ALUMINA YIELD IN THE BAYER PROCESS

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The alumina industry has historically been able to reduce alumina production costs, by increasing the liquor alumina yield. To know the potential for further yield increases, the phase diagram of the ternary system $Na_2O-Al_2O_3-H_2O$ at various temperature levels was analysed. It was found that the maximum theorical precipitation alumina yield is 160 g/l, while that for digestion was calculated to be 675 g/l.

1. INTRODUCTION

In the Bayer process, a caustic soda solution circulates between a high and a low temperature level. In digestion, the high temperature end of the cycle, alumina hydrate is extracted from bauxite, by the caustic soda solution. The liquor from digestion is rich in alumina and is called green or pregnant liquor. The green liquor is cooled to atmospheric boiling point and the bauxite residue, called red mud, is subsequently removed and washed in clarification. The clear green liquor from clarification, diluted with mud wash water, is further cooled and passed to precipitation, the low temperature end of the liquor cycle. Because of the cooling, the liquor is highly supersaturated with alumina and, after the addition of seed crystals, crystalizes alumina trihydrate. After precipitation the alumina trihydrate crystals are removed from the caustic solution. The caustic solution from precipitation has a low alumina content and is called spent liquor. An evaporator removes water from the spent liquor stream to increase the caustic concentration to the digestion requirement. After subsequent heating to digestion temperature the spent liquor is ready for another production cycle.

One of the objectives in alumina production is to enrich the caustic solution in digestion with a maximum of alumina and to subsequently recover this alumina in precipitation. In other words, maximize the alumina production per kilogram or per liter of circulated liquor, i.e. maximize the liquor alumina yield. An advantage of higher yields in reduced capital costs per ton alumina, for digester vessels, heat exchangers, pumps etc. Also such operating costs as digestion steam, pumping power and labour, decrease at higher yields. On the other hand a high yield requires long holding times, interstage coolers, seed filtration, etc. in the precipitation area, that increase costs. Also, a high yield requires a high caustic concentration and some of the associated

effects increase alumina costs. For example, the high liquor viscosity/density has a detrimental effect on mud settling rates, whilst the high liquor boiling point rise has a negative impact on process heat recovery. An additional problem of a higher caustic concentration is the increased difficulty in producing a sandy, smelting grade alumina. In general however, the industry has been successful in reducing production costs of sandy, smelting grade alumina, by increasing yield.

This paper presents the potential for further yield increase by defining, on a theoretical basis, the maximum possible yield.

When there is no caustic added or removed from the liquor, yield is calculated as follows:

$$YIELD = (\Delta A/C) * C$$

A = liquor alumina concentration (g/l)
B = liquor caustic concentration (g/l)
$\Delta A/C$ = change in liquor A/C ratio, between digestion and precipitation (-)

The above formula indicates that yield is affected by caustic concentration and the change in A/C ratio. Because of evaporation and dilution effects, the caustic concentration of the circulating liquor is not constant over the process cycle, so digestion yield is different from precipitation yield. Precipitation yield is based on the caustic concentration of the green liquor flow to precipitation, digestion yield on the caustic concentration of the spent liquor flow to digestion.

The change in A/C ratio is determined by the difference in the A/C ratio in the liquor from digestion (known as blow off ratio) and the A/C ratio in the liquor from precipitation (known as finishing ratio). The maximum theoretical blow off ratio and the minimum theoretical finishing ratio are controlled by caustic concentration and temperature. An important tool in the study of alumina yield is therefore the phase diagram of the ternary system $Na_2O-Al_2O_3-H_2O$ at various temperatures.

This paper first discusses, in section 2, the phase diagram. Subsequently, Bayer process alumina yields are discussed in section 3. The conclusions are presented in section 4.

2. THE PHASE DIAGRAM OF THE SYSTEM $Na_2O-Al_2O_3-H_2O$

2.1. The composition triangle of a ternary system

The phase equilibria, at a certain temperature, of a ternary system are represented in a composition triangle, see figure 1. The three corners of the triangle represent the three components A, B and C, of the ternary system. Points on the sides represent binary mixtures, and points within the triangle represent ternary mixtures.

The length of each side of the triangle is considered as divided into 100 equal parts, each of which represents 1% by weight on the composition scale in each of the binary systems.

