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# Prospects of phase transformations in the Bayer process

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*The mineralogical appearance of the bauxite components and their influence on the yield of alumina, on the loss of caustic and on the separability of red mud slurries.*

*Equivalent solid phases in the presence of CaO, $TiO_2$, $Fe_2O_3$, NaCl and $Na_2CO_3$ in the Bayer cycle. Formation of phases which are favourable from the point of view of losses in caustic and aluminium. Conditions of goethite-hematite transformation, their influence on the alumina yield, on the solubility of $V_2O_5$, on the sedimentability and compactibility of red mud. Possibilities for further development of the Bayer technilogy via directing phase transformation.*

The basic technology of the Bayer process has remained unchanged for many decades. It very nearly appeared that further progress can be expected only in the design of equipment, when — in recent years — more and more problems of chemical technology, phase transformation and kinetics arose, due to the greatly differing properties of bauxites, to the contaminations entering the cycle together with the bauxite and, in consequence, to the greatly differing composition and properties of aluminate liquors.

In the present paper, the parameters of the Bayer process that are of decisive importance with respect to its economics, namely alumina yield, NaOH losses and conditions of red mud separation and wash will be discussed from the view of the transformation of existing phases into more favourable phases.

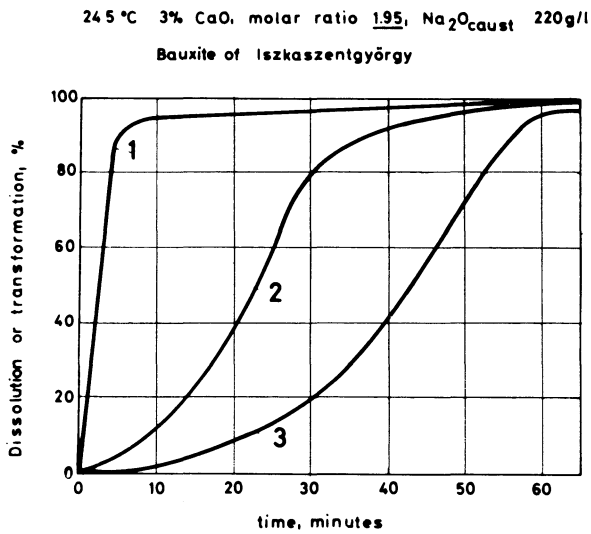
The problems that we particularly wish to emphasize include the technology of processing goethitic bauxites, since such raw materials became increasingly important; problems of NaCl and $Na_2SO_4$ additives in connection with the compensation for caustic losses; the effect of CaO in the Bayer cycle; and finally the determination of the separability of red mud by measuring morphological characteristics.

These problems are rather complex and interdependent, therefore their grouping is arbitrary to a certain extent.

## 1. SOME KINETIC PROBLEMS OF PROCESSING GOETHITIC BAUXITES CONNECTED WITH ALUMINA YIELDS

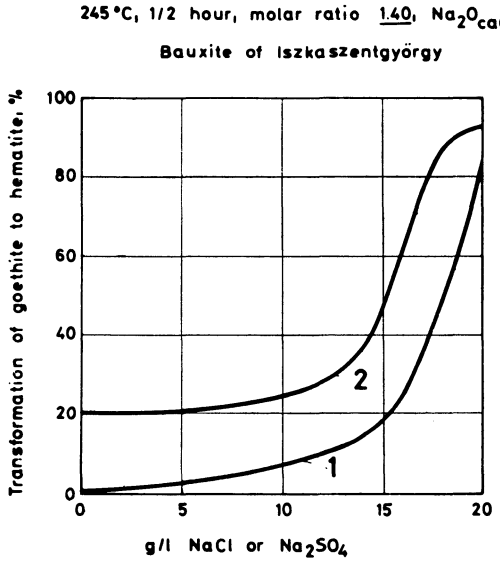
Processing of goethitic bauxites will be demonstrated by the example of a Hungarian bauxite from Iszkaszentgyörgy whose mineralogical composition is shown in Table I.

It is well known that in processing such bauxites, the aluminium content incorporated in the goethite lattice by isomorphous substitution results in undigested alumina losses, while the settling properties of the mud containing goethite lead to unfavourable mud wash conditions [1-5]. These technological disadvantages can be eliminated by transforming goethite into hematite. For this purpose King [6] utilizes the catalytic effect of CaO. In the process (1) developed at our institute [7], [8] we utilize the joint effect of CaO and NaCl or $Na_2SO_4$. However, these salts alone are also capable of reducing the temperature and time of the transformation.




