh	Heat mill. cal.	Working Plant	Total hours
Prior to 1939	< 3	2.2	85	8	325	2.8	14	26
At present in modern plants	5-7	2.5	120	3.5 and approx. 2 resp.	240	1.3	3	8

^{1/} For references in parenthesis, see Bibliography.

6. It should be mentioned that the bauxite caustic soda consumption as a function of the silica content may be expressed by the following simplified formulae:

$$\text{Bauxite (dry)} \frac{t}{t} = \frac{100}{A-S-L_A} \quad \text{Caustic soda (NaOH)} \frac{t}{t} = \frac{\sim 0,8 S + L_N}{A-S-L_A}$$

where A = Al₂O₃ % in the bauxite
 S = SiO₂ % in the bauxite
 L_A resp. L_N = Al₂O₃ resp. NaOH losses other than due to silica.

As can be seen, both bauxite and caustic soda consumptions follow a hyperbolic law, with an even steeper slope in the case of the latter.

II. CHEMISM OF THE BAYER PROCESS

7. A great number of manuals discuss the chemism of the Bayer process: Pearson, Fulda-Ginsberg, Ginsberg-Wrigge, Maselj, Lajner, Kusnyecov, l'Aluminium (Pechiney), Extractive Metallurgy (1-8). This paper restricts its discussion to a review of some more recent results.

Determination of mineral composition of bauxite and its technological aspects

8. According to the mineral form of aluminium-hydroxide, reference is made to gibbsitic, boehmitic or diasporic-bauxites. However, gibbsite boehmit is often encountered next to boehmite diasporic. If the quantity of boehmite resp. of diasporic is rather noteworthy in the gibbsitic-boehmitic resp. boehmitic-diasporic ore (somewhat over 5%), these mixed ores have to be processed as boehmitic resp. diasporic bauxites.

Table 2 shows the chemical composition of some characteristic types of bauxite; their mineral composition appears in table 3. Mineral composition has been determined by X-ray diffractometer (9,10) as well as derivatograph (11,12).

Table 2

Chemical composition of bauxites

Bauxite samples (land of origin)	Loss on ig- nition	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	TiO ₂	Al ₂ O ₃ / SiO ₂ ratio
	%	%	%	%	%	
(1) Indian	31.8	58.8	1.4	0.6	5.0	98.0
(2) Yugoslavian	11.2	53.3	28.0	3.1	3.6	17.2
(3) Greek (diasporic)	14.4	63.4	14.2	4.3	2.7	14.7
(4) Hungarian (from Iszka)	20.7	49.7	19.4	5.8	2.4	8.58
(5) Hungarian (from Halimba)	12.4	51.3	25.5	6.2	2.5	8.25
(6) Greek (boehmite-diasporic)	13.6	54.1	23.1	4.6	2.8	11.70

Table 3

Mineral composition of bauxites

<u>Bauxite samples (land of origin)</u>						
	(1)	(2)	(3)	(4)	(5)	(6)
<u>Mineral</u>	<u>Al₂O₃%</u>					
Gibbsite	58.0	-	-	23.2	2.4	-
Boehmite	traces	51.2	-	21.6	43.7	40.1
Diaspore	-	-	60.4	-	-	10.2
Caolinite	<u>traces</u>	<u>2.5</u>	<u>3.0</u>	<u>4.9</u>	<u>5.3</u>	<u>3.8</u>
Total	58.8	53.7	63.4	49.7	51.3	54.1
	<u>Fe₂O₃%</u>					
Hematite	1.4	25.5	traces	4.9	21.8	12.4
Goethite	traces	1.0	14.2	14.5	3.7	9.6
Pyrite	<u>-</u>	<u>-</u>	<u>-</u>	<u>-</u>	<u>-</u>	<u>-</u>
Total	1.4	26.5	14.2	19.4	25.5	23.1
	<u>TiO₂%</u>					
Anatase	4.2	2.7	2.7	1.6	2.2	2.8
Rutile	<u>0.8</u>	<u>traces</u>	<u>traces</u>	<u>0.8</u>	<u>0.3</u>	<u>traces</u>
Total	5.0	2.7	2.7	2.4	2.5	2.8
	<u>CaO%</u>					
Calcite	traces	-	-	traces	0.6	-
	<u>SiO₂%</u>					
Quartz	0.6	1.0	-	-	-	-

9. Among the samples shown in table 2, No.1 represents the gibbsitic-type Indian bauxite with a relatively high (5%) TiO_2 content. Sample No.2 represents a Yugoslavian type, Al_2O_3 contents of which appears in a boehmitic form; its Fe_2O_3 content is almost exclusively hematite. No.3 is a Greek diasporic bauxite, its iron mineral, however, is goethite. Samples Nos. 4 and 5 represent Hungarian bauxites. In sample No.4 a nearly identical quantity of Al_2O_3 may be found in form of gibbsite and boehmite, its dominating iron mineral being goethite. Sample No.5 represents a hematitic bauxite with a boehmitic character. Sample No.6 is Greek of a boehmite-diasporic-diasporic type. From a technological point of view sample No.4 must be qualified as boehmitic, while sample No.6 as diasporic. Quantitative knowledge of mineral composition of bauxites may foster estimation of their technological behaviour. In this respect not only Al_2O_3 modifications but also mineral forms of accompanying elements are worth attention. Contrary to hematite, the sedimentation deteriorating effect of goethite is, for instance, beyond doubt as well as the higher reactivity of anatase against the digesting liquor as compared to rutile and the divergent solubility of quartz and caolinite at digestion which has lead to the introduction of the "reactive silica" conception. Therefore when selecting digesting conditions the mineralogical form of SiO_2 and TiO_2 should be taken into consideration.

10. Recent research has included investigation of $\alpha-FeOOH-\alpha-AlOOH$ system by means of X-ray diffractometer and electron microscope. According to the investigations of Thiel (13) 8 to 33 mol-percentages of $\alpha-FeOOH$ in the goethite-lattice may be substituted by $\alpha-AlOOH$ molecules. The occurrence of this compound in some bauxites has, no doubt, an influence on their technological behaviour, their digestion and sedimentation characteristics. In the near future with a better knowledge of the mineral composition and morphology of bauxites unequivocal consequences may be drawn as regards technological behaviour of these ores.