The percentage by weight of each component in a ternary mixture, e.g. mixture D in figure 1, is obtained by the construction described below. A line MN is drawn parallel to side BC and the percentage of A is than given by the lenghts BM or CN. The percentage of B is given by the lenghts AO or CP, obtained by drawing line OP parallel to side AC. Similarly, the percentage of C is given by the lenghts AR or BS, obtained by drawing line RS parallel to side AB. Thus:

%   A = BM = CN = SD = PD
%   B = AO = CP = RD = ND
%   C = AR = BS = OD = MD

In a composition triangle a straight line, such as BT in figure 1, drawn from one component corner (i.e. B) to the opposite side (i.e. AC), represents the following compositional aspects. Moving along BT, away from B, results in mixture compositions with a decreasing percentage of component B and an increasing percentage of the other two components, A and C. The relative amounts of A and C remain the same, i.e. the ratio of the other two components A and C is constant.
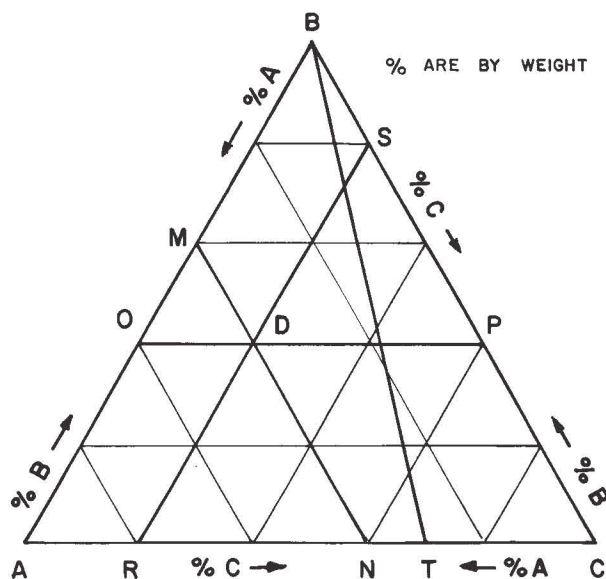

FIGURE I.　THE COMPOSITION TRIANGLE

2.2. The $30^\circ C$ phase diagram of the ternary system $Na_2O-Al_2O_3-H_2O$

As an example the $30^\circ C$ phase diagram of the ternary, system $Na_2O-Al_2O_3-H_2O$ is plotted in a composition triangle, see figure 2. This phase diagram is discussed below.

The area ABC in the phase diagram, enclosed by lines AB, BC and AC is called the solution field and represents the unsaturated liquid phase. The liquid saturation lines are AB and BC.

If the mixture composition moves from area ABC across line AB it enters the area ABD, enclosed by the lines AB, BD and DA. In this area a saturated liquid phase and a solid phase, $Al_2O_3.3H_2O$ exist together. For example, unsaturated liquid, with composition X is diluted with water, to composition Y. This moves the mixture from the unsaturated liquid area to the area of the saturated liquid phase plus solid phase, $Al_2O_3.3H_2O$. As a result, solid $Al_2O_3.3H_2O$ crystallizes. The remaining liquid phase becomes saturated, at a composition determined by the intersection, point Z, of the saturation line AB and the tie-line DYZ.

The weight of solids of composition D and saturated liquid of composition Z, produced by the decomposition of an initial mixture of composition Y, is calculated by the so-called "lever rule" which says:

$$\frac{\text{weight of solids at composition D}}{\text{weight of liquid at composition Z}} = \frac{YZ}{YD}$$

or, the weight percentage of initial mixture (Y) that forms solids (D) is

$$(YZ/DZ) * 100\%$$

and, the weight percentage of initial mixture (Y) that forms saturated liquid (Z) is:

$$(YD/DZ) * 100\%$$

The mixture composition can also move from area ABC across line BC into the area where a liquid phase exists together with sodium containing solid phases $(Na_2O.Al_2O_3. 2,5H_2O$ or $3Na_2O.Al_2O_3.6H_2O)$. However alumina production requires Na_2O – free crystals and the area below the line BC is therefore of no further interest.

The interesting areas in the phase diagram are basically the unsaturated liquid area and the saturated liquid plus solid $Al_2O_3.3H_2O$ area.

The point of maximum Al_2O_3 solubility is the non-variant point B, where the solubility curve of $Al_2O_3.3H_2O$ meets the solubility curve of $Na_2O.Al_2O_3. 2,5 H_2O.$ The $30^\circ C$ non-variant point has the composition:

$Al_2O_3 = 25\%$, $Na_2O = 22\%$, $H_2O = 53\%$.