1. Dissolution of $Al_2O_3$
2. Dissolution and transformation of titanium minerals
3. Transformation of goethite to hematite

▲ Fig. 1




1. without CaO
2. with 3% CaO

Fig. 2 ▲

(1) Patent applied for.

**TABLE I**

*Chemical and mineralogical composition of goethitic bauxite and red muds obtained in the presence of various additives. (Digesting conditions: 220 g/l $Na_2O$caust, 30 minutes, 245 °C, molar ratio after digestion: 1.40)*

| | *Constituent (%)* | *Bauxite (Iszkaszentgyörgy)* | *Red Muds* | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | *1* | *2* | *3* | *4* | *5* | *6* |
| | | | *Without additive* | *20 g/l NaCl* | *20 g/l $Na_2SO_4$* | *3% CaO + 20 g/l NaCl* | *3% CaO + 20 g/l $Na_2SO_4$* | *10 g/l $Na_2SO$* |
| $Al_2O_3$ | Gibbsite | 16,0 | 0,2 | 0,2 | — | — | — | — |
| | Boehmite | 25,5 | 0,3 | 0,4 | 0,5 | 0,3 | 0,3 | 0,4 |
| | Diaspore | 1,3 | 2,0 | 1,3 | 1,3 | 0,4 | 0,4 | 1,2 |
| | Kaolinite | 5,0 | — | — | — | — | — | — |
| | Goethite-maghemite | 2,1 | 3,6 | 0,3 | 0,3 | — | — | 3,7 |
| | Hematite | 0,2 | 0,2 | 0,5 | 0,5 | — | — | 0,4 |
| | OH-sodalite | — | 5,5 | 0,5 | 0,4 | 0,2 | 0,3 | 0,4 |
| | Cl-sodalite | — | — | 4,0 | — | 3,0 | — | — |
| | $CO_3$-sodalite | — | 5,7 | 0,6 | 2,9 | 1,5 | 2,9 | 3,4 |
| | Cancrinite | — | 1,8 | 7,5 | 9,3 | 6,3 | 8,0 | 7,7 |
| | Ca-Al-silicate | — | — | — | — | 2,8 | 3,0 | — |
| | | 50,1 | 18,3 | 15,3 | 15,2 | 14,5 | 14,9 | 17,2 |
| $Fe_2O_3$ | Goethite | 10,2 | 21,5 | 5,3 | 6,2 | 1,7 | 1,3 | 20,0 |
| | Maghemite | 3,5 | — | — | — | — | — | 3,8 |
| | Hématite | 5,0 | 17,7 | 39,2 | 38,0 | 40,4 | 40,4 | 16,5 |
| | | 18,7 | 39,2 | 44,5 | 44,2 | 42,1 | 41,7 | 40,3 |
| $TiO_2$ | Anatase | 1,8 | — | — | — | — | — | — |
| | Rutile | 0,6 | 0,8 | 0,8 | — | — | — | — |
| | Na-titanate | — | 1,1 | 1,6 | 2,0 | 2,0 | 2,0 | 2,0 |
| | Ca-titanate | — | 3,0 | 2,6 | 3,0 | 3,0 | 3,0 | 3,0 |
| | | 2,4 | 4,9 | 5,0 | 5,0 | 5,0 | 5,0 | 5,0 |
| $SiO_2$ | Kaolinite | 5,9 | — | — | — | — | — | — |
| | Quartz | 0,5 | 0,8 | 0,3 | 0,2 | — | — | 0,4 |
| | Na-Al-hydrosilicate + Ca-Al-hydrosilicate | — | 14,1 | 14,0 | 14,5 | 14,4 | 14,3 | 13,3 |
| | | 6,4 | 14,9 | 14,3 | 14,7 | 14,4 | 14,3 | 13,7 |
| $V_2O_5$ | Soluble in alkali | 0,03 | — | — | — | — | — | — |
| | In goethite | 0,04 | — | 0,01 | 0,01 | — | — | 0,09 |
| | In other minerals | 0,03 | — | 0,07 | 0,07 | 0,07 | 0,07 | 0,07 |
| | | 0,10 | — | 0,08 | 0,08 | 0,07 | 0,07 | 0,16 |
| $Na_2O$ | | — | 12,4 | 11,7 | 11,4 | 10,0 | 10,4 | 11,7 |
| $Na_2O/SiO_2$ molar ratio | | — | 0,81 | 0,79 | 0,75 | 0,68 | 0,70 | 0,83 |
| CaO | | 0,6 | 1,4 | 1,2 | 1,4 | 6,1 | 6,3 | 1,2 |
| MgO | | 0,4 | — | 0,6 | 0,8 | 0,8 | 0,6 | 0,6 |
| Cl | | — | — | 0,57 | — | 0,23 | — | 0,1 |
| $SO_3$ | | — | — | — | 2,1 | — | 1,8 | 1,7 |
| Loss on ignition | | 19,2 | 8,6 | 5,8 | 5,1 | 6,0 | 5,2 | 9,6 |
| $Al_2O_3$ yield | | — | 80,5 | 87,2 | 87,2 | 87,2 | 86,7 | 84,1 |

Processing of goethitic bauxites has become of particular importance lately, owing to tropical, e.g. Jamaican bauxites of this type being used for alumina production [9-11].