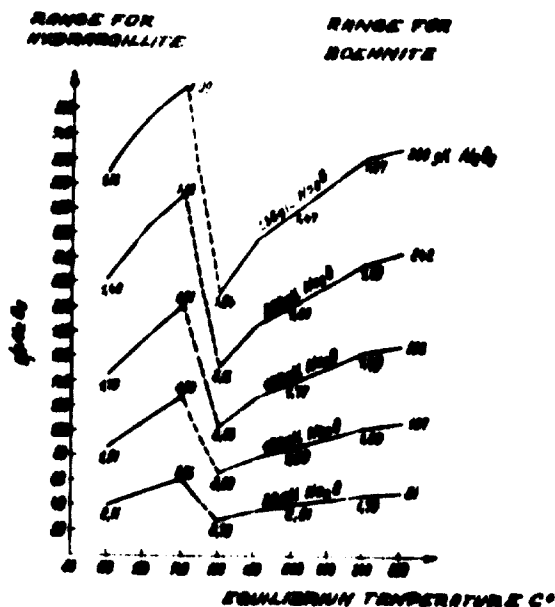
Chemistry of digestion

11. Digestion temperature and composition of digesting liquor may be selected on the basis of equilibrium solubility of various aluminium-oxide forms, but it stands to reason to also take into consideration the behaviour of accompanying components.
12. On basis of data published by Adamson, Bloore and Carr, (8) figure 3 shows equilibrium solubility of gibbsite and boehmite. From the figures it appears that for digestion of gibbsite-containing bauxites, atmospheric circumstances are favourable too, but in order to decrease molar ratio of liquor after digestion and to increase the rate of reaction and the efficiency of the circuit an under pressure work at temperatures ranging up to maximum 145°C is often practised.
13. When digesting boehmite-containing bauxites a higher temperature is necessary in order to attain adequate digestion and circuit efficiency. At present modern plants are already working at digesting temperatures ranging between 220 to 250°C.

Figure 3

Equilibrium solubility of hydrargillite and boehmite as a function of temperature and concentration resp.

Minerals given for the different diagrams are representing the $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3$ molar ratio.

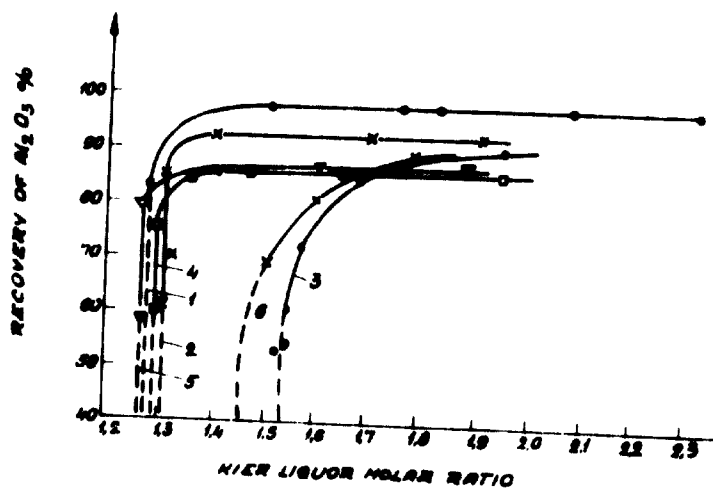


Equilibrium data of diasporic bauxites as compared to gibbsitic and boehmitic ores are far from being fully cleared up. By an adequate modification of the Bayer process and with the addition of about 4% lime to the bauxite, diasporic ores can also be processed at the usual digesting temperatures although for approaching molar ratios attained at digestion of boehmitic bauxites digesting liquor of a higher Na_2O concentration is necessary. According to experimental measurements, diasporic bauxites may be digested without any lime addition at a higher digesting temperature than the usual 280°C . This very fact may be of considerable importance at an eventual realization of tube-digestion on an industrial scale.

14. Figure 4 shows characteristic curves of the digestion of the six special bauxite types. In all cases a one-hour digestion was realized at 240°C in laboratory autoclaves only the gibbsite containing Indian bauxite No.1 was digested at 140°C during three hours - to compensate partly for the lower Na_2O concentration of the digesting liquor. Digestion of the diasporic and diasporic-boehmitic sample (Nos. 3 and 6) was effected by adding 4% CaO . The divergent character of the digesting curve of boehmite type bauxites (samples Nos. 2, 4 and 5) and that of a diasporic character (samples Nos. 3 and 6) is well discernible.

Figure 4

Characteristic curves of digestion



	1 INDIAN BAUXITE	2 YUGOSLAVIA- VIEN Bx.	3 GREEK Bx.	4 HUNGARIAN Bx.	5 HUNGARIAN Bx.	6 GREEK Bx.
DIGESTION TEMPERATURE	140	240	240	240	240	240 C°
DIGEST. TIME	3	1	1	1	1	1 hour
DIGESTING LIQUOR CONC.	141.6	185.6	217.2	227	227	222.5 Na_2O_x
CaO TO BAUXIT	—	—	4	—	—	4 %