THE COMPOSITION
SCALES ARE IN
% BY WEIGHT
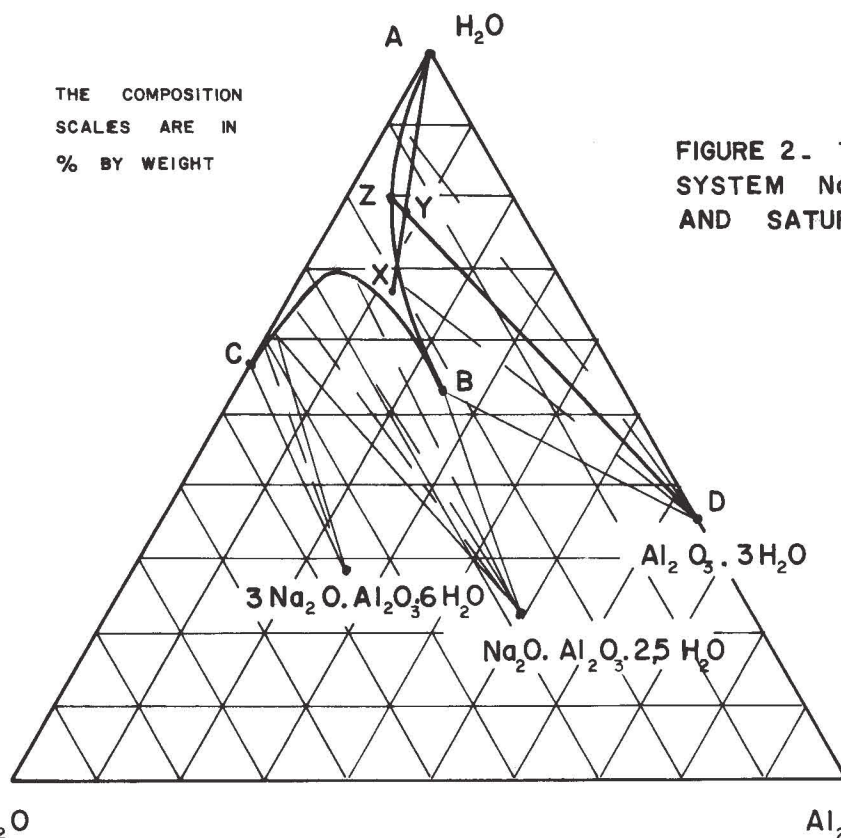
FIGURE 2. THE PHASE DIAGRAM OF THE SYSTEM $Na_2O - Al_2O_3 - H_2O$ AT 30°C AND SATURATION PRESSURE

2.3. The effects of temperature on the phase diagram

The phase diagram of the ternary system Na_2O-Al_2O_3-H_2O for various temperatures is depicted in figure 3. (Data are from references (1) and (2)).

Figure 3 indicates that for increasing temperatures the solution field widens, whilst the alumina trihydrate solubility curve straightens out and approaches a constant Al_2O_3/Na_2O ratio. Also the non-variant point moves to higher percentages Na_2O and Al_2O_3 indicating that more Al_2O_3 can be dissolved.

3. BAYER PROCESS ALUMINA YIELDS

3.1. Alumina dissolution in digestion

In digestion alumina hydrate is dissolved in the caustic solution, so extraction is achieved in unsaturated liquid. The phase diagram indicates that the maximum amount of alumina is in solution at the non-variant point. At temperatures above 150°C the non-variant point has an almost fixed location, with composition:

$Al_2O_3 = 33\%$, $Na_2O = 24\%$, $H_2O = 43\%$

In Bayer plant terminology, with concentrations presented at a standard temperature of 25°C, the composition of the non-variant point is:

Alumina	= 550 g/l
Caustic (as Na_2CO_3)	= 690 g/l
Alumina/Caustic	= 0.800

The non-variant point is represented by point Q in figure 4.