Reaction kinetics and phase transformation processes occurring when goethitic bauxites are processed are presented in Figures 1 and 2. The constitution of typical red mud samples is shown in Table 1.

It may be seen from Figure 1 that in the presence of CaO, three successive reactions proceeding simultaneously only in a slight degree can be observed during digestion, viz. the dissolution of alumina-containing minerals, the dissolution of titania minerals and their partial transformation into calcium titanate, and finally the transformation of goethite into hematite. While the first reation is complete after 5 minutes at 245 °C, the transformation goethite to hematite reaches an appreciable rate only after half an hour, when the dissolution of titania minerals and their conversion to calcium titanate has made substantial progress. This is demonstrated by the fact that the reaction proceeds through an intermediate phase formed with the Ca ions even in the case of relatively high molar ratios (1.95 in our experiments).

Figure 2 represents the effect of the salt additives NaCl and $Na_2SO_4$. Industrial liquor from the Almásfüzitó Alumina Plant containing 220 g/l $Na_2O$ caust and an important percentage in soda (12%) was used for digestion. The figure demonstrates that in this case, if the amount of the salts in question attains a definite value, practically complete conversion is reached in half an hour, at a molar ratio close to the equilibrium value (1,40). In the presence of CaO, the effects add up. The plots show that in the case of NaCl or $Na_2SO_4$ addition, the transformation goethite to hematite proceeds along a different mechanism.

From the phase composition of typical red mud samples in Table I, it may be seen that the relatively stable goethitic diaspore (substitution 22 mol % Al) can be transformed also without CaO, solely by adding NaCl or $Na_2SO_4$; indeed, the rate of reaction is higher in this case, because no other reactions consuming CaO/e.g. formation of calcium titanate, calcium phosphate [11] will proceed and no secondary losses due to the formation of calcium aluminate will occur.

Diaspore, however, as may be seen from the data in Table I, is dissolved only in the presence of CaO.

In addition to alumogoethite and diaspore, corundum and other $Al_2O_3$ phases containing no combined water are occasionally observed. These phases cannot be digested at usual operating temperatures and concentrations. Even at temperatures exceeding 240 °C, a substantial increase of the digestion molar ratio would be required to dissolve these phases [12].

## 2. COMPENSATION OF CAUSTIC LOSSES BY NaCl AND/OR $Na_2SO_4$ AND CaO ADDITION

The anion incorporated in sodalite and cancrinite type compounds depends on the absolute and relative concentration of the salt contaminates in the recycled digesting liquor. This gave us the idea (for which a patent was applied for) that to compensate caustic losses partially, NaCl or $Na_2SO_4$ additives might be used.

Figure 3 represents the distribution of sodium aluminium silicates vs. digestion temperature in the absence of additive and in the presence of 20 g/l NaCl and 20 g/l $Na_2SO_4$, resp. The data refer to industrial liquor from the Almásfüzitó Alumina Plant processing Iszkaszentgyörgy bauxite, also taking into account data and samples presented in Table I