15. In addition to the equilibrium solubility of mineral form and the rate of solubility, the Al_2O_3 recovery of the Bayer process is determined by the silica content of bauxite. Namely, the SiO_2 content is transformed into sodium-aluminium-silicate at the digestion stage and the soda and aluminium losses bound in the red mud may be calculated on the basis of the sodium-aluminium-silicate composition. According to recent research results (3, 6, 7, 8, 15) the sodium-aluminium-silicate formed at digestion is of a sodalite structure having a regular crystalline system, lattice-constant which varies between 8.86 to 8.96 Å according to the infiltration of foreign ions.
16. Composition of sodium-aluminium-silicate depends on the solution concentration as well as the digestion temperature, but for practical calculations average composition may be characterized by the $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 1,7\text{SiO}_2$ formula with sufficient accuracy. In the zeolitic structure of hydroxi-sodalite foreign ions may be incorporated not only in the lattice inter-spaces but substitution of Si-atoms by Al-atoms is possible in the silicate lattice itself (3). Cation deficiency thus developed has to be compensated by alkali intake. Therefore Na_2O bound in the sodium-aluminium-silicate compound may even attain a value of 0.7 g/g SiO_2 .
17. In order to decrease caustic soda losses, one of the practicable methods is to add lime prior to digestion or causticisation of red mud with burnt lime. The latter method is applied in Hungary on an industrial scale. In both cases a calcium-aluminium-hydrosilicate $\cdot 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot k\text{SiO}_2 \cdot l\text{H}_2\text{O}$ is formed having an identical structure with that of $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ and Na_2O loss is decreasing (39).
18. Among the accompanying components of bauxite, TiO_2 merits special attention. With digesting liquor anatase, and to a lesser extent rutile, react and an unsoluble sodium containing titanium compound is formed increasing the soda loss of the Bayer process. According to investigations of Ivekovic and Uselac (17) hexatitanate pentatitanate is formed but in general the transformation is not complete. On one per cent of TiO_2 -contents they are reckoning with a smaller caustic soda loss value than 1.3 kg $\text{Na}_2\text{O}/\text{t}$ of bauxite.
19. Hungarian researchers (18) have ascertained that the measure of transformation of anatase and rutile into sodium-titanate as well as the bond of Na_2O beside digestion temperature and its duration depends fundamentally on both concentration and molar-ratio of the digesting liquor, that is on the activity of OH^- ion.

20. At the digestion of bauxite, the reaction of aluminium and titanium minerals with the digesting liquor takes place at different rates but simultaneously with one another. Soda loss brought about by the titanium content depends on the measure and rate of approximation of the equilibrium molar-ratio. If the solubility rate of aluminium minerals is sufficiently high and the deviation from the equilibrium molar-ratio is rather small, at the end of the alumina solution, Na_2O losses due to TiO_2 content do not exceed the value of 0.1 kg $\text{Na}_2\text{O}/\text{kg TiO}_2$ at the digestion of bauxite. The major part of anatase and especially that of rutile are generally unaltered into the red mud and thus soda loss of 0.05 kg $\text{Na}_2\text{O}/\text{kg TiO}_2$ may be attained.

21. On the basis of X-ray diffractograms, the qualitative phase composition as well as the hematitic and goethitic character of the red muds and finally the presence of sodalite and cancrinite phases can be well determined. By means of the highly sensitive diffractometer the digestion of bauxite is also controllable, as even lesser quantities than 1% of hydrargillite, boehmite or diasporite are well perceptible.

22. Red muds shown in Table 4 belong to the sections giving a maximum Al_2O_3 recovery of the digesting curves.

Table 4
Composition of red muds
(X-ray diffractograms)

Sample No.	Loss on ignition %	Al_2O_3 %	Fe_2O_3 %	SiO_2 %	TiO_2 %	Na_2O %	CaO %
1	12.0	10.5	8.9	1.6	53.2	1.7	-
2	4.8	9.2	64.1	6.6	7.2	5.9	-
3	12.3	10.0	39.0	7.6	8.0	5.3	12.9
4	10.0	13.0	42.8	12.1	5.6	10.1	-
5	5.4	13.0	53.1	11.4	5.0	9.8	-
6	8.8	11.5	43.1	9.1	7.0	6.7	10.0

23. The Fe_2O_3 content of bauxites varies between extraordinary broad limits (2 to 30%). Although after digestion iron minerals can invariably be traced in the red mud, their role is still rather significant. At the processing of bauxites having high Fe_2O_3 content the specific quantity of red mud is quite considerable, thus requiring surplus equipment and more washing-water. In addition, certain iron minerals first of all goethite deteriorates the sedimentation rate of the mud thus causing surplus costs as well.

24. Red mud of bauxites having a high Fe_2O_3 content may be taken into consideration as iron ores as well, especially in countries poor in iron ores along with the simultaneous recovery of the Na_2O and Al_2O_3 contents of red mud (19).

25. Among the accompanying elements a considerable amount of vanadium, phosphorus, fluorine and gallium dissolve in the digesting liquor, also sulphates. Concentrated in the liquor circuit these components cause technological troubles as well as soda losses. Contents in organic substances of bauxites belong among the detrimental contaminations which are easily soluble in the digesting liquor, and enriched in the circuit they may cause difficulties at salt separation and evaporation. On account of the relatively high organic substance contents of Hungarian bauxites, considerable work was carried on in Hungary (20), but by the introduction of intensive salt-separation the problems thus arising were essentially eliminated. Among the elements mentioned, recovery of the valuable vanadium and gallium contents had been solved on an industrial level.

Role of the mineral composition of red mud at settling

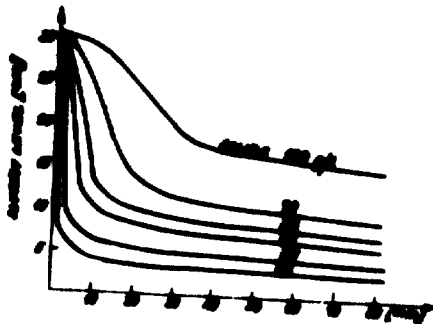
26. The settling operation and the separation of red mud from the liquor are distinct physical procedures the efficiency of which, however, depends to a considerable extent on the red mud structure and its mineral composition. The rate of settling is first of all decreased by the sodium-aluminium-silicate and goethite content of red mud but a considerable part is played by the grain structure of the mud and its degree of dispersity. In the settling operation of red mud the role of iron minerals is well illustrated by the comparison of settling curves of the hematitic mud of Halimba and the goethitic mud of Isskassentgyörgy (Bittó) (see figure 5); as indicated, the settling tendency of the goethite-containing ore of Isska is considerably worse.

27. Roasting of bauxite at a temperature exceeding 300°C , in addition to burning of organic substances, has a favourable effect from the point of view of settling, because of the goethite to hematite transformation. At present, however, advantage is given to wet grinding for reasons of energetics.