3.2. Liquor decomposition in precipitation

To recover the dissolved alumina, the liquor composition must move from the non-variant point into the two phase area of the phase diagram. The phase diagrams indicate that this requires dilution with water. This dilution is represented in figure 4, by moving from point Q, along line QA, to point A. The amount of dilution required for maximum yield can be determined by applying the lever rule to the phase diagram at precipitation temperature.
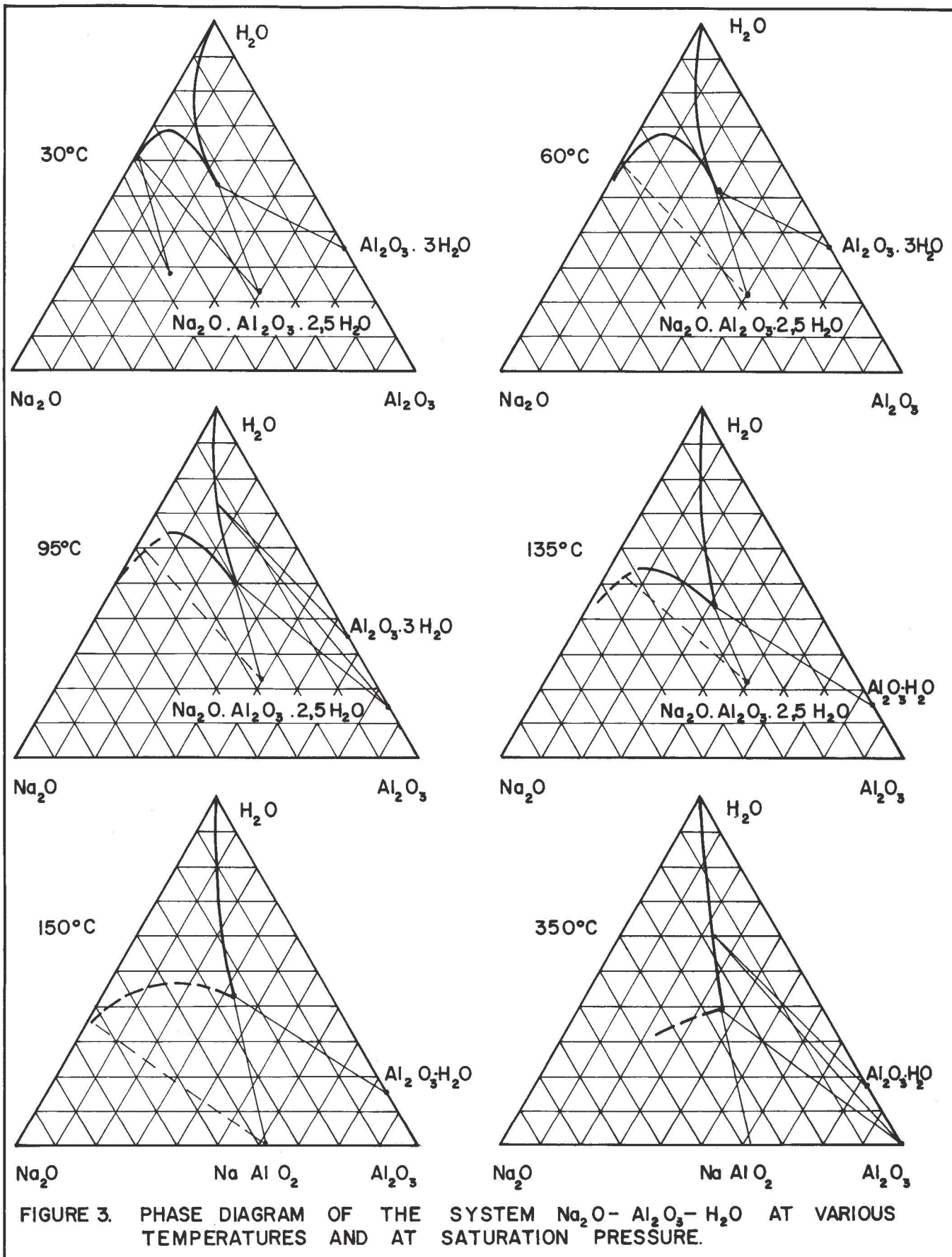
With decreasing temperature the two phases field widens so, according to the lever rule, higher yields of alumina trihydrate will result. Assume now that 30°C is the lowest possible precipitation temperature.

The curved line AB in figure 4 shows the 30°C saturation line. Based on the lever rule the maximum amount of crystallized alumina trihydrate is obtained from a kilogram liquor, if the liquor to precipitation is diluted to that composition Y, where YD/DZ has a maximum value. Trial and error indicates that YD/DZ has its maximum value, if the composition of Y is approximately:

$Al_2O_3 = 16,5\%$, $Na_2O = 12\%$, $H_2O = 71,5\%$

or:

Alumina	= 211 g/l
Caustic (as Na_2CO_3)	= 265 g/l
Alumina/Caustic	= 0.800

FIGURE 3. PHASE DIAGRAM OF THE SYSTEM $Na_2O-Al_2O_3-H_2O$ AT VARIOUS TEMPERATURES AND AT SATURATION PRESSURE.

