

Basic Principles of Bayer Process Design

A. N. ADAMSON, E. J. BLOORE, and A. R. CARR

The British Aluminium Co. Ltd., London, England

Data used in Bayer process design are presented, with an account of the methods used in evaluation of bauxites as a source of alumina, and of plant design, with particular reference made to extraction, silica, mud separation, decomposition, causticization, flow of fluids, and heat transfer.

1. Introduction

The chemical considerations affecting the Bayer process for the production of alumina have been summarized by Pearson.¹ The process can be operated over a wide range of conditions of temperature, liquor concentrations, etc. The choice of conditions involves a complex economic assessment, using such factors as raw material consumption and costs, operating and capital costs. This paper presents an account of the methods used in making this assessment and fundamental data used in designing a plant. The data are generally presented as correlations, representing the best fit for the mass of laboratory and works data collected during the many years that the British Aluminium Co. has been recovering alumina from bauxite by the Bayer process, and where possible with reference to other manufacturers' data. The scope of this paper is limited to the liquor circuit only, and does not deal with the factors affecting the chemical and physical nature of the alumina hydrate produced, nor of its calcination.

Fundamental to this study is the nature of the bauxite used. Generally, alumina occurring in bauxite in trihydrate form is readily attacked at low temperatures by liquors of relatively low soda concentration, while monohydrated alumina is economically extracted only at higher temperatures using liquors of higher soda concentration. Notable in modern practice is the increasing importance of mixed ores with alumina present in both trihydrated and monohydrated form, e.g., in bauxites from North Australia, Jamaica, and West Africa. It may well prove uneconomic in some cases to recover monohydrated alumina,

particularly if the alumina plant is located on or near the bauxite field. Alternatively, mixed ores can be treated in the same manner as pure monohydrate ores.

On the other hand, extraction conditions can be chosen, suitable for the economics of the plant as a whole and not as dictated solely by the extraction of alumina. For instance, extraction at a high temperature (up to 240°C) has been used to give, simultaneously and economically under certain conditions, high alumina extraction efficiency and a large proportion of the evaporation of water necessarily introduced into the circuit for the washing of residues and products. This process, as applied to a particular bauxite, also gives a residue of relatively good settling and filtration characteristics, and rapid desilication of the liquor.

Extraction conditions are usually chosen to facilitate the process of removal of silica. Silica combined as clay and other silicates dissolves early in the extraction process. Silica present in the bauxite as quartz is generally not attacked during extraction at lower temperatures, but is attacked to an increasing extent at higher temperatures. Silica dissolved during the extraction process must be eliminated from the solution as sodium aluminum silicate, and is therefore responsible for loss of soda from the circulating liquor and for reduced recovery of alumina from the ore. The choice of extraction conditions is usually such that quartz attack is at an economic minimum, and that optimum desilication of the product liquor is effected.

Extraction conditions must also be such that the product liquor can readily be converted to the feed liquor for decomposition, the so-called new, green, or rich liquor, of composition dictated by chemical and economic considerations.

Separation of the bauxite residue after extraction and liquor desilication is generally carried out after conversion of the liquor from extraction to the new liquor composition and cooling to atmospheric boiling point. Primary separation can be carried out in continuous settling and thickening equipment, followed by clarifying filters, or in filters only, depending on the settling and filtration characteristics of the residue. The residue as removed from the thickeners or filters is associated with valuable soda and alumina in solution in the wetting liquor, and this is generally recovered by continuous countercurrent decantation washing with water. The wash from this process is generally added to the liquor from extraction to give a liquor of new liquor concentration. If the alumina/soda ratio of the liquor from extraction is higher than that of new liquor, old or spent liquor from the decomposition step will also be added at this dilution step.

Where extraction is carried out in two stages, the slurry from the monohydrate extraction is fed to the washing and disposal system direct, and the wash produced combined with the slurry from the trihydrate extraction to give new liquor and mud, the latter being separated for treatment in the monohydrate extraction stage.

New liquor composition is determined not only by considerations affecting the decomposition step but also by alumina losses and scale deposition due to premature decomposition in the liquor clarification process.

Liquor from the clarification step is cooled before feeding the decomposers, conveniently by heat interchange with old or spent liquor from decomposition and mud washes or water.

Decomposition is effected in what are basically stirred tanks, of which the design and operation at various plants throughout the world vary widely. The process can be operated batch fashion, the seed being retained in the tank after each batch, returned as a separated thick slurry in old or spent liquor, or introduced into the new liquor feed as a filtered, but not washed, cake. From a chemical viewpoint, these variations affect the effective starting liquor composition. The process can also be operated continuously, the main variations being in the steps taken to regulate the intermediate stocks of seed hydrate within the system, and in the position of withdrawal of product hydrate from the system.

Product alumina hydrate from the decomposition system is separated and washed free of soluble soda and alumina. The wash is generally combined with the old or spent liquor from the system, the combined liquor returning to the extraction step.

Carbon compounds enter the liquor circuit from organic constituents of bauxite and as carbon dioxide from the atmosphere, and they must be removed from the circulating liquor.

In some cases other impurities (notably, vanadium, phosphorus, and zinc) tend to accumulate in the plant liquors and are removed by suitable chemical means.

Soda losses from the circulating liquor are made good by the addition of caustic soda or of sodium carbonate with subsequent causticization.

Water introduced into the cycle, mainly as mud and hydrate wash water, must be removed. Modern practice tends toward liquor cooling simultaneous with flash evaporation removing some or all of this water.

For economic operation, it is essential to regard the Bayer process as a closely integrated circuit, each section exerting an effect on the process as a whole.

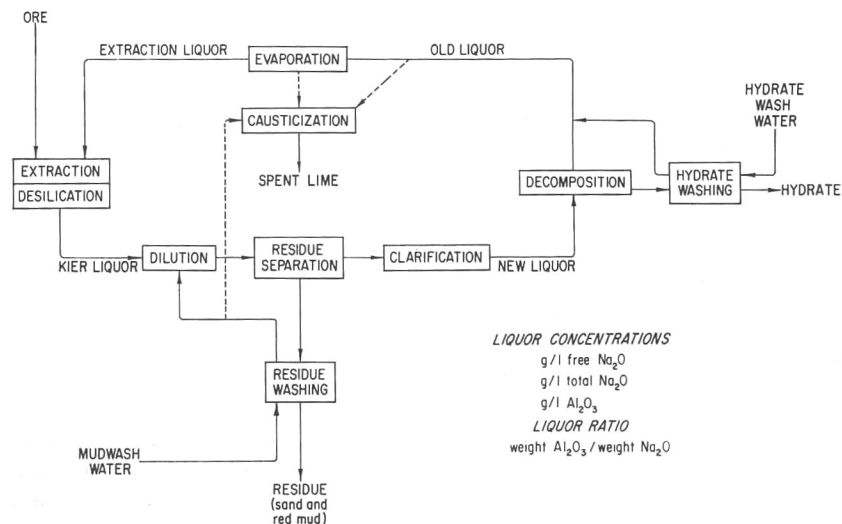


Fig. 1. Diagram of Bayer process, showing terminology. (Decomposition is referred to as precipitation in American practice.)

There are variations in nomenclature in alumina-producing companies. Figure 1 is a diagrammatic representation of the Bayer process, marked to identify some of the terms used in this paper.

Soda concentrations are expressed in terms of equivalent Na₂O, g/liter, alumina concentrations, Al₂O₃ g/liter. Liquor ratio is expressed as weight Al₂O₃/weight Na₂O. (*Editors note:* To correct ratios to American practice multiply by 0.585.)

2. Evaluation of Bauxite

Methods for evaluating a bauxite field are constantly undergoing improvements, and the methods used in the recent assessment of the North Australian deposits are of general application.

Field Survey

For survey work, rapid methods suitable for field use are required and a high degree of accuracy is relatively unimportant. Field analysis determines total silica, quartz (the difference between these being the reactive silica), extractable trihydrate alumina, and total extractable alumina, both mono- and trihydrate. The latter determinations are based on extraction of ore using 100 g/liter Na₂O pure caustic solution for 15

min in a small rotating cylinder heated by gas flame, at 120°C, with ore charge adjusted to give approximately 0.8 Al₂O₃/Na₂O weight ratio in the final liquor for trihydrate, and for 30 min at 180°C to 0.4 ratio for total extractable alumina. Determination of alumina extracted is by volumetric analysis of the resultant liquors. Accuracy is of the order of 0.6% on the ore.

Detailed Survey

For more detailed studies, more extensive work is carried out on composite samples representative of a particular part of the field. Extractions for times up to 3 hr are carried out at various temperatures, usually 120, 180, and 230°C, using extraction liquor of 200 g/liter free Na₂O, 0.50 Al₂O₃/free Na₂O weight ratio, and sufficient ore to give a final ratio of about 0.8. This procedure at 120°C gives the trihydrate only, and at 180 and 230°C the total extractable alumina, while the whole series establishes the pattern of the quartz attack. In making the assessment, the results are corrected for silica remaining in solution, using the ore and mud analysis, assuming that in practice this silica would be deposited on the mud as 2Na₂O·2Al₂O₃·3SiO₂.

Extraction tests are then carried out under the conditions which may be used in the final process, and practical values estimated for extractable alumina, soda loss, mud quantities, etc. Mud settling and/or filtration characteristics are also determined during this work.