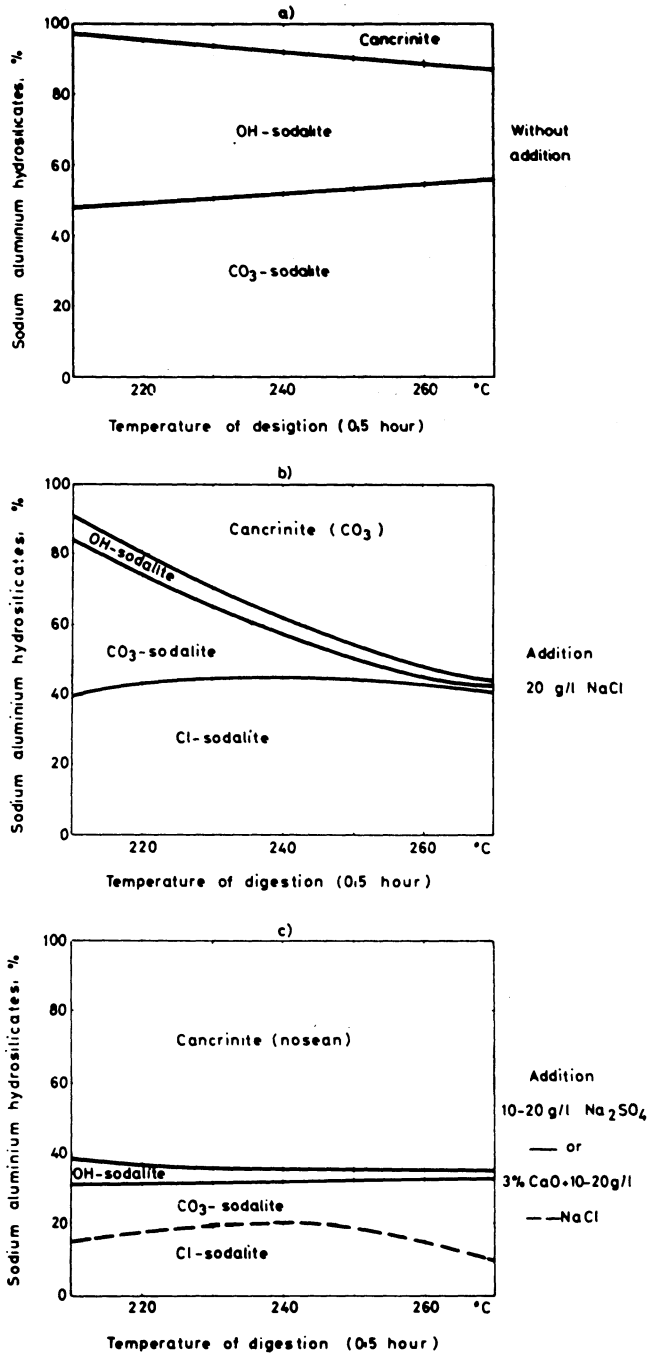



Fig. 3

and Figures 1 and 2. It may be seen from Figure 3 that the salt additives promote the formation of chloride-sodalite and cancrinite, resp. The formation of cancrinite is also favoured by CaO addition.

However, CaO — besides its mentioned effect on the phases — reacts with the aluminate liquor and with some components of red mud. The composition of the resulting compounds noticeably affects caustic consumption and alumina yield and defines the minimum amount of CaO required for phase transformation.

Data from the literature as well as our own studies demonstrated that the addition of CaO to aluminate liquor results in the formation of a phase having the composition $3\ CaO\ .\ Al_2O_3\ .\ 6H_2O$. If the aluminate liquor also contains dissolved $SiO_2$, hydrogarnets

with the composition $3CaO \cdot Al_2O_3\text{-}kSiO_2 \cdot (6\text{-}2k)H_2O$ will be formed, these being solid solutions of the above-mentioned calcium hydroaluminate and calcium aluminium silicate $3CaO \cdot Al_2O_3 \cdot 3SiO_2$.

At conditions close to those of desilication preceding bauxite digestion

($Na_2O$ caust = 150 — 200 g/l, $\alpha$ caust = 1.65, T = 90 °C)

the maximum value of $k$ is 0.3 [13]. In the experiments carried out under digestion conditions

($Na_2O$ caust = 220 g/l, $\alpha$ caust = 1.68, T = 210 °C, t = 1 hr)

we found a value k = 0.77. A higher $k$ value was only obtained by causticization of sodium aluminium hydrosilicates in aqueous or aluminate-free caustic slurries. In these experiments the value of $k$ approached 2.

The solubility of tricalcium hydroaluminate increases substantially with increasing temperatures [14]. In concentrated aluminate liquor ($\alpha$ caust = 1,7, $Al_2O_3$ = 280 g/l) at temperatures between 245 and 300 °C it does not appear as a solid phase at all [15]. Hence, the $SiO_2$-content of the hydrogarnets may show a relative increase in the high temperature stage of digestion owing to the dissolution of calcium aluminate, although the formation of calcium aluminium silicate will be more intense.

In calcium aluminium silicates, depending on the value of $k$, the amount of CaO required for the replacement of caustic and the $Al_2O_3$ loss will change as compared to the phase $3(Na_2O \cdot Al_2O_3 \cdot 2SiO_2) \cdot Na_2X \cdot nH_2O$ usual in the Bayer cycle. In the hydrogarnets formed in digestion, the amount of CaO required to replace 1 part by weight of $Na_2O$ is higher by a factor of 3.2, while the $Al_2O_3$ loss calculated on $SiO_2$ will be increased 2,5-fold.