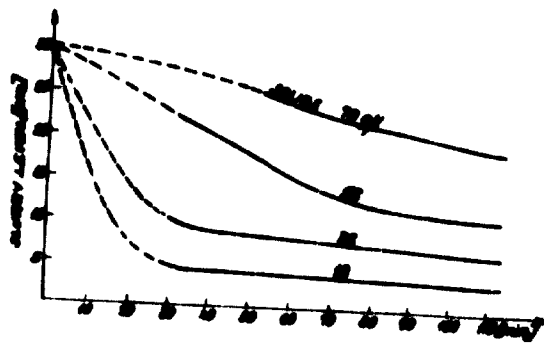
Figure 5

Sedimentation of the red mud of Hungarian bauxites

HEMATITIC



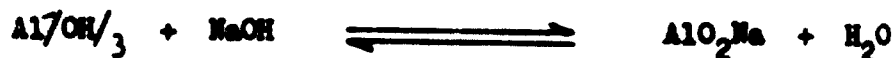
GOETHITIC



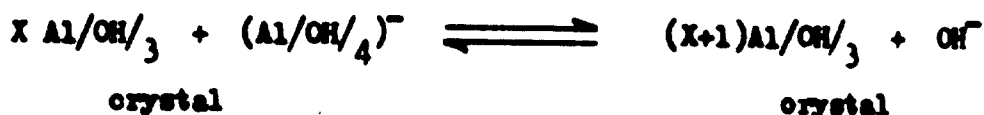
28. At the settling and at the following counter-current-washing, Na_2O and Al_2O_3 adsorption of red mud must be taken into consideration as this increases soda and alumina loss of the Bayer process although it is considerably less than that bound in the sodium-aluminium-silicate. The extent of adsorption depends on the solvent concentration as well as the adsorbing ability of the mud thus on its mineralogical composition and morphology; therefore values being characteristic for all bauxites red mud types have to be expressed by formulae characterising the given material (8).

Decomposition kinetics

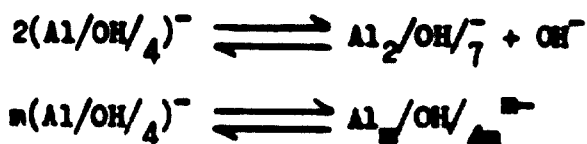
29. One of the most important processes of the Bayer process is the separation of aluminium-hydroxide from the sodium-aluminate solution, which, in the presence of alumina-hydrate used as seed, is a crystallization taking place during stirring. In fact the following equilibrium reaction is at stake:



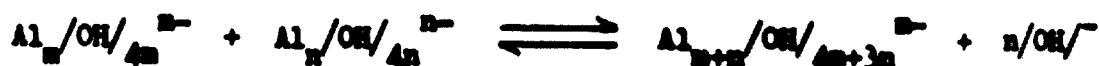
30. According to a considerable number of researchers, aluminate ions may be found in the form of complex anions in the $(\text{Al/OH/}_4)^-$ solution. Some consider only the existence of the monomer possible, and according to them the basic reaction at the decomposition is the following:



Other researchers (3, 6), point to the possibility of complex aluminate anion polymerisation which, for instance, is based on the following formula:



The decomposition reaction is thus:



31. The rate of decomposition is determined first and foremost by the temperature, caustic Na_2O concentration of the solution, initial Al_2O_3 concentration of the solution, Na_2CO_3 -content and the seeding. In practice, however, the aim is not only to attain maximum decomposition rate but an adequate grain-size-composition of the product is of similar importance. Increasing of the separation rate requires a seeding material of the finest possible grain-size, whereas the filtration of product-hydrate, its washing and calcination calls for a coarser grain-size. Utilization of extremely fine active seeding hydrate has not become popular, but in general for increasing the decomposition rate larger quantities of seeding materials 3 to 5 fold of the separated hydrate is used.

32. Shimozato (21) has analysed thoroughly both theoretical and practical aspects of the decomposition process. According to his statements the rate of decomposition is proportionate to that of the crystal increment and core formation. On the other hand the rate of crystal increment is determined by the product of the square of over-saturation referring to the aluminium-oxide of the solution and of the active surface of seeding material. Similarly, reference (22) may be found for the mathematical expression of temperature variation giving a maximum hydrate separation rate in the function of the various characteristics of decomposition.

$$T = K \left(\frac{1}{i}\right)^n \quad \text{and} \quad T = K' \left(\frac{1}{\alpha}\right)^{n'}, \text{ where}$$

T = temperature

i = time of decomposition

α = molar ratio of the solution

n' , n , K , K' = Constants depending on Na_2O concentration and the seeding ratio.

Role of liquor contaminations at evaporation

33. Although no chemical process takes place at evaporation, nevertheless the increase of Na_2O concentration considerably decreases solubility of soda, fluorine, phosphore, vanadium and arsenium compounds. Solution of solid caustic soda by concentrated liquor has proved to be an especially effective method to decrease the carbonate sodium level after which the salt thus precipitated is separated by centrifuge from the solution.

Calcination

34. The calcination process of alumina hydrate is described by the following equation:

$2\text{Al}(\text{OH})_3 = \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$. Reaction heat amounts to 381 kcal/kg Al_2O_3 . In fact, however, water separation takes place gradually and the end-product of $\alpha\text{-Al}_2\text{O}_3$ is arrived at by numerous transitory modifications.

35. Phase transformation taking place in the course of calcination has rather extensive literature and the widespread research of Saalfeld (24), Torkar (25) and Wefers (26) are worth mention. Recently with a view to decreasing calcination temperature and turning out of products with favourable physical characteristics, calcination by means of mineralization, mainly by adding AlF_3 , has become popular.

The calcination process may also be realized in a steam atmosphere at high pressure and temperature which may eventually result in a fundamental alteration of present technology (6).

36. Requirements of chemical purity and physical properties of alumina are ever increasing, especially in the production of aluminium wires with fair conductivity. In the near future one may expect increase of conditions as regards physical properties, precursory signals of which are already appearing in the recently elaborated ISO standards as well as the endeavours for standardisation in the Comecon countries.

III. PROCESS ENGINEERING

Technology

37. Parameters of the two main variants of the Bayer process are shown by the following data completed on the basis of Barrand's work (7).

<u>Variant</u>	<u>Trihydratic</u>	<u>Monohydratic</u>
Digestion temperature	105-145	200-250
Digesting liquor concentration	100-130	180-280 Na ₂ O g/l
Molar-ratio after digestion	1.5-1.6	1.5-1.75

The Na₂O-Al₂O₃-H₂O system

38. In order to illustrate the two different technologies the Na₂O-Al₂O₃-H₂O system (4) appears to be extremely suitable (figure 6: a and b).