Rapid Assessment

During the investigation of North Australian ores it was found that an estimate of ore quality, sufficiently close for preliminary economic studies, could be obtained by calculation from the dry ore analysis, once the pattern of quartz attack had been established.

Using dry ore analysis, if the reactive silica $S\%$ is present as kaolinite, Al₂O₃·2SiO₂·2H₂O, and this with a proportion p of $Q\%$ quartz is attacked to form 2Na₂O·2Al₂O₃·3SiO₂; then

$$\text{alumina present as hydrates } X_h\% = \text{total alumina in ore } X\% - 0.85S$$

$$\text{water present in hydrated alumina } L_h\% = \text{total combined water in ore } L\% - 0.30S$$

$$\text{alumina present as trihydrate } X_t\% = 2.833L - 0.50X_h = 2.833L - 0.50X - 0.425S$$

$$\text{total extractable alumina (monohydrate + trihydrate)} = \text{total alumina in ore } X\% - (S + pQ) 1.133$$

$$\text{total extractable trihydrate} = \text{alumina present as trihydrate } X_t\% - 0.283S - 1.133pQ = 2.833L - 0.50X - 0.708S - 1.133pQ$$

$$\text{soda loss as Na}_2\text{O}/100 \text{ parts ore} = 0.689 (S + pQ)$$

This quick assessment gives values for extractable trihydrate of 94–100% of those determined by extraction and full analysis, 102–105% of the total extractable alumina, 103–140% of the soda loss/100 parts ore during low temperature extraction (120°C), 93–105% of the soda loss at higher temperatures. This accuracy is satisfactory for preliminary economic assessments.

These methods can also be used for investigations on the beneficiation of bauxite. While, in the British Aluminium Co. operations, this is at present confined to the reduction of clay minerals in Ghana ore by wet washing, other methods for further reduction of the silica and quartz contents are constantly being sought.

3. Extraction

Hydrated alumina occurs in bauxite as gibbsite or hydrargillite, Al₂O₃·3H₂O, and as boehmite and diasporite, Al₂O₃·H₂O. Generally, for economic operation, extraction of monohydrate is carried out at temperatures above 160°C, and with relatively concentrated solutions up to 320 g/liter free or caustic Na₂O. The solubility of trihydrate is higher and extraction can be carried out at temperatures up to 150°C using weaker solutions. At temperatures above about 140°C, and at a rate increasing with temperature and soda concentration, trihydrate is converted to monohydrate, so that a solution prepared under trihydrate conditions, if containing alumina in excess of that soluble under monohydrate conditions, and if heated above 140°C, will deposit monohydrate.

The maximum solubilities of alumina under extraction conditions are shown in Figures 2 and 3 for trihydrate and monohydrate conditions, respectively, in the form of equilibrium ratio (weight Al₂O₃/weight free or caustic Na₂O) curves. The equilibria are not substantially affected by the presence of sodium carbonate, sodium chloride, or organic materials. However, recent work suggests that the monohydrate equilibria are sensitive to the species present and that ratios higher than shown in Figure 3 can be obtained on complete extraction, under monohydrate conditions, of such diverse materials as Ghana bauxite, French bauxite, and synthetic monohydrate alumina.

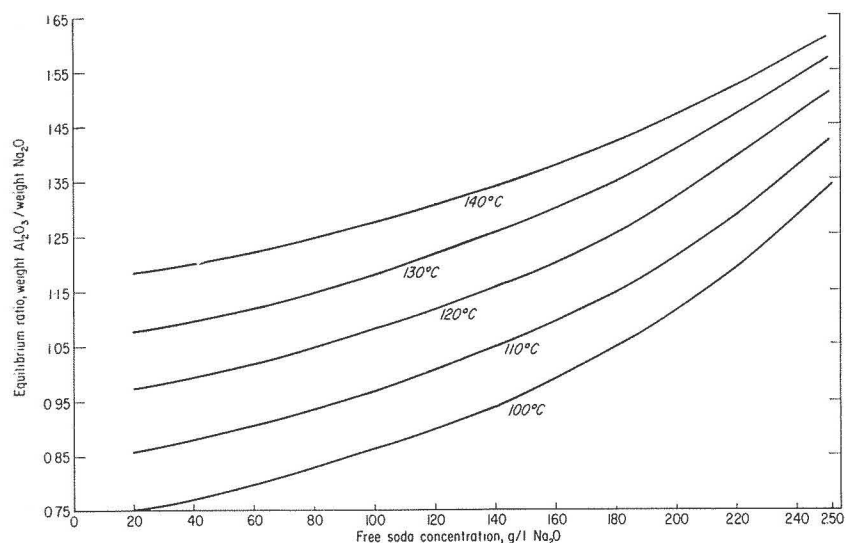


Fig. 2. Equilibrium ratios for trihydrated alumina over a temperature range of 100 to 140°C.

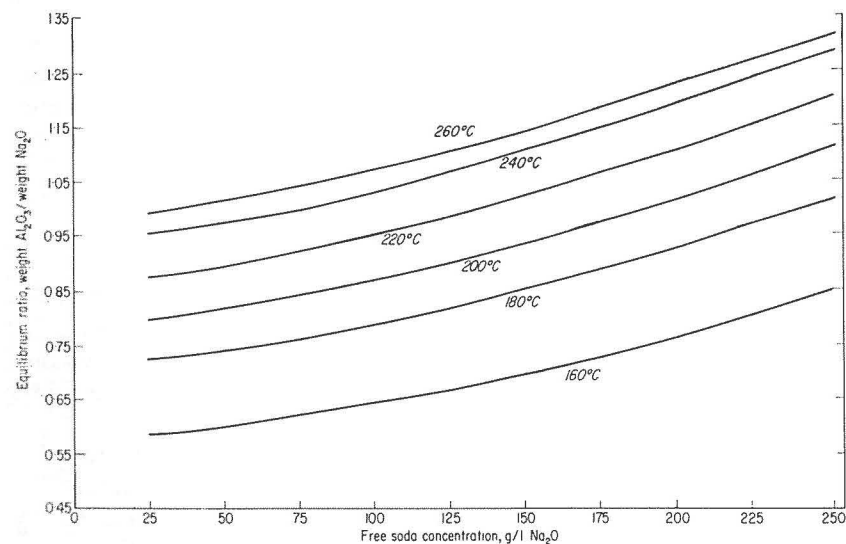


Fig. 3. Equilibrium ratios for monohydrated alumina over a temperature range of 160 to 260°C.

While it has been established² that extraction obeys a kinetic law similar to that governing decomposition (see Sec. 6), in practice extraction conditions are based on the attainment of the required extraction efficiency under production conditions for the particular ore and also desilication of the solution after alumina extraction. Particularly when extracting trihydrate, the latter often establishes the detention time at extraction temperatures (see Sec. 4).

Reference has been made in the Introduction to the extraction of trihydrate and monohydrate alumina ores and of mixed ores containing alumina in both forms. The first work carried out by the British Aluminium Co. on the treatment of mixed ores was concerned with the treatment of some British Guiana ores containing up to 5% of the alumina as monohydrate. In these the trihydrate alumina was extracted at 130–140°C, and the mud residue, after removal of quartz-bearing sand fraction, treated with milk of lime at 160–170°C. The soda recovered from decomposition of sodium aluminum silicate by lime dissolved some of the monohydrate alumina. When ores containing higher proportions of monohydrate were received, the trihydrate extraction residue was treated at the higher temperature with additional soda added, either as caustic soda make up liquor or as a plant liquor. For a time this latter process was followed by the lime extraction process to give a recovery of soda from the residue.

However, and subject to the overall economics, it is occasionally preferable to regard a mixed ore as a simple monohydrate ore and to fix the extraction conditions on this basis, or alternatively to regard the ore as a trihydrate ore and to regard the monohydrate alumina as non-recoverable.

4. Silica

Silica occurs in bauxite in two main forms: (1) reactive silica, as minerals such as kaolinite $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, readily attacked by caustic liquors, with solution of silica (this attack is very rapid under extraction conditions); (2) quartz, not readily attacked by caustic liquors at low temperatures, but increasingly attacked at higher temperatures.

British Guiana bauxites contain a high proportion of quartz, but this is of relatively massive form, is not attacked, and therefore does not lead to soda and alumina loss during trihydrate extraction at 140°C. It can readily be separated as a sand from the residue after trihydrate extraction. This sand can be rejected and the sand- and quartz-free residue can then be worked at higher temperatures for recovery of mono-

hydrate alumina. On the other hand, Republic of Guinea (formerly French Guinea) bauxite contains quartz of very fine grain, uniformly distributed throughout the ore, and attacked to an appreciable extent (with consequent soda and alumina loss) at temperatures over 120°C. The quartz in North Australian ore is of intermediate nature, fine grained, uniformly distributed throughout the ore, not readily separated after trihydrate extraction, but virtually unattacked at temperatures up to 140°C. At 190°C, the quartz in this ore is dissolved to the extent of about 10% per hour, while at higher temperatures the attack is more rapid.

Simultaneously with solution of silica, and particularly if there is a seed such as red mud present, desilication of the solution occurs with the formation of sodium aluminum silicate. Since, in the reduction process, silica present in the alumina will be reduced to silicon and contaminate the product metal, it is necessary to reduce the silica in the liquor after extraction to such a value that contamination of hydrate produced during decomposition is minimized.