In studies of the interaction between lime and titanium minerals it must be considered that anatase reacts with the digesting liquor only at temperatures exceeding 180 °C, while the dissolution of rutile becomes intense at temperatures above 210 °C and is completed during the normal digestion time of 1 hour only at 240 °C. The major part of the phases formed consists of $Na_2Ti_3O_7$ and $Na_2Ti_3O_7 \cdot 2H_2O$, while a smaller part ($\sim$ 20%) is $Na_2Ti_2O_5$. If free CaO or $Ca(OH)_2$ is present, $CaTiO_3$ will be formed in all cases. If the amount of CaO is insufficient, the sodium titanates of the above-mentioned compositions will be simultaneously formed.

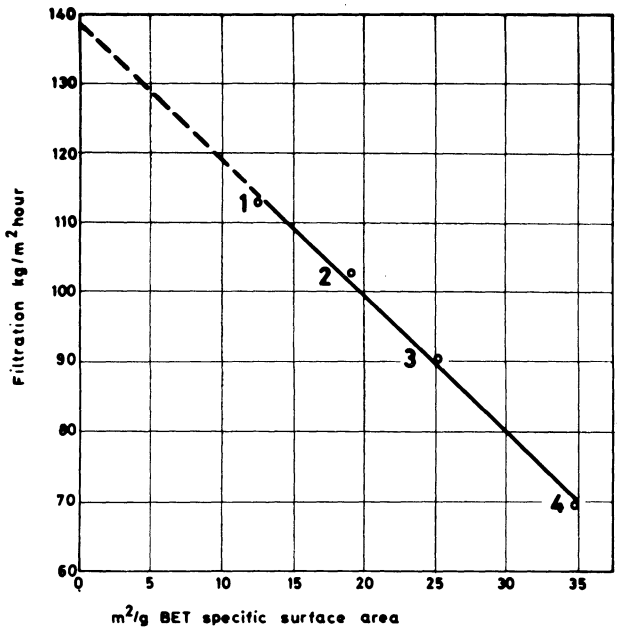
## 3. SEPARABILITY AND WASHABILITY OF RED MUD

Owing to the difficulties in laboratory modelling, the results of filtration and settling tests cannot be readily applied to industrial conditions. We attempted to characterize the separability of red mud by means of its morphology and specific surface area.

Figure 4 presents the results of filtration tests *vs.* specific surface area measured with the BET method, for some typical red muds. Although the mineralogical composition of the muds largely differs, the data yield a good approximation of a straight line, confirming the reliability of the method. The diagram also indicates that by transforming the goethitic mud of the Iszkaszentgyörgy bauxite into hematitic mud, the filterability of the mud is increased by about 25%.

Studies on the speicific surface area and pore size distribution of red mud and its individual constituents allow to throw light on the problem of washability from another view.

In Figure 5 specific pore volume vs. pore radius, measured with a mercury porosimeter, is plotted for the red mud of a largely dolomitic bauxite (Ca + Mg $\approx$ 8%) and for some of its constituents. The same data are presented in Figure 6 where pore size frequency is plotted instead of pore volume. The envelope curves of the column diagram up to pore radii of 200 nm are shown separately.




Filtration at 300 g/l solids.

1. Hematitic mud (transformed) from Iszkaszentgyörgy Bauxite
2. Hematitic-goethitic mud from Halimba Bauxite
3. Goethitic mud from Iszkaszentgyörgy Bauxite
4. Mud from dolomitic Halimba Bauxite

Fig. 4

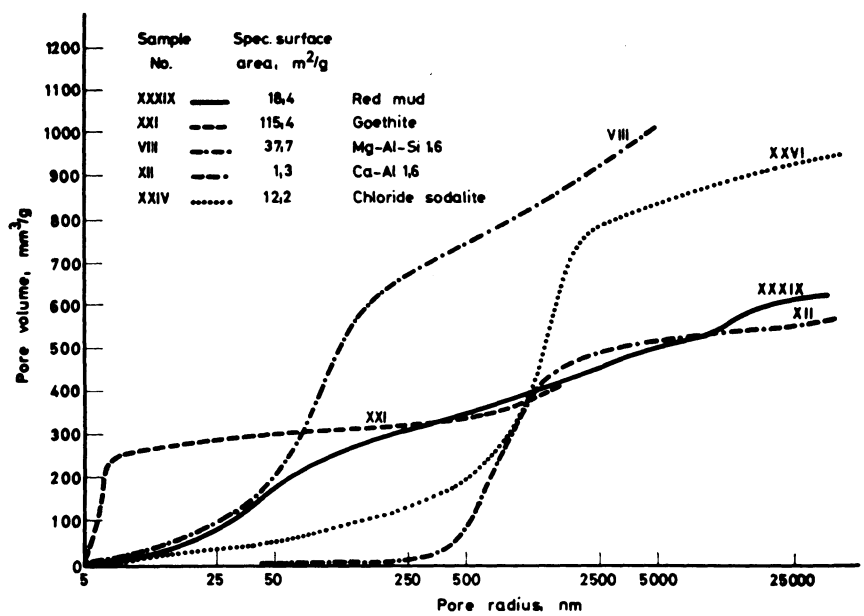



Fig. 5

The porosity of the studied substances is well observable on the scanning electron micrographs in Figure 7.