THE COMPOSITION
SCALES ARE IN
% BY WEIGHT
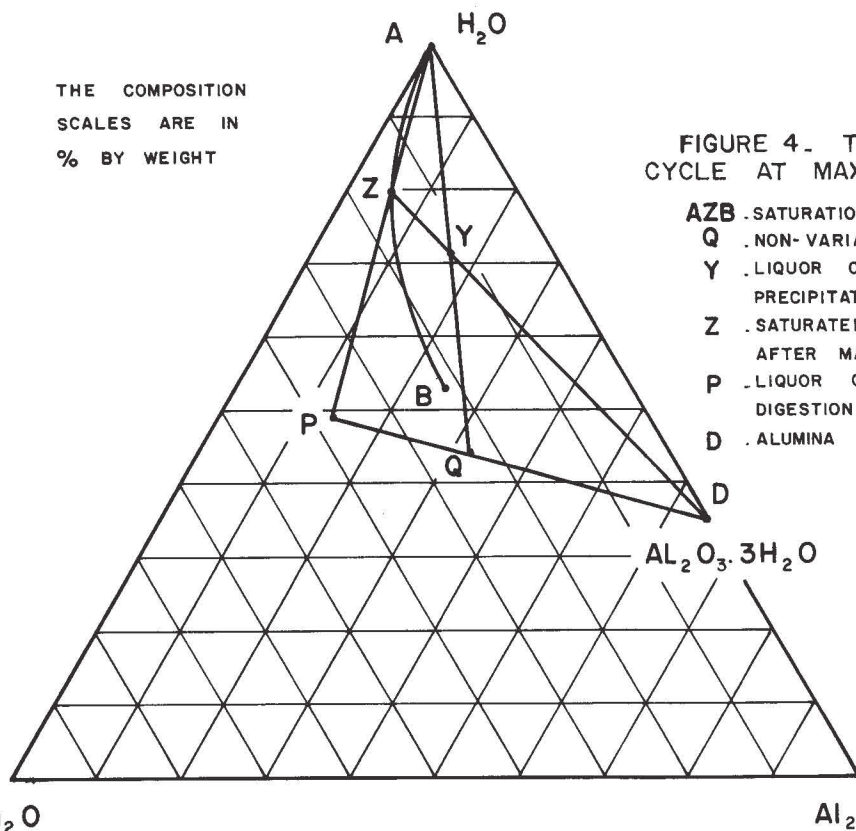
FIGURE 4. THE BAYER PRODUCTION
CYCLE AT MAXIMUM YIELD CONDITIONS

AZB .SATURATION LINE AT 30°C
Q .NON-VARIANT POINT FOR T>150°C
Y .LIQUOR COMPOSITION FOR MAXIMUM
     PRECIPITATION YIELD
Z .SATURATED LIQUOR COMPOSITION
     AFTER MAX. PRECIPITATION YIELD
P .LIQUOR COMPOSITION FOR MAXIMUM
     DIGESTION YIELD
D . ALUMINA TRIHYDRATE COMPOSITION

The diluted liquor decomposes into solid alumina trihydrate (point D) and saturated liquor (point Z). Based on the lever rule, 100 weight units of diluted liquor decompose in 19.4 weight units of alumina trihydrate and 80.6 weight units of saturated liquor, as calculated below:

(YZ)/(DZ) * 100% = 19.4% (by weight) of alumina
                   trihydrate
(YD)/(DZ) * 100% = 80.6% (by weight) of saturated
                   liquor

The saturated liquor composition (point Z) is:

Al_2O_3 = 5%, Na_2O = 15%, H_2O = 80%

or:

Alumina   = 60 g/l
Caustic (as Na_2CO_3)   = 315 g/l
Alumina/Caustic   = 0.190

3.3. Precipitation yield

Based on the data in paragraph 3.2, the maximum precipitation yield is calculated below.