Sodium aluminum silicate is a zeolitic compound, and therefore definition of its formula, and hence of the soda and alumina losses due to silica is difficult. Recent evidence suggests that the formula is $3\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot n\text{H}_2\text{O}$. Further reference to this is made in Section 5.

Silica in Sodium Aluminate Solutions

Leiteizen³ has published data showing that there is a maximum solubility of silica (SiO_2) max, g/liter, in sodium aluminate liquors and has given the relation

$$(\text{SiO}_2) \text{ max} = 0.0005 (\text{Na}_2\text{O}) (\text{Al}_2\text{O}_3) \quad (1)$$

where (Na_2O) is the concentration in g/liter Na_2O of caustic or free soda and (Al_2O_3) is the concentration of alumina.

Desilication of sodium aluminate solutions appears to follow the monomolecular law

$$-dS/dt = K'(S - S_\infty) \quad (2)$$

or

$$\log_{10}(S - S_\infty) = -Kt + C \quad (3)$$

where S is the silica concentration of the solution in g/liter, SiO_2 ; S_∞ is the equilibrium silica concentration in g/liter, i.e., the concentration of

silica after infinitely long desilication; K is the rate constant; t is the time in hours; and C is the constant of integration.

Determination of equilibrium silica concentration is complicated by the very slow approach to equilibrium, particularly at lower temperatures, and therefore is usually estimated from analysis of desilication curves. Results indicate that the equilibrium silica concentration, S_∞ g/liter, is independent of temperature but related to the caustic or free soda, (Na_2O) g/liter, and alumina concentration (Al_2O_3) g/liter, according to

$$S_\infty = 0.000026 (\text{Na}_2\text{O})(\text{Al}_2\text{O}_3) \quad (4)$$

The rate constant K can be expressed by a relationship of the form:

$$\log_{10}K = B - 2000/T - 1.5 \log_{10}(\text{Al}_2\text{O}_3) \quad (5)$$

where T is the temperature, °K, and B is a constant.

It will be noted that the soda concentration, except insofar as it regulates the alumina concentration, does not appear in this relationship.

The term B in this relationship depends on the quantity of desilication agent present, and the nature of this agent. It has been established that desilicating agent quantity affects linearly the magnitude of the rate constant K . Apart from this concentration effect, the precise nature of B has not been established. Experimental work is used to determine its value for a particular bauxite residue or sodium aluminum silicate seed.

In the case of a Ghana bauxite (SiO_2 1.2–1.5%) as used at one of the British Aluminium Co. plants, the value of the constant B in eq. (5) for desilication using extracted mud as seed (the quantity being that arising during extraction) is of the order of 7.82.

Application in Practice

The important aspects of silica control in modern plants are not only the limitation of contamination of the product hydrate but also the minimization of scale deposition on liquor (as opposed to bauxite slurry) heat exchanger surfaces and associated equipment.

From eq. (4) it follows that if a liquor, fully desilicated to equilibrium, is diluted, or if, as in the process of decomposition, its alumina/soda ratio is reduced, the resultant liquors will have silica contents in excess of their silica equilibria. These liquors will therefore tend to deposit silica at a rate defined by eq. (5).

A silica-unstable liquor can be converted into a silica-stable liquor by concentration. In the case of a liquor, free soda concentration N_1 , alu-

mina/free soda weight ratio R_1 , desilicated to equilibrium at N_1 , R_1 , being decomposed to a liquor alumina/soda ratio R_2 , this latter liquor can be concentrated to a silica-stable liquor, free soda concentration N_2 , where N_2 can be expressed by

$$N_2 \geq N_1(R_1/R_2) \quad (6)$$

Since the volume of liquor involved in the decomposition process is given by

$$1000/N_1(R_1 - R_2) \text{ m}^3/\text{metric ton Al}_2\text{O}_3 \text{ deposited} \quad (7)$$

the volume of evaporation required to concentrate the liquor from soda concentration N_1 to soda concentration N_2 and give a silica-stable liquor is

$$1000/N_1 R_1 \text{ m}^3/\text{metric ton Al}_2\text{O} \text{ deposited} \quad (8)$$

of which part is contributed by the decomposition process. The total required evaporation is reduced by increasing starting liquor soda concentration and ratio, but it is independent of the finishing liquor ratio.

The silica content of new liquor should be as low as practicable. Ideally this is effected by the extraction process being carried out at a soda concentration not exceeding that of new liquor, and to an alumina/soda ratio similar to that of new liquor. The fact that extraction generally occurs at the top temperature of the cycle can be used to give the highest available rate constant K , eq. (5). Detention time at this temperature can be provided to ensure that the outlet silica concentration is close to equilibrium. However, such extraction conditions may prove uneconomic in other respects, and extraction be effected at high soda concentration and alumina/soda ratio. Desilication is then carried out on kier liquor after dilution and ratio correction, generally on liquor of new liquor composition at atmospheric boiling point. The desilication rate can then only be increased by increasing the concentration of bauxite residue, e.g., by recirculation, or by providing additional sodium aluminum silicate seed.

In practice, the old or spent liquor from the decomposition process must be heated to extraction temperature. It may also be concentrated to remove from the circuit part or all of the wash water necessarily introduced. The most economical form of heat transfer equipment is that in which the old or concentrated old liquor is heated indirectly, by new liquor or steam, for example. The rate of silicate scale formation on the old liquor side of such heaters will be defined by eqs. (4) and (5). To minimize scale formation it is possible to desilicate old or spent liquor

over sodium aluminum silicate scale, but no case of this being carried out in practice is known.

Stabilization with respect to silica of old or spent liquor by concentration would involve a magnitude of evaporation which generally is uneconomic. It is usual therefore to fix upper temperature limits for the heating in steam/liquor or liquor/liquor heat exchangers of old or spent liquor, both before and after concentration. Heating of the liquor above these temperature limits can be achieved by direct steam injection, with the attendant disadvantage of increasing the evaporation necessary, or by heating the liquor as a slurry with bauxite. The latter course has been adopted by British Aluminium Co. plants.

For concentration of old or spent liquor, reverse feed multiple effect vacuum evaporators are peculiarly suitable, as increasing liquor temperature and hence desilication rate constant is being progressively offset by increasing liquor concentration and hence equilibrium silica concentration.

5. Residue Separation

As noted in the Introduction, separation of the bauxite residue after extraction and liquor desilication is generally carried out after conversion of the kier liquor to new liquor composition and cooling to atmospheric boiling point. An important aspect of residue separation is the recovery of valuable soluble soda and alumina from the liquor wetting the residue.

New Liquor Composition

While the economics of the decomposition process generally require a high alumina concentration or alumina/soda ratio in the new liquor, it is important that the new liquor should not be so unstable with respect to alumina that there is excessive premature decomposition of alumina hydrate in the mud separation and new liquor cooling processes. This decomposition results not only in loss of alumina but also in the formation of scale.

The potential of a liquor to decompose can be defined by the decomposition rate equation (14). Defining the decomposition potential of the liquor in the mud separation process is practiced, using this equation with appropriate values introduced, at unity seed area normality. Experience is used to establish the values of decomposition potential which will result in acceptable alumina loss and scale formation.

Sand Separation

Part of the residue from extraction of certain ores has the physical characteristics of, and is loosely referred to as, sand. The chemical nature of the sands vary widely. They may, as in British Guiana bauxite residues, contain an unattacked quartz fraction, or, as in French bauxite residues, be predominantly iron oxide. Generally they are composed of hard, nonflocculating particles, of size >300 mesh and of relatively high settling rate. They are therefore readily separated in continuous settling equipment, the bowl and rake classifier being suitable. Some recovery of valuable wetting liquor can be obtained in the rake compartment of such a classifier, but high efficiency recovery demands additional equipment, either of the countercurrent washing type or by filtration, e.g., horizontal tilting pan rotary vacuum filters.

Mud Separation by Settling

Sedimentation theory has been summarized by Anderson and Sparkman.⁴ Generally, the Coe and Clevenger analytical methods are not applicable to the design of equipment for the settling of red mud residue, due to formation of different floc structures at different starting solids concentrations, and analysis using the more recently developed Kynch method shows greater promise. Such analysis is at present only used as a guide to plant design, and experience is used in fixing plant sizes.

Red mud can generally be flocculated by starch and similar compounds. Starches from various sources have been used with various treatments to crack the starch grains before addition to the slurry. The pretreatments have varied in respect of the caustic concentration of the cracking liquor, temperature, and time of treatment. In the case of Ghana bauxite residue, various starches can be used, with pretreatment by adding a water suspension of the starch to hot (70°C), old or spent liquor, very short treatment time, followed by addition to the slurry in such a way that rapid and thorough dispersion is obtained.

The settling characteristics of bauxite residue vary with extraction conditions. Usually, increasing extraction temperatures give residues of improved settling characteristics, but this is by no means always the case. For instance, while French and Ghana bauxite residues exhibit improved settling characteristics at higher extraction temperatures, residues from North Australian ores show progressively poorer characteristics with increasing extraction temperatures. Design must therefore be based on laboratory work using residue prepared under the expected extraction conditions, but final plant sizing includes an experience factor.