The amount of liquor retained in the solid phase depends on the total volume of pores, while its removal by washing depends — at a given temperature and concentration gra-

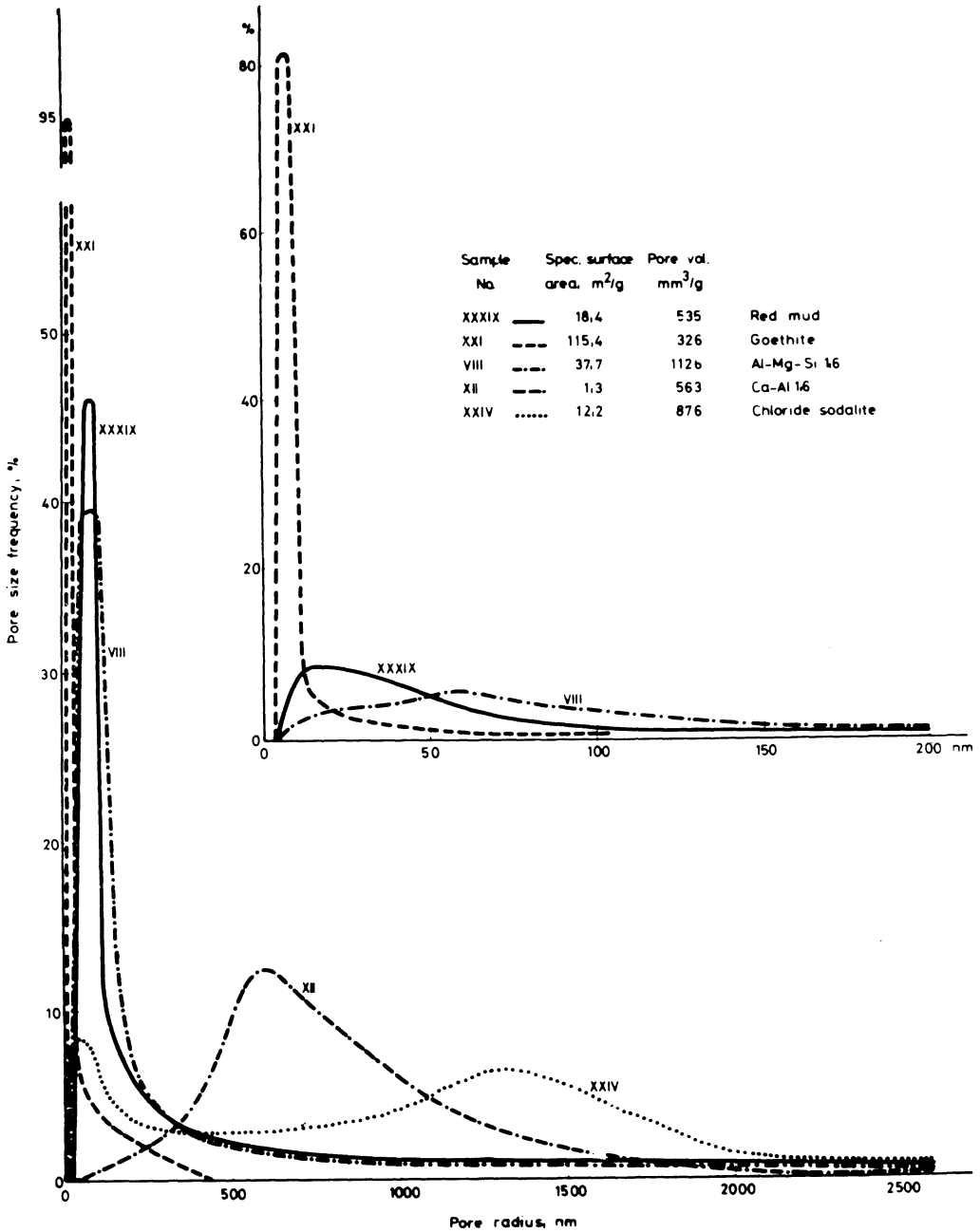


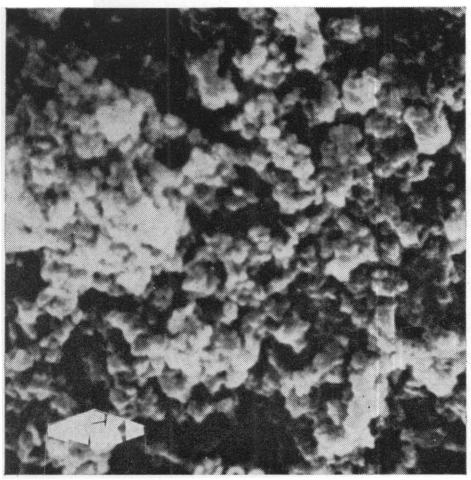

Fig. 6

dient — solely on the flow cross-sectional area, which in turn is controlled by pore size.