In the figures the Al₂O₃ content of aluminate liquors is plotted against caustic Na₂O content. The straights starting from the origin represent identical molar ratios:

Na₂O moles / Al₂O₃ moles, or
identical weight ratios (in brackets):

Al₂O₃ / Na₂O expressed as Na₂CO₃.

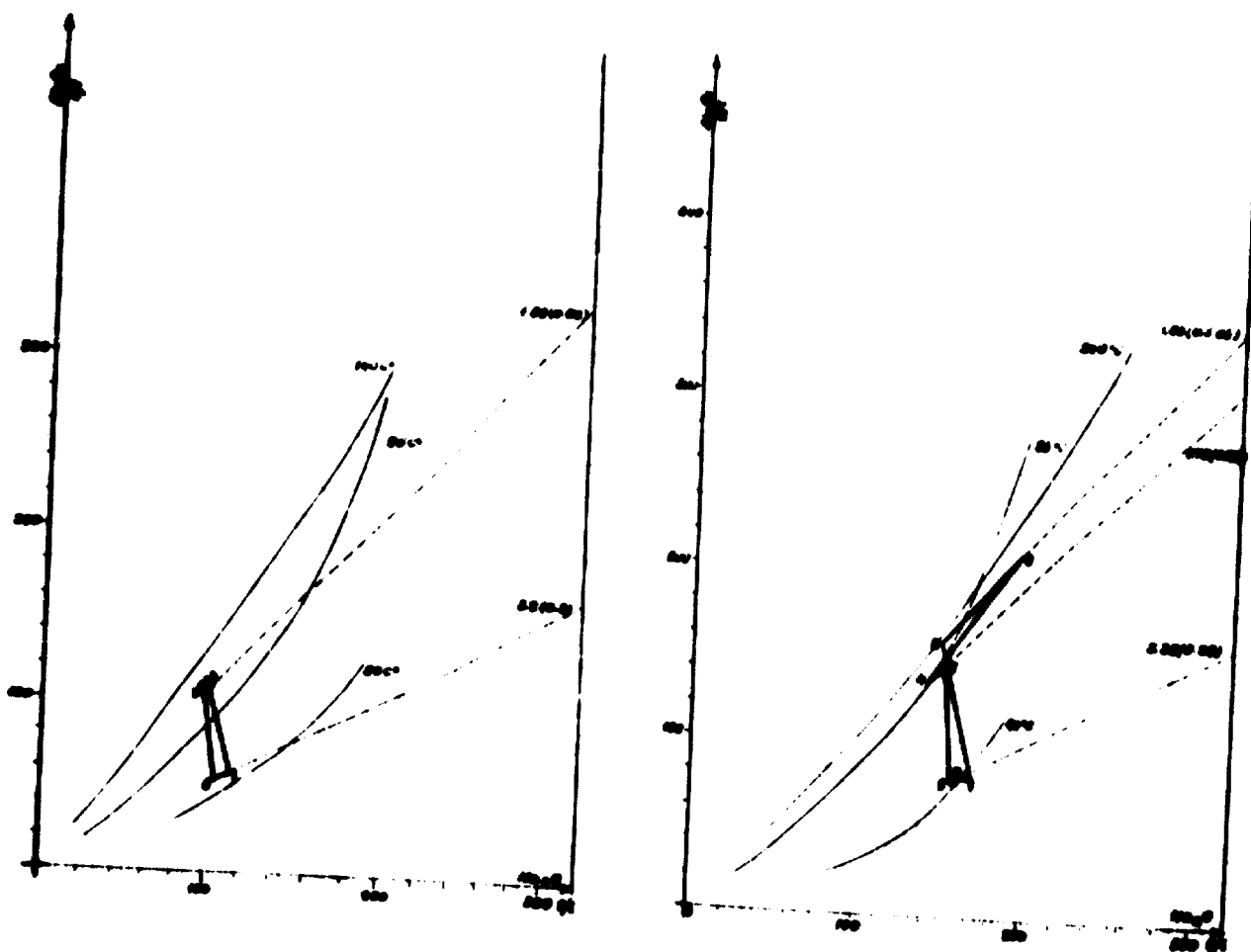
Dilution is represented by approaching the origin; concentration by departing from it. The equilibrium isotherms belonging to the characteristic temperatures are also plotted in the diagrams. Points situated above the isotherms represent supersaturated solutions, able to precipitate alumina hydrate. Points situated

below the isotherms, however, represent unsaturated solutions, able to solve alumina hydrate under certain conditions. The quantity of Al_2O_3 precipitated resp. dissolved in a process is given by the difference of the ordinates; the reciprocal value of this difference is proportional to the rate of plant liquor circuit. In the case of trihydratic Bayer process (figure 6(a)) composition of digesting liquor is indicated by point 1. After adding bauxite, soda and lime to the solution, straight 1-2 will represent the digestion, causticisation of soda and bond of Na_2O occurring simultaneously.

Figure 6

(a) Bayer cycle for trihydrate-type bauxite, low concentrated liquor

(b) Bayer cycle for monohydrate-type bauxite, minimum evaporation



39. In the course of flashing following digestion the solution is concentrated along straight 2-3, then follows the dilution represented by straight 3-4. Flash cooling of aluminate liquor is symbolised by straight 4-5, while straight 5-6 is showing hydrargillite separation occurring in the course of the decomposition. From point 6, when the evaporation of the solution is affected, we get back into point 1. Making up of soda may occur by adding solid or liquid caustic soda or a caustic soda solution gained by causticisation of sodium carbonate by lime. With bauxites having higher boehmite content such a process variant resulted from which digestion is carried out at a low concentration but a high temperature.

40. With the monohydrate European process, high concentration and medium temperature was applied at the outset, but in consequence of equipment development higher temperature and parallel with it lower concentration could be used (figure 6 (b)). Comparison of figures 6 (a) and 6 (b) well illustrates the considerable approachment to one another of the two basic process types.