Wash Thickening of Red Mud

The rigorous equation governing wash thickening is

$$\frac{S_{r-1} - L}{N_r} = W + D_v - M_v \tag{9}$$

where S_{r-1} is the total quantity of soda, tons Na_2O , withdrawn in the underflow with the mud from stage $(r - 1)$ and fed to stage r with overflow from stage $(r + 1)$; L is the soda finally lost from the system, tons Na_2O ; N_r is the soda concentration in stage r , g/liter, Na_2O ; W is the wash ratio, $\text{m}^3/\text{ton mud}$; D_v is the underflow consistency, $\text{m}^3 \text{ liquor}/\text{ton mud}$; M_v is the water finally discarded with the mud, $\text{m}^3/\text{ton mud}$; S_{r-1} , the total quantity of soda in the underflow, is made up of two components: (a) the soda present in the liquor = $D_v N_{r-1}$ and (b) soda in excess of (a) which can be termed adsorbed soda for convenience.

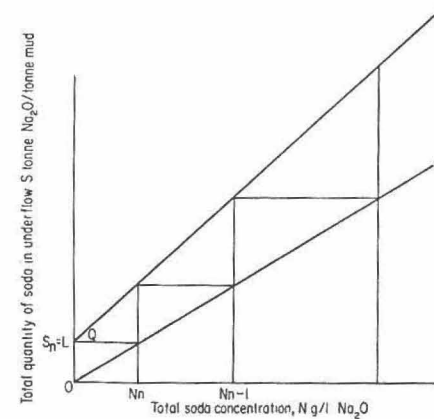


Fig. 4. Graphical solution of wash thickening.

There is some evidence that the sodium aluminum silicate component of red mud is zeolitic in character and therefore its chemical composition varies, in particular with the concentration of soda in the liquor wetting it. There is evidence that sodium aluminum silicate has a formula approximating $3\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot n\text{H}_2\text{O}$, although it is possible that the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio increases slightly with increasing extraction temperature. Soda in excess of this basic formula is referred to as the adsorbed soda. It has been established that there is a relationship between the

adsorbed soda and wetting liquor soda concentration. In the case of a Ghana bauxite mud studied, this relationship was

$$N_a = 0.2138N_t^{0.305} \quad (10)$$

where N_a is the adsorbed Na_2O , % dry mud and N_t is the total soda concentration in the wetting liquor, g/liter Na_2O .

The magnitude of the adsorbed soda, as determined for this Ghana bauxite mud and as expressed in eq. (10) is given as

Adsorbed soda, % Na_2O /dry mud	0.1	0.2	0.3	0.4	0.5	0.7	1
Wetting liquor, total Na_2O g/liter	0.1	0.8	3	8	16	49	160

The attainment of equilibrium on changing the wetting liquor concentration appears to be very rapid.

The wash thickening, eq. (9), can be solved graphically for the case where the underflow consistency D_v is constant throughout the wash thickener system, and where the final soda loss L and hence final total soda concentration N_n are defined, using a plot of total soda against soda concentration, as in Figure 4. In this, curve OP represents $S = D_v N + N_a$ and QR is a line of slope $(W + D_v - M_v)$, origin $S = L$, and represents $S = (W + D_v - M_v)N + L$. The series of steps between the two lines necessary to pass from the original soda N_0 to the final soda N_n can be obtained, and the liquor conditions in each stage determined. It may be considered preferable to use a log-log plot, particularly if N_n is very small compared with N_0 .

For preliminary estimation an approximate equation can be used. Since generally the adsorbed soda and the final soda loss are of similar magnitude, eq. (9) can be rewritten:

$$\frac{S_{r-1} - L}{N_r} = \frac{D_v N_{r-1} + N_a - L}{N_r} = W + D_v - M_v \quad (11)$$

or approximately

$$\frac{N_{r-1}}{N_r} = \frac{W + D_v - M_v}{D_v} \quad (11a)$$

The number of wash thickening stages n will then be the solution of

$$\frac{N_0}{N_n} = \left(\frac{W + D_v - M_v}{D_v} \right)^n \quad (12)$$

where N_0 , N_n are the total soda concentrations in g/liter Na_2O , respectively, of the liquors in the slurry fed to the wash thickener and that required in the final discharge slurry.

In practice, it has been found that hydrostatically controlled series tray wash thickeners give a wash ratio lower than predicted by the foregoing. Their use is being discontinued as circumstances permit, in favor of separate single stage units, with the alternative in some cases of tray thickeners with sealed compartments, the underflow being extracted from each stage.

Mud Separation by Filtration

The filtration characteristics of certain bauxite residues are such that direct filtration is used to separate the residue from the extraction liquor after conversion to new liquor composition. This practice has now been discontinued in Britain in favor of mud concentration by settling and thickening, followed by clarification of the hot new liquor by filtration.

This filtration step is sensitive to extraction and mud separation conditions and all the reasons for variations in the concentration, size, and filtration characteristics of the solids are by no means known. The use of a filter aid is practically essential. Despite extensive experimental work, the only satisfactory filter aid known is a calcium compound and in particular spent lime from the causticization step. The use of this is accompanied by alumina loss and scale formation, as is discussed in Section 7.

In practice, filters of the Kelly type are used, operating at pressures up to 25 lb/in.² gage. The filtration medium is a closely woven metal cloth, with a precoat of either paper or spent lime.

6. Decomposition

Pearson⁵ has given the evidence for the decomposition rate equation

$$-\frac{dx}{dt} = KA_t \frac{(x_t - x_\infty)^2}{(a_\infty + x_\infty)^2} \quad (13)$$

where K is a parameter dependent on temperature only; A_t is the area of seed surface, sq m/l, at time t , hours; x and x_∞ are the molar concentrations of NaAlO_2 at time t and at equilibrium, respectively; and a_∞ is the molar concentration of NaOH at equilibrium.

Batch Decomposition

If X is the concentration of alumina in g/liter Al_2O_3 and N is the concentration of free or caustic soda in g/liter Na_2O , then

$$-\frac{dX}{dt} = KA_t \frac{31^2 (X_t - X_\infty)^2}{51 N_\infty^2} \quad (14)$$

The seed area in eqs. (13) and (14), A_s , is expressed in square meter seed surface/liter liquor. For convenience seed area is expressed in terms of a normality α_s , normal seed having an area of 10 meters²/liter liquor.

If then $X_t - X_\infty = Z_t$, eq. (14) can be expressed as

$$\begin{aligned} -\frac{dZ}{dt} &= \frac{10K \cdot 31^2}{N_\infty^2 \cdot 51} \cdot \alpha_s \cdot Z_t^2 \\ &= K' \alpha_s Z_t^2 \end{aligned} \quad (15)$$

which can be integrated to give

$$1/Z_t = 1/Z_0 + K' \alpha_s t \quad (16)$$

where Z_0 is the value of Z_t at $t = 0$, i.e., $X_0 - X_\infty$.

This equation can be solved, in the general case of varying temperature and hence rate constant K' , varying equilibrium alumina concentration and varying seed, by a step calculation over time intervals sufficiently short that $K' \alpha_s$ is substantially constant.

The calculation of deposition and ratio are complicated by the volume decrease of liquor as alumina is removed from solution. Empirically it has been found that the deposition D and alumina/free soda weight ratio R_t at time t can be expressed to an acceptable degree of accuracy by

$$D = (X_0 - X_t)(1 + 0.00098X_t) \quad (17)$$

$$R_t = (X_t/N_0)[1 - 0.00098(X_0 - X_t)] \quad (18)$$

Theory of Continuous Decomposition

The above treatment refers to batch decomposers only. Continuous concurrent decomposition has been analyzed using stirred-tank reactor theory. For if X_{r-1} , X_r are the alumina concentrations in g/liter in the $(r - 1)$ th and in the r th decomposers, respectively; Q is the liquor flow in meter³/hr, through n decomposers each of volume V meter³; t is the overall reaction time in hours; then in the r th decomposer, the alumina balance is

$$X_{r-1}Q = X_rQ + K' \alpha_s (X_r - X_\infty)^2 V \quad (19)$$

Since $t/n = V/Q$ is the retention time in each decomposer and, as before, $X - X_\infty = Z$, eq. (19) can be expressed as

$$K' \alpha_s (t/n) Z_r^2 + Z_r - Z'_{r-1} = 0 \quad (20)$$

where

$$Z'_{r-1} = X_{r-1} - X_\infty$$

The equilibrium alumina concentration in stage r is $X_{\infty r}$. Analysis of a complete system can therefore be made by a step calculation using the quadratic eq. (20).

Calculation of Practical Decomposition Rates

It has been established that the decomposer tanks cool according to Newton's law

$$dT_t/dt = -k(T_t - T_e) \quad (21)$$

where T_t and T_e are temperatures in °C at time t , hr, and at equilibrium (ambient temperature), respectively; and k is the cooling constant, a function of the plant only. Variation of temperature during decomposition can then be predicted.

Pearson⁶ has referred to the equilibrium composition of sodium aluminate solutions and to the effect of poisons in the liquor. He points out that the effect of the latter in the decomposition of works sodium aluminate solutions is to give false values for the equilibrium. Data for equilibrium alumina concentration in works liquors, over the range 40–60°C, can be expressed by the relationship:

$$\log_{10} X_\infty = \bar{3}.5814 + 0.02113T + (1.788 - 0.007T) \log_{10} N_0 + 0.00064 X_0 \quad (22)$$

where T is the temperature in °C, N_0 is the starting soda concentration in g/liter, and X_0 is the starting alumina concentration in g/liter.

Above 60°C, values of X_∞ tend to be higher than those given by this relationship, the error at 70°C being about 5%.