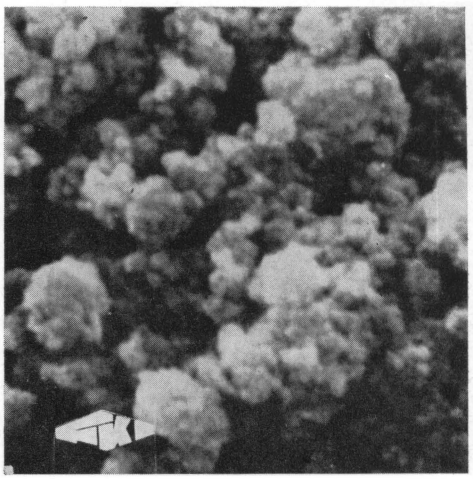
Figure 8 presents curves referring to the extent of washability of the liquor in the pores of individual phases. The dash line presents the amount of removable caustic calculated from the quantity and concentration of the adhering liquor, after individual wash stages. The continuous line represents actual values obtained by washing chloride-sodalite and goethite. Washing experiments were carried out by preparing a slurry of wet mud (separated by centrifuging from the mother liquor) corresponding to 10 g dry matter in 25 ml distilled water and agitating for 5 minutes at 90 °C. Subsequently the slurry was separated by centrifuging for 25 minutes.

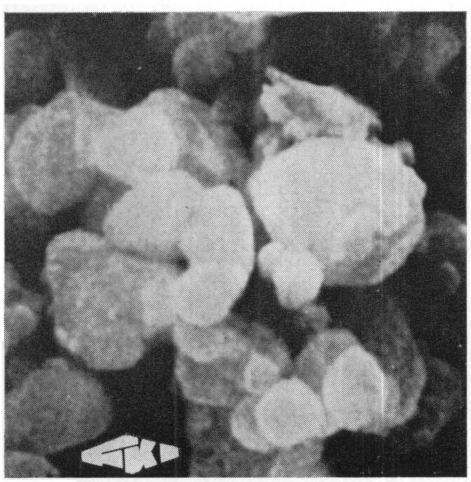
The coincidence of calculated and experimental values in the case of chloride-sodalite indicates that equalization of the concentrations of the wash liquor and the liquor bound

a: Bauxite (Sample Kd-T-3).

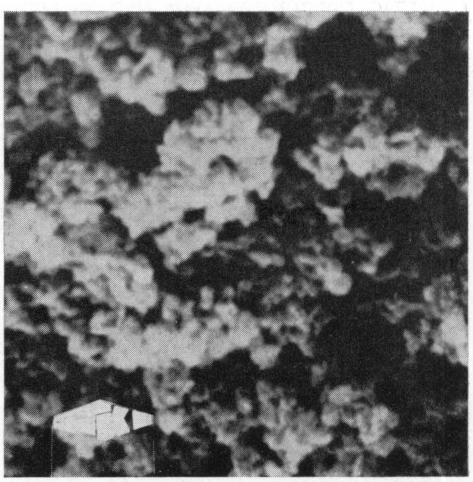


b: Red mud (Sample No. XXXIX).





c: Ca-Al 1,6 (Sample No. XII).



d: Mg-Al-Si 1,6 (Sample No. VIII).