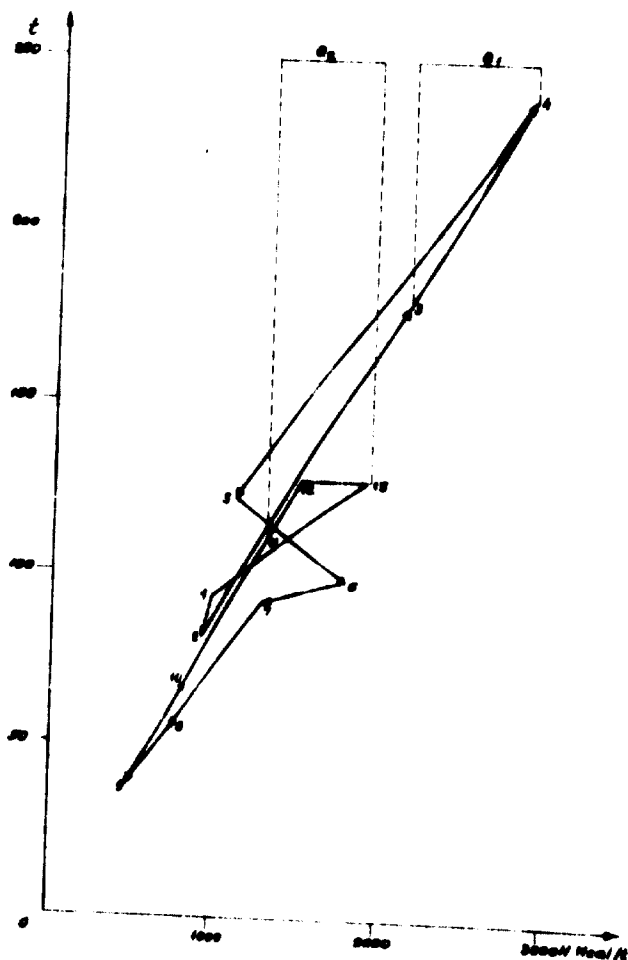
Thermal economy

41. From the caloric point of view the Bayer process represents a series of counter-current heatings and cooling. This is well apparent on basis of figure 7 in which there is characterized individual solutions according to their thermal content referring to 1 t alumina and temperature (on basis of 42). By mixing bauxite in the digesting liquor (1), temperature and thermal content of the latter decreases, (1-2).

42. Slurry thus obtained is heated in counter-current way (2-3) by the heat which results from the flashing of the digested slurry. In the last heating section (3-4) high-pressure and high-temperature steam has to be used (Q_1). The flashing slurry (4-5) transmits its heat to the slurry to be heated. Then follows the dilution (5-6) which entails decrease of temperature and increase of thermal content. At the elimination of the red mud, part of the heat content goes into waste (6-7). In the course of flash cooling of the aluminate liquor (7-8) a considerable quantity of heat is released. Heat released in course of decomposition (8-9) represents a nonrecoverable loss for the time being. Spent liquor is heated first by steams of the evaporation (10-11); for heating up to the temperature of the first body of the evaporator (11-12) and for evaporation carried out at this temperature (12-13) low pressure steam is required (Q_2).

43. Concentrated and cooled liquor is again indicated by point 1. From the figure one may draw the consequence that the lower the steam consumption of the circuit, the higher the efficiency of the recovery $\frac{2-3}{4-5}$ resp. $\frac{9-10}{7-8}$ and the lower the quantity of water to be evaporated.

Figure 7
i-t diagram of the Bayer cycle



Optimization

44. The rentability of alumina production can only be improved by a careful and complex optimization. For example, the optimization of digestion heat-recovery alone requires economic comparison of numerous variants of thermal technique, independently from the other plant-units. From the point of view of steam economy, the increase of the number of flashing stages as well as that of the pre-heater surfaces appears to be advantageous, however, it entails considerable investment costs.
45. In figure 8 the preheating surface area is plotted vrs. the number of heat recovery stages, while numbers indicated in the figure show Forint-costs of the digestion reckoned on 1 t of alumina. Points of identical rentability are linked by means of curves. The optimum amounts to 240 Forints/t, at 12 stages and at approximately $6,5 \text{ m}^2 \text{ h/t}$ preheating surface. From a practical point of view in the present case we have chosen 9-stages and $9 \text{ m}^2 \text{ h/t}$ preheating surface, rentability is only 0,4% less advantageous (39). The preheating of the slurry is limited by that fact that above a certain temperature the reaction rate of the silica precipitation is increased to such an extent that a scale is formed in the preheaters which diminishes the heat transfer.
46. This, however, can be eliminated to a certain extent by a careful desilication prior to digestion, which calls for surplus tanks and higher slurry-stocks and results in thermal losses in connexion with heating. Another solution is separate heating of part of the liquor used for digestion; from the point of view of thermal technique this method is not so economic as the heating of the total quantity of slurry, but it offers considerable advantages with a view to maintenance. For rentability calculations economic questions of all the other plant units have to be taken into consideration; this question may only be solved by optima calculations carried out by a modern computer. Nowadays when making projects for alumina plants or for the extension of existing plants optima in accordance with local circumstances are approached by means of computers. Complete material-, thermal-, and finally economic balance programmes are fed into computers and by changing some of the factors an approach to the most economic solution is given within the limits set forth.

Bauxite preparation

48. At present, high capacity wet grinding ball-mills are almost exclusively used operating in either closed or open circuits. Elimination of the adherent moisture of bauxite by means of drying is justified generally only when it yields decrease of transportation costs. Introduction of autogenous milling seems to be an up-to-date means of development and successful tests are already in course. Some types of autogenous mills allow for crushing to be dispensed with; it may be expected that both of the procedures crushing and milling will be carried out in one equipment (44).

Digestion

49. The trend of development was at first aimed at continuity which rendered multistage flashing possible and accordingly application of heat recovery. Following this, increase of digestion temperature was more and more put into the limelight and in the near future introduction of digestion at a temperature exceeding 250°C may be expected. From the technological point of view one of the solutions is the so-called tubular digestion which, however, raises some peculiar problems the solution of which may be envisaged in the near future (45, 46). There are possibilities for the development in the field of preheaters, autoclaves (decrease of deposits, elimination of dead space, increase of heat transfer etc.) as well as the decrease of flashing tank volume by means of better steam selection, self stirring or by other means.