Smoothed data for the rate constants

$$K' = \frac{10K \cdot 31^2}{N_\infty^2 \cdot 51} \quad (\text{see eq. 15})$$

fit closely the relationship

$$\log_{10} K' = -\frac{3525}{T} - 2 \log_{10} N_0 - 0.1R_0 + 12.0796 \quad (23)$$

where $R_0 =$ starting $\text{Al}_2\text{O}_3/\text{free Na}_2\text{O}$ weight ratio $= X_0/N_0$ and T is the temperature in °K. Application of these data with eq. (16) or (20) as applicable gives decomposition curves close to those obtained in practice.

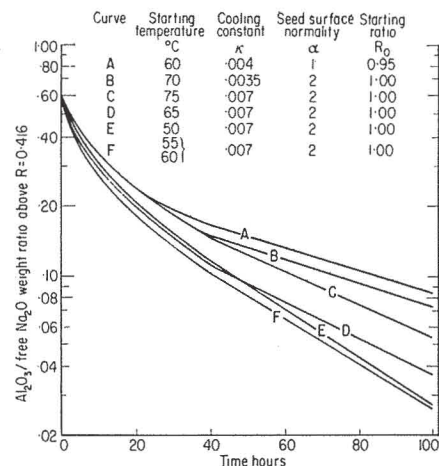


Fig. 5. Decomposition of 130 g/liter sodium aluminate solutions under various conditions.

It has further been found that practical and theoretical decomposition data when plotted in the form $\log(R_t - R_\infty)$ or $\log(X_t - X_\infty)$ against time, give straight line plots for times over 40 hr. The values of R_∞ and X_∞ used in these plots were chosen to give the best fits for the plots, but the preliminary assessments of their values were obtained by extrapolation of data for X_∞ down to the ambient temperature assumed. Examples of these plots are shown in Figure 5.

7. Causticization of Sodium Aluminate Liquors

The caustic liquors circulating in the Bayer process are continuously suffering a reduction in caustic soda/total soda ratio, or purity, due to pickup of carbon dioxide, partly from degradation of organic impurities in the bauxite, and partly from the atmosphere. In addition, if the make up soda is added to the liquor circuit as sodium carbonate, carbonate enters from this source. This carbon dioxide must be removed from the system, on a long-term basis, at the same rate at which it enters.

The method used exclusively by the British Aluminium Co. is causticization of part of the liquor stream by quicklime. It follows that the particular liquor is chosen such that, for the quantity available and the increase in purity obtained by causticization, the resultant carbon dioxide removal offsets the pickup. Liquors that have been used include solution of salts from salting out evaporators (operated at 300 g/liter,

free Na_2O , 340 g/liter, total Na_2O), washes from the red mud wash thickening system, kier liquor during extraction of alumina from bauxite, and old or spent liquor after decomposition.

Figure 6 shows the variation in maximum purity (per cent of Na_2O present as NaOH) attainable with soda concentration when causticizing soda and sodium aluminate solutions at 95–100°C. Curve A shows the results obtained by Littmann and Gaspari⁷ under conditions where complete conversion to equilibrium was claimed, curve B the results by Goodwin⁸ and Olsen and Direnga,⁹ Lunge,¹⁰ whose results are similar to

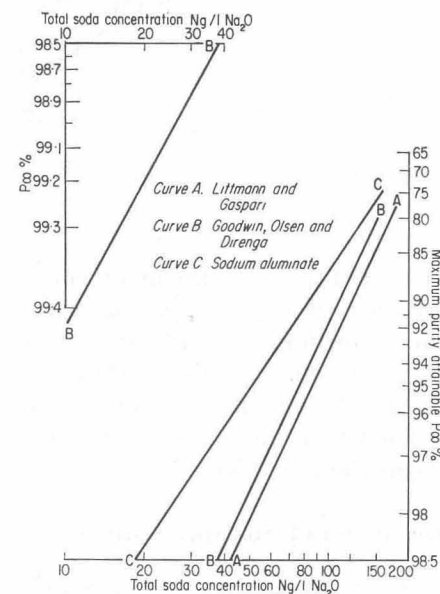


Fig. 6. Causticization—maximum purity attainable.

those of Littmann and Gaspari, claimed that increase in temperature had little effect on the equilibrium. Some tests on causticization of aluminate solutions at 275°C, simultaneous with extraction, show that the purities attainable approach the Littmann and Gaspari data.

Causticization of aluminate solution under works conditions (e.g., 95–100°C) with relatively short reaction times indicates that the maximum purity attainable, P_∞ %, is related to the total Na_2O concentration as shown by curve C in Figure 6 or by

$$\log_{10}(99.5 - P_\infty) = 1.632 \log_{10}(\text{Na}_2\text{O})_t - 2.0635 \quad (24)$$

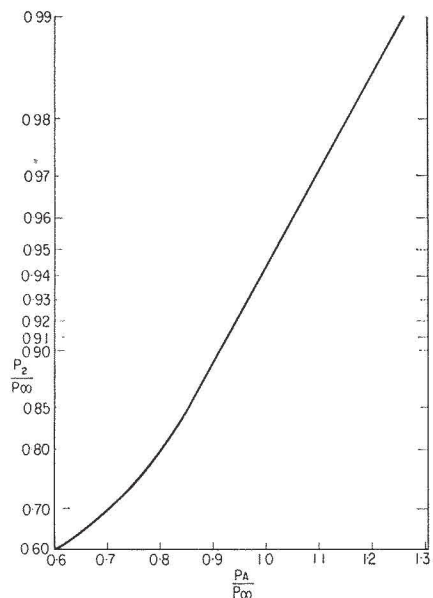


Fig. 7. Causticization—purity attained.

Results indicate that the purity P_2 attained under works conditions (i.e., 95–100°C up to 1 hr reaction time) and the purity aim P_A (i.e., the purity that would be attained if all the quicklime added were converted to calcium carbonate) are related according to Figure 7. It will be noted that the plot of P_2/P_∞ against P_A/P_∞ gives a single curve for all soda and alumina concentrations, and that for values of P_A/P_∞ above 0.85

$$\log_{10}(1 - P_2/P_\infty) = 1.6523 - 2.896P_A/P_\infty \quad (25)$$

This relationship also applies at 275°C.

The excess lime, not present as carbonate after the reaction, can be expressed as

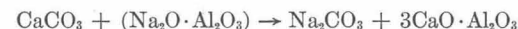
$$(\text{Na}_2\text{O})_t(P_A - P_2) \text{ 56/6200 g/liter CaO} \quad (26)$$

This lime reacts, to an extent depending on reaction time, concentration, and temperature, with alumina from the solution, to give tricalcium aluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. There is evidence that this reaction is not complete, even under the conditions of high alumina concentration and extended reaction time, but complete reaction would lead to an alumina loss of

$$0.548 (\text{Na}_2\text{O})_t(P_A - P_2)/100 \text{ g/liter Al}_2\text{O}_3 \quad (27)$$

There are two important back reactions which affect the overall causticization:

1. If spent lime from causticization at a certain soda concentration is mixed with liquor of a higher soda concentration, there is a tendency for the reaction of calcium carbonate with sodium aluminate, giving reduced liquor purity and alumina loss according to:



2. If, on the other hand, the spent lime is mixed with liquor of lower concentration, there is a tendency for the reaction of calcium aluminate with sodium carbonate, giving increased liquor purity and alumina recovery according to



These reactions are to be expected from the basic principles enumerated previously.

For instance, a one-hour treatment at boiling point (107°C) of 160 g/liter total Na_2O , 86% purity, 0.82 Al_2O_3 /total Na_2O weight ratio, new or green liquor with calcium carbonate sludge from causticization led to a drop in liquor purity to 75% and of Al_2O_3 /total Na_2O weight ratio to 0.77.

Conditions have not yet been found favoring the completion of the back reaction to calcium aluminate, some calcium carbonate and a small amount of free lime remaining. It is suspected that the calcium aluminate can be formed as a coating over the solid particles, leading, in the case of causticization of aluminate liquors, to a low efficiency of utilization of lime, and in the case of the back reaction of calcium carbonate to calcium aluminate, to incomplete reaction.

8. Flow of Fluids

Viscosity

The variation of viscosity of water with temperature can conveniently be represented by the linear plot of log viscosity against an empirical temperature scale. The variations of log viscosities of 20, 40, and 60% sucrose solutions with temperature are also linear with respect to this temperature scale. The negative slopes of the lines increase regularly with increasing sucrose concentration, and a fan of lines can be obtained. It has been established that the viscosities of industrial sodium aluminate solutions can be represented similarly.

The viscosities of industrial sodium aluminate solutions at 60°C have been found to approximate

$$\log_{10} \mu_{60} = \bar{1}.672 + 0.00260 (\text{Na}_2\text{O} + \text{Al}_2\text{O}_3) \quad (28)$$

where μ_{60} is the viscosity of the solution at 60°C in centipoises, $\bar{1}.672$ is the \log_{10} viscosity of water at 60°C in centipoises, Na_2O is the total soda concentration in g/liter, Na_2O , and Al_2O_3 is the alumina concentration in g/liter, Al_2O_3 . The variation of log viscosity with temperature for a solution of a given viscosity at 60°C can then be predicted from the water/sucrose solution data.

Flow of Flashing Liquors

Bayer process liquors froth readily with air. Similarly, froths can be generated with steam and the liquor or slurry may be transported as a froth. A Bayer liquor-steam mixture rising in a sloping pipe acts as a froth and does not, as water, give slug flow.