$[(A/C)_{in} - (A/C)_{out}] * C_{in}$ = (0.800 − 0.190) * 265 =

= 160 g/l

3.4. Digestion yield

After precipitation, water is removed from the liquor, to increase again the liquor caustic strength, as required for digestion. This removal of water is represented in figure 4, by moving from point Z, along line AP, to point P. Point P is the intersection of lines AZ and DQ and, according to the lever rule, gives the required liquor to digestion composition, which is:

Al_2O_3 = 12,5%, Na_2O = 38,7%, H_2O = 48,8%

or:

Alumina   = 210 g/l
Caustic (as Na_2CO_3)   = 1110 g/l
Alumina/Caustic   = 0.190

Dissolution of alumina trihydrate in digestion brings the liquor composition back to the previously defined non-variant point with composition:

Al_2O_3 = 33%, Na_2O = 24%, H_2O = 43%

or:

Alumina   = 550 g/l
Caustic (as Na_2CO_3)   = 690 g/l
Alumina/Caustic   = 0.800

Based on the data in this paragraph, the digestion yield is calculated below.

$[(A/C)_{in} - (A/C)_{out}] * C_{in}$ = (0.800 − 0.190) * 1110 =

= 675 g/l

4. CONCLUSIONS

The phase diagram of the ternary system $Na_2O-Al_2O_3-H_2O$ at various temperature levels was analysed and used to determine the maximum theoretical alumina yield in the Bayer process.

The liquor from digestion has a maximum possible alumina/caustic ratio of 0.800 at a caustic strength of 690 g/l and at a digestion temperature above 150°C. Under these conditions the dissolved alumina content is 550 g/l.

Decomposition of this liquor from digestion, by dilution to a caustic strength of 265 g/l and cooling to 30°C, results in a maximum precipitation alumina yield of 160 g/l and an alumina/caustic ratio of 0.190 in the liquor from precipitation.

Concentration of this liquor from precipitation to a caustic strength of 1110 g/l and heating to a temperature above 150°C, allows dissolution of alumina trihydrate to arrive at a digestion alumina yield of 675 g/l. The resulting liquor from digestion has again the composition stated above.

Operating under maximum yield conditions involves excessive evaporation of the liquor to digestion, followed by excessive dilution of the liquor to precipitation. It seems attractive to limit the extend of evaporation and dilution and operate under conditions with a considerably reduced digestion yield. As a result the liquor to precipitation will have an alumina/caustic ratio somewhat below the maximum of 0.800. Consequently the precipitation yield will be somewhat below the 160 g/l maximum value.

In current industrial practice the precipitation yield is 40-80 g/l. One of the challenges for the alumina industry is now to find economic solutions, to narrow the gap between theoretical and actual alumina yield, whilst maintaining alumina quality.

APPENDIX

Concentration conversions from percentage by weight to gram per liter are based on the following formula:

$$D = 1.016 + 8.98 * 10^{-4} * C - 2.5 * 10^{-7} * C^2 + 4.9 * 10^{-4} * A$$

D = Liquor density at 25°C (kg/l)

A = Alumina (Al_2O_3) concentration at 25°C (g/l)

C = Caustic (NaOH) concentration at 25°C (g/l)

The liquor density formula is based on data taken from references (3), (4), (5) and (6).

REFERENCES

1. T.G.Swansiger - "Crystallization of $Na_2Al_2O_4.2,5H_2O$", Light Metals 1978, pp. 1-17.

2. K.Wefers - "Zur Chemischen Technologie des Bauxitaufschlusses" Teil 1: Das System $Na_2O-Al_2O_3-$ - H_2O, Metallwissenschaft und Technik, 21 Jahrgang, Heft 5, Mai 1967, pp. 422-431.

3. A.S.Russel, J.D.Edwards, and C.S.Taylor - "Solubility and Density of Hydrated Aluminas in NaOH Solutions", Journal of Metals, Oct 1955, Vol. 7, pp. 1123-1127.

4. C.Misra and E.T.White - "A Mathematical Model of the Bayer Precipitation Process for Alumina Production", proc. "Chemeca'70" Conference, Melbourne, Australia, 1970, pp. 52-76.

5. T.Ikkatai and N.Okada - "Viscosity, Specific Gravity and Equilibrium of Sodium Aluminate Solutions". Extractive Metallurgy of Aluminum, G.Gerard and P.T.Stroup, eds., (Interscience Publishers, New York, 1963) Vol. 1, pp. 159-173.

6. Tables from "International Critical Tables", Vol. 3 page 79.