Settling, washing filtration

50. Development of settling tanks points again towards using one-chamber equipment by means of which good settling and a better compression of red mud can be attained than with multichamber equipment. In alumina plants equipment of large size is already sited in the open air having a diameter of 30 to 36 m with flat or conical bottom and lateral or central mud discharge.

51. A method frequently applied for washing of red mud is filtration. On the basis of economic consideration one has to determine whether multi-stage settling and/or one- or more-stage filtration should be chosen. In general, filtration of red muds is rather difficult, on the other hand, however, the mud of some bauxite types can be filtered with relatively good efficiency. With a view to the fact that filtration ability of red mud improves with the decrease of liquor-phase concentration, it appears to be serving the purpose to effect red-mud washing first by means of settling and then to filter the partly washed mud.

52. Filtration of red mud is effected by means of vacuum-drum-filters or by filtering equipment operating under pressure. Modern vacuum filtering equipment is of continuous operation and guarantees a relatively high specific capacity (100-150 kg/m² hour) but can only be applied for red muds lending themselves to a relatively good filtration. Modern vacuum-drum-filters are manufactured with a filtering surface of 40 to 80 m² and are equipped with a device for removal of the thin filter-cake. Moisture content of red mud filtered on a vacuum-filter amounts to 42 to 60% depending on mud characteristics. Red muds of a very fine grain-size can be filtered with higher filtering pressure only but in this case equipment working under pressure and operating batchwise is used.

53. Specific yield of modern pressure-filters using filtering cloth made of synthetic material is 30 to 60 kg/m² hour and guarantees a filtering-cake of 38 to 48% moisture content. Traditional leaf-filters are manufactured at present with a filtering surface of 230 m² per unit. Specific space requirement of pressure filters is considerably less than in the case of vacuum-drum-filters; their operating costs reckoned on an identical filtering capacity are approximately equal to those of the vacuum-drum-filters.

54. Because the storage of red mud has caused serious trouble attempts have been made for the utilisation of red mud in iron metallurgy but a precondition of this, however, is its transportability. Neither drum-filters nor the traditional pressure filters guarantee a treatable and transportable non-adhering red mud. It is well known that red muds become treatable only with a moisture content below 30% which can be attained by means of drying after filtration.

55. This problem is solved adequately by the AJKO-type air cushion pressure filter developed in Hungary, operating automatically, requiring no drying and guaranteeing the necessary moisture content below 30% by means of mechanic pressure following filtration. Filter-cakes of red mud thus obtained may be stored in thick layers in prismatic form, but they may also be transported directly to the possible site of utilisation. According to experience acquired, in the case of vacuum filters one filtering stage substitutes approximately two washing stages, and in the case of filtration, with a low moisture content, three washing stages.

Decomposition

56. At present decomposition is carried out in the majority of cases in air-lift agitated tanks sited in the open-air, energy consumption of which is considerably lower than that of mechanically agitated tanks and can be connected in series without difficulty. Additional saving may be expected from propeller-agitators. Here development points towards increase of tank-sizes (2-3000 m³).

57. The technological solution by which only hydrate quantity in line with production is carried further from one tank to another while the rest of the hydrate remains in the slurry-tank as constant seed, merits attention. By this procedure filtration of seed which is costly and requires numerous equipment can be eliminated. For hydrate filtration, disc-filters which require small space have become more and more popular. At present they are made with 240 m² filtering surface and have operating costs considerably lower than that of drum-filters. Adequate classification of alumina-hydrate is a rather important factor and can be effected by hydro-separators which entail low operating costs; however, requiring big space and guaranteeing poor separation, by hydrocyclones having high energy consumption and by rake-classifiers.

Evaporation

58. Evaporation was first carried out by equipment adapted from other industrial branches, especially from the caustic soda industry. However, evaporation of alumina plant liquors produces special problems, with direct-current equipment an increased silica separation results as a consequence of low concentration and high temperature prevailing in the first body. The low temperature and high concentration reigning in the last bodies favours soda separation. One solution is to use counter-current or mixed equipment and to apply self-evaporation of the evaporated thick liquor by a maximum utilisation of the flashed steams. Such modern type equipment operating with low specific steam and practically without maintenance needs no spare equipment. Distribution of temperature and concentration is such that in the course of evaporation neither silica nor sodium carbonate are precipitated in noteworthy quantities. In the course of development of this equipment bodies having a heating surface of 1400 m² are used already. The question of salt separation which has caused considerable trouble has been solved by the introduction of self-discharge centrifuges.

Calcining equipment

59. The development of calcining equipment was first reflected in an increase of size; at present generally 75 to 110 m furnaces operate in alumina plants. One interesting trend of development is the preliminary drying of the hydrate which allows for a uniform production to be turned out with low energy consumption (43). Another trend is introduction of dust cyclones using the heat of flue-gases for hydrate pre-heating and that of alumina for recuperation. In this case shorter furnaces may be used with a rather advantageous specific energy (capacity: 900 t/day, fuel oil requirement 110 kg/t).

60. Numerous experiments have been carried out in view of fluid bed calcination of alumina, but such equipment is not yet operating on an industrial scale. On the other hand, however, fluidisation may very well be used to recuperate alumina heat and for the transport of alumina.

V. AUTOMATION

Development of analysing procedures

61. With the development of the Bayer process, setting up of quick, continuously operating automatic analysers became imperative in order to determine the composition of bauxite, red mud and alumina as well as that of liquors of different concentration in the circuit. As regards plant control and regulation, methods based on the measurement of physical parameters are finding acceptance.

62. For analysing bauxite and red mud, the use of an X-ray vacuum-spectrograph is again gaining ground (27, 28). In possession of adequate calibration curves, the method has proved very suitable in cases of series investigations. For quick determination of Al_2O_3 and SiO_2 -content of bauxite in Hungary, a method based on the selective activating of neutron energy has been elaborated (29). With a view to increasing accuracy of slurry adjustment, the radiometer flow gauge is applied which in addition to determining thickness and solid content of digesting liquor, can be used on other places of the circuit as well (3).