This principle has been used in the transfer of flashing slurries from extraction and in the interconnecting pipes between flash vessels. In the latter application, the slurry flow control valve is sited at the outlet of a flash vessel and is sized for slurry flow. Interconnecting pipework to the following flash vessel is designed for the flow of the froth resulting from the flashing of the slurry, the extent of this flashing depending on the pressures varying throughout the length of the pipe. Advantage is taken of the fact that the density of the froth is considerably lower than that of the liquor from which it is formed to obtain elevation of the slurry and to obtain better control characteristics in the control valve. In addition, since practically all the flash occurs in the interconnecting pipework, wear is substantially in this pipework and not in the flash vessel itself. It is possible that the flash steam is more readily obtained at a high degree of cleanliness.

The original installation was designed by using the standard fluid flow theory¹¹

$$\Delta P = G^2(v_2 - v_1)/g + fG^2v_{av}L/2gm + KL\rho_{av} \quad (29)$$

= change in kinetic energy + friction loss + head of froth

where ΔP is the difference in pressure between two points, lb/ft²; g is the acceleration constant, ft/sec²; v_{av} is the weighted average specific volume of the inlet and outlet, specific volumes v_1, v_2 , respectively, in ft³/lb; G is the mass flow, lb/sec ft²; f is the friction factor (Fanning);

m is the hydraulic radius, ft; KL is the change in height between inlet and outlet, ft; ρ_{av} is the weighted average density of the inlet and outlet, densities ρ_1, ρ_2 , respectively, lb/ft³; and L is the length in ft.

The calculation was by trial and error solution over a series of sections, chosen for convenience, to be each bend, entry, straight pipe discontinuity, or each foot of pipe.

Analysis of a particular installation of 6 in. pipe of commercial roughness showed that the pressure drop gave results in line with theory, if a friction factor f of 0.0041 was assumed. This value is in line with that expected for high Reynolds numbers.¹² In making the analysis, the exit loss traditionally applied is not applicable, but rather the change in kinetic energy term of eq. (29) defines the exit loss from the pipe.

In some applications, it is preferable to suppress flashing in pipework which can then be sized for liquid flow. Where applicable, the suppression can be obtained by siting a flow control valve at the pipework exit, but where this is not feasible, suppression is obtained by installing at the exit a wear-resistant orifice of suitable dimensions.

9. Heat Transfer in the Bayer Process

The Bayer process can be represented diagrammatically as shown in Figure 8.

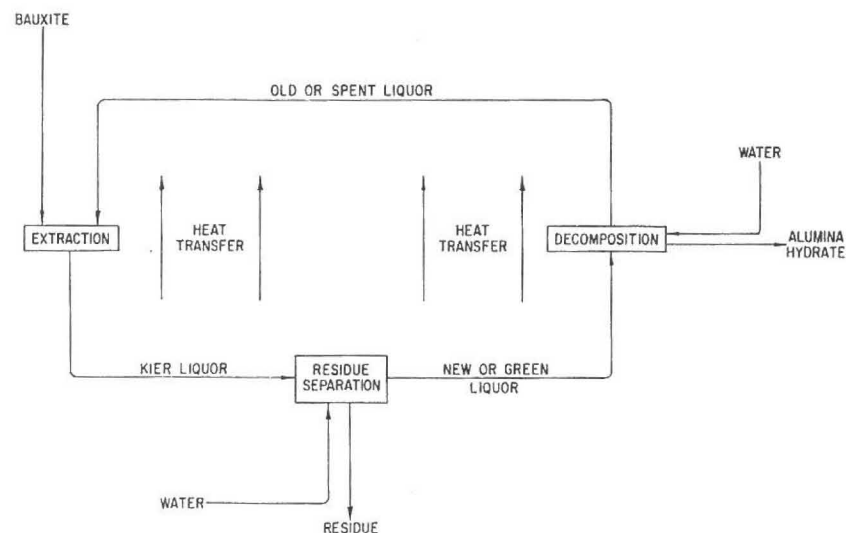


Fig. 8. Diagrammatic representation of the Bayer process. (Decomposition is referred to as precipitation in American practice.)

The temperature of the liquor leaving the extraction step is in the range of 105 to 250°C, depending on various chemical factors. Mud separation is generally carried out at atmospheric boiling point. The new or green liquor feeding the decomposers is in the range of 50 to 75°C. Water is introduced into the circuit to recover valuable liquor from waste red mud and to wash the alumina hydrate product and must be removed from the circulating liquor.

There is clearly scope for the practice of regenerative heat transfer from the kier liquor/new liquor side of the cycle to the old or spent liquor side. This transfer can be continuous in countercurrent liquor/liquor heat exchangers, or discontinuous in flash steam/liquor heaters, or by flash evaporation/direct injection. Factors, such as deposition of scale, generation of power, and the magnitude of the heat losses from the plant must be considered along with the more basic processes of extraction, desilication, decomposition, causticization, and the water required to wash the product hydrate and red mud.

Analysis of Heat Transfer Process

The heat transfer process can be analyzed graphically or, in simpler cases and if certain assumptions are made, by direct algebraic methods. The complete graphical analysis is shown in Figure 9. In the following analysis, the term "liquor" may in practice refer also to a slurry of liquor and bauxite, bauxite residue, or hydrate.

When liquor is heated, the variation of its total heat with temperature can be represented by a line such as *ABC*. In practice, the liquor volume may vary, as when heat transfer by direct injection of steam is practiced or when liquor is withdrawn from the system, e.g., for wet milling of bauxite. There will also be heat losses due to convection, noncondensable gases, and to the heat of reaction, e.g., if bauxite slurry is being heated under conditions giving solution of alumina. Therefore, consider the relationship between the increase in temperature of the liquor and the heat supplied to practical heaters as shown by line *AB'C''*.

Heat from an external source must be supplied if heat transfer is to be effected in a closed circuit. The theoretical heat input can be calculated from the overall heat balance of the system and must be supplemented by the losses in the liquor heating and cooling systems. These quantities are denoted and shown by *S_t*, *L_H*, *L_s*, and *L_c*.

In Figure 9 liquor originally at temperature *T₀*, heat zero, is heated to temperature *T₁*, heat *H₁* above zero, by heat *H'₁* supplied to heat exchangers which incur a heat loss *L_H*, and is then further heated to

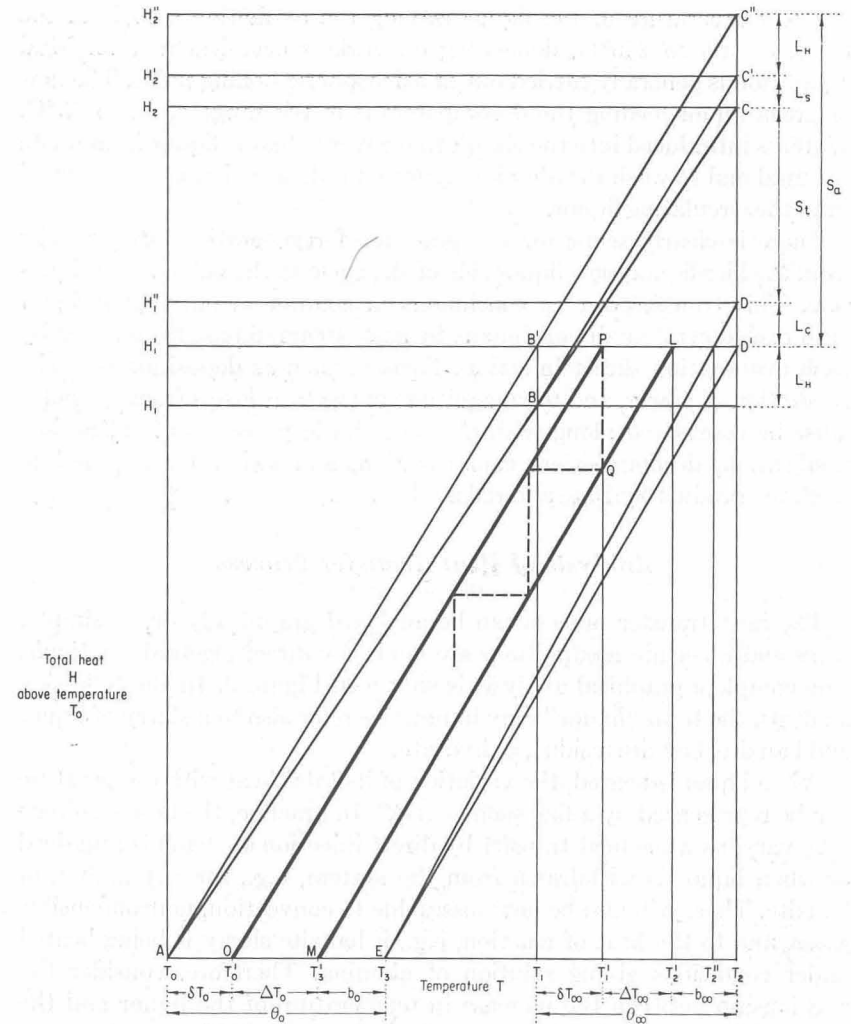


Fig. 9. Graphical solution of heat transfer.

temperature *T₂*, heat *H₂* in heat exchangers supplied with heat (*H'₂* - *H₁*) from an external source, these final heaters incurring a heat loss *L_s*, *L_H* and *L_s* being due to convection, noncondensable gases, etc., and to any heat of solution or reaction.