Fig. 7. Scanning electron micrographs

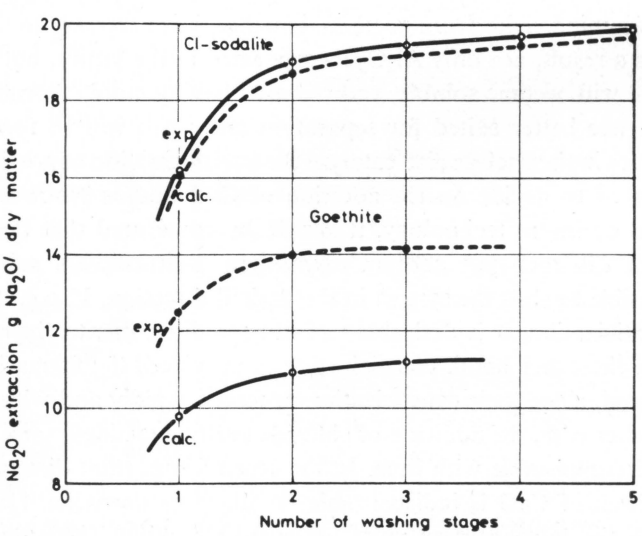



Fig. 8

to the solid phase has taken place. In the case of small-pore goethite, the washing period under the given experimental conditions is too short for equalization to take place, i.e. liquor having a higher concentration than the wash liquor remains in the pores. To effect complete equalization of concentrations, 5 hours were required in the case of goethite, under otherwise similar experimental conditions.

If the size of the pores and the presence of interconnected voids in the substance allows mixing of the liquor occluded in the pores with the wash liquor, dilution and removal of the occluded liquor is feasible. At small pore radii, however, the dissolved matter can leave the pores only by diffusion.

Laboratory tests with red muds led to the result that the above-listed experimental conditions (5 minutes agitation and 25 minutes centrifuging at 90 °C) are satisfactory for washing substances having a mean pore diameter of 250 nm, while with substances having mean pore diameters below 50 nm, a part of the occluded liquor cannot be removed.

Based on this finding, the contradictory observations made from time to time both in industrial practice and in laboratory experiments concerning aluminate liquor "adsorbed" on red mud can be explained. Since the morphological properties of the red muds in question were not defined satisfactorily, it appears that differences in porosity caused the observed phenomena, viz. that in some cases the occluded solution could be removed during the given wash period, while in other cases this period proved insufficient.

Based on the described concept, an explanation is also found for the experience often made in practice that important hydrolysis losses appear even in cases when the temperature of the wash line and the molar ratio of the aluminate liquor do not account for these losses. This can presumably be caused by the fact that the diffusion rate of NaOH is higher than that of the aluminate. Therefore the NaOH concentration in the pores decreases faster than the aluminate concentration, the molar ratio decreases and sodium aluminate is decomposed.

Another important consequence for industrial practice is that when small-pore red muds are being washed on filters, the amount of unremoved occluded aluminate liquor will substantially increase, unless sufficient residence time is allowed before each filtration to enable satisfactory diffusion. In unfavourable cases, several hours may be required.

## 4. CONCLUSIONS

To increase alumina yields from goethitic bauxites, it is necessary to transform goethite into hematite. As a result, not only $Al_2O_3$ incorporated in the lattice, but also the valuable vanadium content will become soluble, and red mud having more favorable morphological properties and hence better suited for separation and wash will be formed. Since NaCl or $Na_2SO_4$ additives in themselves also catalyze the transformation of goethite into hematite, the choice is free as to decide on the addition of CaO and/or NaCl and $Na_2SO_4$, resp. In elaborating an optimum technology, it should be considered that the washability and causticizability of different-type sodium aluminium hydrosilicates substantially differs, and that it is possible to shift the system in the desired direction, If, e.g., the red mud shall not undergo causticization, it is desirable to form sodalites, due to their favourable wash properties. If, on the other hand, causticization is provided, the formation of cancrinites should be promoted, since their causticization proceeds rapidly and with an almost 100% yield [8]. In the latter case, the addition of chloride must be avoided, since chloride-sodalite is practically undecomposable with lime. In the case of important diaspore content in the bauxite, the addition of CaO is indispensable for diaspore digestion. However, increased alumina losses in the hydrogarnets must be calculated with. The amount of CaO and technology should be elaborated so as to ensure that total $TiO_2$ be converted to calcium

titanate and hydrogarnet formation be reduced to a minimum; also, the $SiO_2$ content of the hydrogarnets should be as low as possible.

NaCl and/or $Na_2SO_4$ addition may also be utilized for soda salt precipitation. In this case, the above-noted advantages will be attained without increasing the total salt content of the cycle. In addition, common salt will be used instead of solid caustic for soda salt precipitation.

Finally we wish to underline the improved morphological properites of red muds formed in the presence of CaO, NaCl and $Na_2SO_4$, resp.: reduced specific surface area and microporosity, and hence their improved separability and washability.

The application of the discussed research results in the Hungarian alumina plants has been commenced in the form of industrial-scale experiments. Particularly important results are presumably to be expected under the conditions of tube digestion, where the advantages offered by higher temperatures can fully be utilized — owing to the short residence time — only by accelerating and controlling the phase transformation processes.

We believe that a relevant utilization of NaCl and $Na_2SO_4$ will open up new prospects for the further development of the Bayer technology.

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