63. Endeavours have been made to maintain automatic, continuous and instrumental control of aluminate liquors which is of paramount importance from the point of view of automation. In this field attention has been focused on automatic titrating equipment based on the potentiometric method, and on equipment based on the measurement of physical constants. The purpose appears to be well served

especially by the measurement of conductivity of aluminate solutions by means of which both caustic Na_2O -content (eventually after dilution) and mol-ratio can be ascertained (30, 31).

64. From the extent of endeavours being exerted throughout the world it can be concluded that the problem of continuous, automatic analysis of liquors of different concentrations occurring in the Bayer process should be solved in the near future which is of decisive importance both from the point of view of automation as well as optimisation.

Computer control of alumina plants

65. The conception of computer-controlled alumina plants has already reached such a stage that its general acceptance may be expected within a few years. This can be ascribed to the following factors:

- (a) Substantial development of measuring and analysing instruments. Accuracy and speed of same is at present already sufficient to be connected to process-controlling computers.
- (b) Both mathematical and statistical methods-application made possible by the computers are apt to furnish suitable flow-equations.
- (c) In the majority of plants part-procedures are automatized and their connexion to a central computer system can easily be realized.

In practice off-line type computer controlling is in the course of preparation or being introduced in several important alumina plants. The basis of the mathematical model necessary for computer control is achieved by material and heat balances of alumina plants as well as by economic programmes.

66. In the material balance programme those relations are built which can be elaborated by reaction-kinetics, laboratory measurements, plant measurements and the statistical analysis of same. On the basis of data fed in, the programme calculates all data of alumina plant material balance such as concentrations, specific weight, mol-ratios and water-values.

67. The heat balance programme indicates for a material balance variant at will, heat requirements of the process on the basis of heat parameters as well as equipment built in. Furthermore it shows heat-technical data of various stages of counter-current heat-recuperating systems, including condensed waters. The economic programme contains material prices and those of the different energy sources as well as investment and repair costs, and the varying parts of self-costs based on an operating method at will.

68. On the basis of operation conditions given by means of the three above-mentioned programmes, production costs may be calculated and their variation determined in case of initial conditions being changed. A special optimizing programme supplies the most suitable variation on the basis of economic results. It also indicates set points and can adjust them as well in case of on-line control which is the final goal of the present development.

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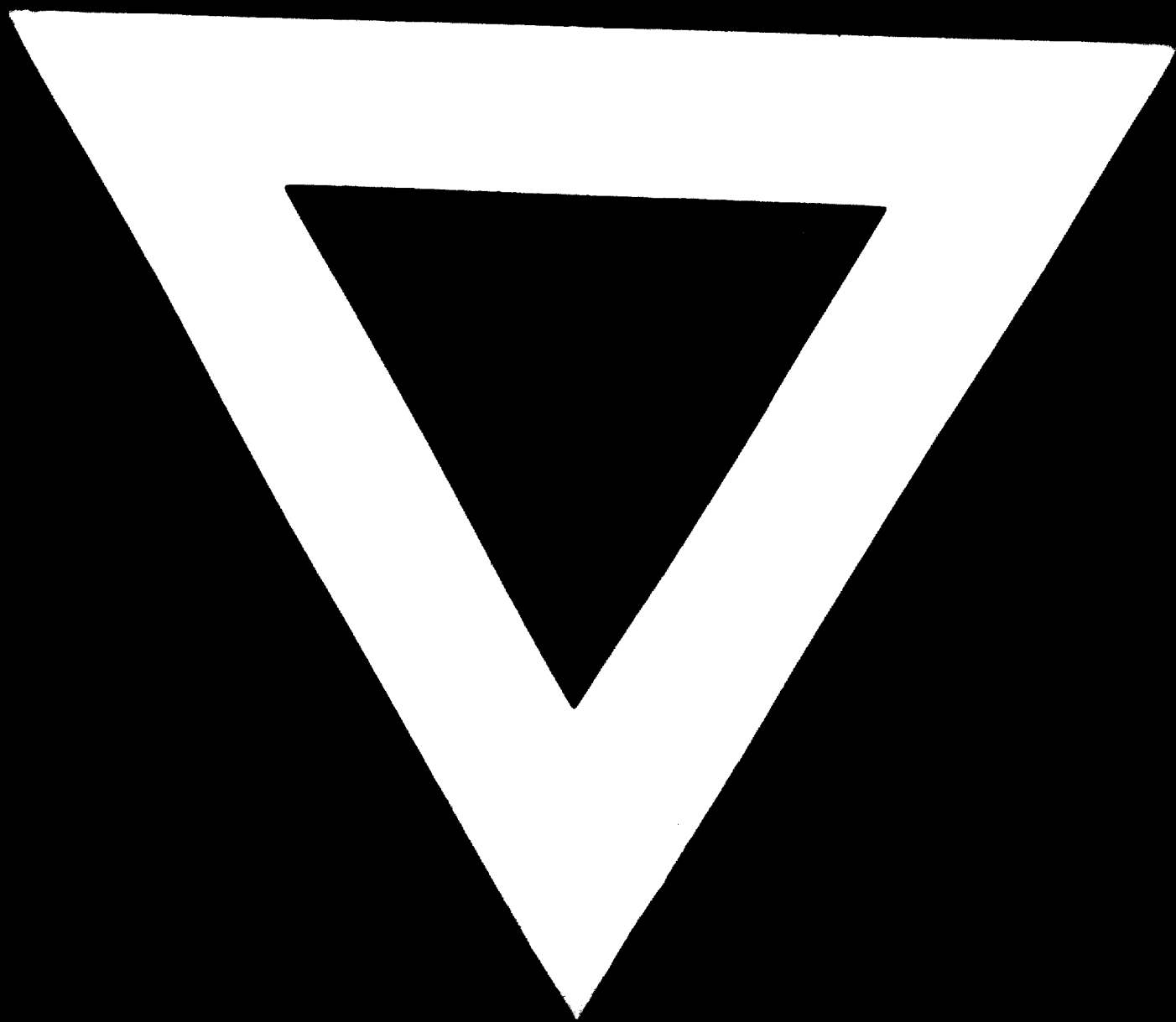
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