The heated liquor, and possibly condensate from the final heaters if these are indirectly steam heated, can be cooled by the quantity *H''₁* and the heat transferred to the feed liquor. This quantity *H''₁* equals the

heat supplied to the heaters, H_1' , plus losses during the cooling process L_c , due to convection, heat of concentration, etc. It will be noted that if cooling is by flash evaporation, and the resultant condensates are also cooled by flash evaporation in parallel with the liquor, the effective quantity of liquor cooling remains constant throughout the cooling process.

For convenience the cooling process is shown by the line DE where D is the starting liquor temperature T_2 , heat H_1'' , E is the final liquor temperature T_3 , heat zero. In cooling, loss L_c is incurred. Also, if heat transfer is by flash evaporation/indirect steam liquor heaters, the heat will not be available between temperatures T_2 and T_3 , but between these temperatures less the boiling point rise and the temperature loss due to the pressure loss in the flash steam vapor lines, entrainment separators, etc. (i.e., the heat will be available only at the temperatures at which the flash steams condense). Heat transfer by direct injection involves equalization of vapor pressures, and hence the boiling point rise loss is not incurred.

In Figure 9 the line LM represents the availability of heat from the cooling process and is the line DE corrected for heat losses during flashing, and for temperature losses, where applicable, due to the boiling point rise and pressure loss.

In the case where heat is exported from the cooling liquor system (e.g., as steam to another process, boiler feed water, etc.) the effective quantity of cooling liquor will not remain constant throughout the flashing process.

The solution for the case of continuous liquor/liquor heat transfer is straightforward.

The simplest solution for the discontinuous flash heat transfer process is to assume that in the heat exchangers a terminal temperature difference, either fixed or regularly variable with liquor exit temperature, is required. If this temperature difference is δT_0 at liquor temperature T_0 , δT_∞ at liquor temperature T_1 , an operating line, OP can be drawn, where O is temperature $T_0' = T_0 + \delta T_0$, heat zero, P is $T_1' = T_1 + \delta T_\infty$, heat H_1' . Then in the first flash stage, liquor will flash to give steam condensing at T_1' and transfer heat equivalent to PQ . Subsequent stages will be given by the series of steps between the operating lines OP , LM . Conditions of the steam and liquors at all points in the system can now be determined.

Using certain assumptions, an algebraic solution can be obtained. Generally,

$$H = Q \cdot s \cdot T \tag{30}$$

where H is the heat content of liquor or slurry, Q is the quantity of liquor or slurry, s is the specific heat, and T is the temperature.

If s can be assumed constant over the temperature range considered, then

$$dH/dT = Qs \tag{31}$$

Considering the case of a constant liquor quantity, say Q_H , of specific heat s_H being heated, then the slope of the line AB , Figure 9, say (H) , will be

$$(H) = Q_H s_H \tag{32}$$

If it can be assumed that the heat losses during heating, L_H (due to convection, noncondensable gases, and reaction) can be expressed in terms of an efficiency

$$\eta_H = 1 - L_H/H_1' \tag{33}$$

then the slope of the operating line OP , say $[H]$, will be

$$[H] = \frac{Q_H s_H}{\eta_H} \left\{ 1/1 + \frac{\delta T_\infty - \delta T_0}{T_1 - T_0} \right\} \tag{34}$$

In practice, design will probably be based on constant terminal temperature difference throughout, i.e., $\delta T_\infty = \delta T_0$. Equation (34) then reduces to

$$[H] = Q_H s_H / \eta_H = (H) / \eta_H \tag{35}$$

On the liquor cooling side, consider the case of constant effective liquor quantity, say, Q_c effective specific heat s_c . As noted previously, the effective liquor being cooled may be made up of the actual liquor from the process and condensate from the indirect steam/liquor final heater. Also, in the case of flash evaporation of liquor with parallel flashing of the condensate arising from it, the effective liquor quantity remains constant throughout the flashing process, if there are no exports from the system as a whole of steam, condensate or liquor, nor heating within the system by direct injection. If, further, the heat loss L_c due to convection within the liquor cooling circuit and to heat of concentration can be expressed in terms of an efficiency

$$\eta_c = 1 - L_c/H_1'' \tag{36}$$

then, as for the heating circuit, the slope of DE in Figure 9, say (C) , can be expressed as

$$(C) = Q_c s_c \tag{37}$$

and the slope of the operating line LM , say $[C]$, as

$$[C] = Q_c s_c \eta_c \left\{ 1/1 - \frac{b_\infty - b_0}{T_2 - T_3} \right\} \quad (38)$$

where, b_∞ and b_0 are, respectively, the temperature losses due to boiling point rise and pressure loss in the vapor lines at start and finish of a flash evaporation process.

Many worked examples have shown that over the range of conditions usually operated the boiling point rise does not vary appreciably during flash evaporation, the increase in the boiling point rise due to increasing soda concentration being offset by the decrease due to decreasing temperature. Equation (38) can then be simplified to

$$[C] = Q_c s_c \eta_c = \eta_c(C) \quad (39)$$

It can be shown that if heat transfer is discontinuous (e.g., by flash evaporation) the required number of stages n is given by

$$n = \frac{H_1'}{[H](\Delta T_0 \text{ or } \Delta T_\infty)} = \frac{(T_2 - T_3) \text{ or } (T_1 - T_0)}{\Delta T_0 \text{ or } \Delta T_\infty} \quad (40)$$

if $[H]/[C] = \eta_c \eta_H(C)/(H) = 1$, and

$$n = \frac{\log(\Delta T_\infty/\Delta T_0)}{\log([H]/[C])} = \frac{\log[1 + \{1 - \eta_c \eta_H(C)/(H)\}(T_2 - T_3)/\Delta T_0]}{\log(H)/\eta_c \eta_H(C)} \quad (41)$$

if $[H]/[C] = \eta_c \eta_H(C)/(H) < 1$ and > 1 but $< 1 + \Delta T_0/(T_0 - T_3)$ where $T_2 - T_3$ is the temperature range over which the liquor is cooled; $T_1 - T_0$ is the temperature range over which the liquor is heated; ΔT_0 is the difference between the temperatures of the liquors entering and leaving the system $T_3 - T_0 = \theta_0$, say, less the boiling point rise of the liquor, temperature loss due to pressure drop in the vapor pipes of each stage and the terminal temperature difference of the heaters (the sum of these assumed constant throughout); (H) and (C) are, respectively, the heat equivalents of the liquor or slurries being heated and cooled, in the case of (C) including, e.g., final heater condensate if this is flashed in parallel with the liquor; η_H is the ratio of the increase in heat of the liquor or slurry passing through the heaters to the heat supplied to the heat exchangers, and allows for losses due to convection, non-condensable gases, heat of reaction, etc.; η_c is the ratio of heat available at the heaters to the decrease in heat of liquor or slurry during cooling, and allows for losses due to convection, heat of concentration, etc.

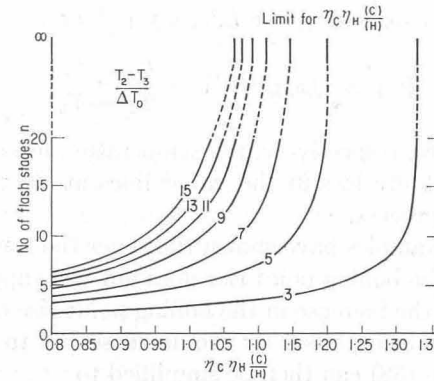


Fig. 10. Flash evaporation—number of stages required.

The values of n , the number of flash-heater stages, from eqs. (40) and (41) are shown in Figure 10.

The total heat supplied to the preheaters will be

$$\eta_c(C)(T_2 - T_3) \quad (42)$$

For discontinuous heat transfer, the heat transferred in the r th stage will be

$$\frac{(H)}{\eta_H} \Delta T_0 \left\{ \frac{1}{\eta_c \eta_H} \frac{(H)}{(C)} \right\}^{r-1} \quad (43)$$

The liquor or slurry enters the final heater at a temperature

$$T_1 = T_0 + \eta_c \eta_H [(C)/(H)](T_2 - T_3) \quad (44)$$

For discontinuous heat transfer, the terminal temperature difference in the heaters has been defined as δT throughout. The starting temperature difference in the r th stage will be

$$\delta T + \Delta T_0 \left\{ \frac{1}{\eta_c \eta_H} \frac{(H)}{(C)} \right\}^{r-1} \quad (45)$$

The log mean temperature difference in the r th stage will therefore be

$$\frac{\Delta T_0 \left\{ \frac{1}{\eta_c \eta_H} \frac{(H)}{(C)} \right\}^{r-1}}{\log_e \left[1 + \frac{\Delta T_0}{\delta T} \left\{ \frac{1}{\eta_c \eta_H} \frac{(H)}{(C)} \right\}^{r-1} \right]} \quad (46)$$

If U_r is the heat transfer coefficient in the r th stage, the heat transfer area required in the r th stage will be

$$\frac{(H)}{\eta_H} \frac{1}{U_r} \log_e \left[1 + \frac{\Delta T_0}{\delta T} \left\{ \frac{1}{\eta_c \eta_H} \frac{(H)}{(C)} \right\}^{r-1} \right] \quad (47)$$

Where heat exchange is by flash evaporation, the evaporation is equivalent to that obtained by loss-free flashing from temperature T_2'' to T_3 , i.e., to a temperature drop of $\eta_c(T_2 - T_3)$. Calculations show that, almost exactly over the range of water temperature 100–250°C, a liquor flashes 10% of its volume for a drop of 50°C in the water temperature, where the water temperature is the temperature of water exerting a vapor pressure the same as that of the liquor, or the liquor temperature less boiling point rise, over the range of soda concentrations encountered in practice.

If the thermal efficiency of the final heater is defined as previously, with allowance for losses in the heater due to convection and heat of reaction, as in

$$\eta_s = 1 - L_s/S_t \quad (48)$$

the total heat input to the system $S_a = S_t + L_H + L_s + L_c$ will be given by

$$S_a = \frac{(H)}{\eta_s} \left\{ \theta_0 + (T_2 - T_3) \left(1 - \eta_H \eta_c \frac{(C)}{(H)} \right) \right\} \quad (49)$$

where θ_0 is the temperature difference between the inlet liquor to the heaters and the outlet liquor from the coolers.

Similar methods can be used for the analysis of more complex systems with quantities of liquor varying within the system, direct injection heating of liquor at one or more stages by flash or live steam, withdrawal of heat as steam or condensate at intermediate points in the system, etc.

Factors Affecting Heat Transfer

For countercurrent liquor/liquor heat transfer it is necessary to have available, either from the convection and other heat losses from the whole Bayer circuit or by deliberate heat rejection from the system, a temperature difference $\delta T = \theta$ between the inlet and outlet liquors, equivalent only to that required in the heat exchangers. Flash evaporation simultaneous with liquor cooling requires a temperature difference between inlet and outlet liquors greater than that required in the heat exchangers alone by the boiling point rise plus ΔT_0 , the magnitude of this

last difference regulating the number of flash stages required. Heat transfer by flash evaporation/direct injection similarly requires the heat exchanger temperature difference and ΔT_0 , but since the heat transfer process depends on equalization of vapor pressures, an additional temperature difference equivalent to the boiling point rise is not required. In each case the temperature difference must be preserved throughout the heating/cooling system, the condition for this being

$$\Delta T_0 > (T_2 - T_3) \{ \eta_H \eta_c [(C)/(H)] - 1 \} \quad (50)$$

Having established the necessary temperature difference, then for a heat consumption equivalent to this temperature difference, a flash evaporation/heater system can be designed to give an evaporation/feed liquor ratio proportional only to the temperature range over which the liquor is flashed. This range may be defined by the extraction temperature and the temperature of the new or green liquor entering the decomposers.

Extraction may be carried out at some temperature higher than that required from considerations of extraction alone to give the desired amount of evaporation. The heat input to the system is defined by the temperature difference plus losses.

It follows that for a high evaporation/feed liquor ratio to be obtained in a single flash/heater system, high pumping pressure and high pressure heaters and flash vessels will be required. It may in some cases be possible to increase, by recirculation, the feed liquor quantity or alternatively to install a two-stage flash evaporation/heater plant, but both of these, while operating at lower pressure, will require a higher temperature difference to give the total evaporation obtained in a single unit without recirculation.

It will be noted that the term $\eta_H \eta_c (C)/(H)$ should be kept to a minimum for economic design. Consideration can be given to the following methods of achieving this.

1. In the case of the system applied to the extraction of alumina, heating the slurry of all liquor supplied to extraction with the bauxite, thereby giving an effective quantity of material being heated as nearly equal as possible to that being cooled, and also supplying some of the heat of solution of alumina from the cooling liquor.

2. Avoiding heating by direct injection of steam, with the attendant increase in the quantity of liquor being cooled relative to that being heated, and introduction into the liquor water which must at some stage be evaporated.

3. Avoiding the necessity of using the flash system to recover heat from the condensate arising from an indirectly steam heated final heater, for example, by using oil or other suitable fluid as the heat transfer medium in this heater.

4. Where practically and thermodynamically feasible, supplying steam users elsewhere in the plant with the flash steam of the lowest suitable pressure.

Heat Transfer Data

Data used in heat transfer calculations are shown in Figure 11 (the product of specific heat and specific gravity of sodium aluminate liquors), Figure 12 (boiling point rise), Figure 13 (heat of concentration).

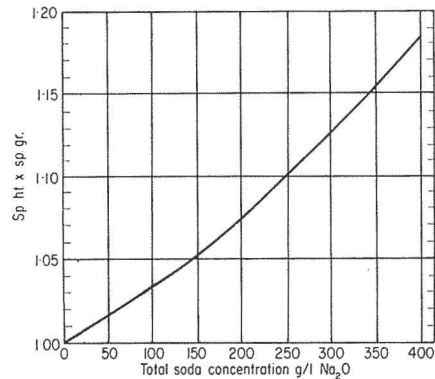


Fig. 11. Product of specific heat and specific gravity for sodium aluminate solutions.

Within the range of liquor compositions encountered, the boiling point rise appears to be dependent on total soda concentration only and independent of alumina concentration. Data for boiling point rise of caustic soda solutions¹³ fit the relations

$$bpr_0 = 0.0063N + 0.000109N^2 \tag{51}$$

$$bpr_{100} = 0.0272N + 0.000084N^2 \tag{51a}$$

where bpr_0 , bpr_{100} are the boiling point rises in °C at water temperatures (temperatures at which water exerts a vapor pressure the same as that of the liquor) of 0 and 100°C, respectively, and N is the total Na_2O concentration in g/liter.

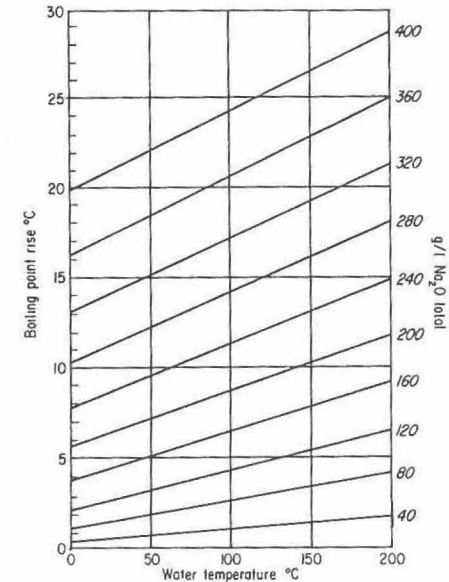


Fig. 12. Boiling point rise of caustic soda solutions.

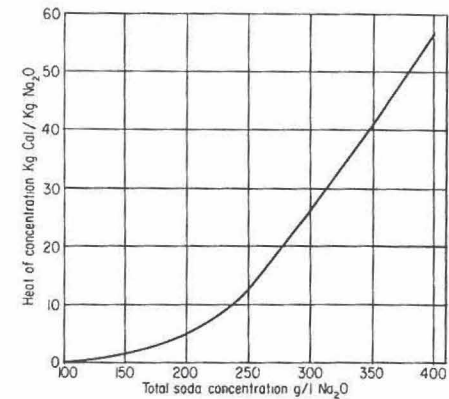


Fig. 13. Heat of concentration of caustic soda.

Over the range of 0 to 150°C, linear extrapolation with temperature of the coefficients of N and N^2 in eqs. (51) and (51a) gives values for boiling point rise in close agreement with data on works liquor.

Data on the heat of concentration of caustic soda solutions are taken from the *International Critical Tables*,¹³ as quoted conveniently in Hougén and Watson.¹⁴

The heat of solution of trihydrate alumina is taken at 170 kcal/kg Al_2O_3 , and for monohydrate as 70 kcal/kg Al_2O_3 .

Analysis of liquor density determinations shows that solution of alumina increases the volume of the solution, the apparent density of Al_2O_3 in solution being 2.58.

The authors are indebted to the British Aluminium Co. Ltd. for permission to use their records; to their colleagues in the works, laboratories, and research laboratories who carried out work and who assisted with the preparation of this paper. They also wish to thank friends in other alumina-producing companies who have given them the benefits of their work and experience.

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Discussion

L. F. Brennecke (*Aluminum Co. of America*): It is mentioned that there is a continual reduction in caustic soda/total soda ratio due to pickup of CO_2 , partly from degradation of organic impurities in the bauxite and partly from the atmosphere. How many grams per liter of caustic are neutralized by each.

A. R. Carr: From long-term plant studies we estimate that the CO_2 pickup is of the order of 0.6 ton CO_2 /100 tons Al_2O_3 for the Ghana bauxite currently in use in our plants and 0.4 for French bauxite. The CO_2 pickup from the air in the main circuit is so small that it is masked by other factors, but it must be borne in mind that our plants do not use air agitation of liquor, and to combat frothing entrainment of air

with liquor is as far as possible prevented. One of our plants uses a closed circuit mud disposal system, in which the CO_2 pickup is of the order of 0.95 ton CO_2 /100 tons Al_2O_3 .

An important source of CO_2 in the main circuit is the back reaction of sodium aluminate liquor with calcium carbonate, where this material is used as a filter aid. As mentioned in the section on causticization, if lime residues are washed countercurrently before disposal with carbonate containing liquor, some removal of CO_2 from plant liquor is effected.

S. Ostap (*Aluminium Labs. Ltd.*): It is mentioned that zinc accumulates in plant liquors. Have you actually found this to occur?

A. R. Carr: Zinc buildup was controlled by sodium sulfide additions.