

BOEHMITIC REVERSION IN A DOUBLE DIGESTION PROCESS ON A BAUXITE CONTAINING TRIHYDRATE AND MONOHYDRATE.

Jean-Michel LAMERANT¹ and Yves PERRET²

¹ Aluminium Pechiney
Alumina Technology
PO Box 54 -13541 Gardanne Cedex –France

² Aluminium Pechiney
Process and Development Department
PO Box 62 -13541 Gardanne Cedex –France

ABSTRACT

Gardannes's Bayer Plant has been modified to process Boké bauxite with a double digestion.

This bauxite gives a ratio: soluble alumina in the first digestion (140-150°C) to soluble alumina in the second digestion (225-240°C) close to 6, but this ratio is lower in industrial exploitation. The first digestion dissolves the trihydrate but causes simultaneous precipitation of monohydrate due to high boehmite content of muds (about 30%.) This reaction continues during muds settling, without affecting their separation. The effects of factors such as supersaturation, temperature and residence time have been studied in lab experiments. Above a given supersaturation threshold, boehmitic reversion accelerates quickly. Plant process parameters have been optimized taking into account this situation.

INTRODUCTION

At present, a few alumina refineries use a double digestion process to leach their bauxites.

This type of process is interesting when the ratio boehmite/gibbsite (i.e. $AlOOH / Al(OH)_3$) is typically in the range 0.07 to 0.3

With lesser boehmite, it is not worth investing in a high temperature digestion. But if boehmite content is too high, medium temperature digestion has a low productivity, and a lot of alumina, dissolved from the gibbsite, precipitates on the seed of boehmite.

Gardanne's plant has been modified in 1998 to process Boké's bauxite with a double digestion.

Three of the six existing files of high pressure autoclaves, formerly designed to leach bauxites at 240-245°C, have been split into two similar halves, so that the plant is now equipped with 6 short files able to reach 140-150°C, and 3 long files able to reach 240°C

A predessilication unit has been added in order to control soluble silica after the first digestion.

Gardanne's Bayer cycle has no evaporator. Flash tanks evaporate enough water for the overall balance, because bauxite slurry is preheated indirectly without water condensation in the liquor.

As a result, the steam consumption is low, only about 4.8 giga Joules per ton of alumina.

The specific flow entering the first digestion depends on the boehmite to gibbsite ratio of the bauxite, as already explained, but also on the boehmitic reversion.

This reversion can be important, and several factors such as final alumina to caustic ratio, temperature and residence time, may have a great influence on it.

In the same way, boehmitic reversion can continue during muds settling.

Of course, these reversions should not reduce final alumina extraction because high temperature digestion redissolves the boehmite.

However, liquor saturation can be reached, causing a decrease of the yield.

Finally, boehmitic reversion and boehmite content in the bauxite notably influence plant performance as well as plant capacity.

THEORY OF BOEHMITE CRYSTALLISATION

A lot of studies have been performed on gibbsite crystallisation, but few have been done on boehmite crystallisation [1 to 5], especially at temperatures above atmospheric ebullition.

The kinetic equation that we use for $AlOOH$ crystallisation is similar to the one for $Al(OH)_3$:

$$d [Al_2O_3] / dt = k S ([Al_2O_3] - [Al_2O_3]_{eq})^2 \exp(-9540/T - 0.38 I)$$

but:

- ▶ k is about 20 times lower than the gibbsite kinetic coefficient
- ▶ the term $\exp -0.38 I$, which is the Ionic Strength of the solution, is below one, and diminishes again the speed of the reaction.

Overall, boehmite crystallisation is one to several hundred times slower than gibbsite for the same supersaturation.

In practice, such a model is not really useful to make good previsions.

First, the exponent 2 applied to $(Al_2O_3 - Al_2O_3_{eq})$ is not fully satisfying, and 2.5 or even more fit better with many experimental data. But the main problem is the estimation of S, which is the seed's active surface area.

S is almost impossible to measure in a bauxite or in a mud, and even if the geometric area were known, it can be inactivated by adsorbed impurities while in contact with the liquor.

A contrario this area can increase a lot if boehmite nucleation appears during gibbsite digestion.

These phenomena are observed in some experimental tests described hereafter.

EXPERIMENTAL

The lab work consisted in two series of tests:

- digestion tests in agitated small bombs (75 ml of suspension), varying the ratio solid/liquor, the temperature and the residence time.
- settling tests on suspensions from digestions, varying the initial alumina to caustic ratio and the residence time.

1-Digestion tests

The starting material was a dessilicated Guinean Boké's bauxite from the dessilication unit of the plant. This solid had the following composition:

Tot Al_2O_3	Boehmite Al_2O_3	Gibbsite Al_2O_3	TiO ₂
53.71%	5.06%	46.4%	3.27%
Fe ₂ O ₃	SiO ₂	CaO	
11.04%	1.19%	1.84%	

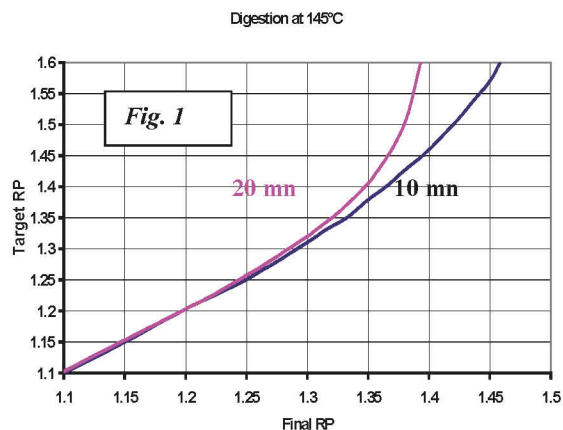
The liquor was a plant spent liquor, analyzed as:

$$\text{Caustic } Na_2O = 175g/l \quad \text{RP} = Al_2O_3/Na_2O = 0.616$$

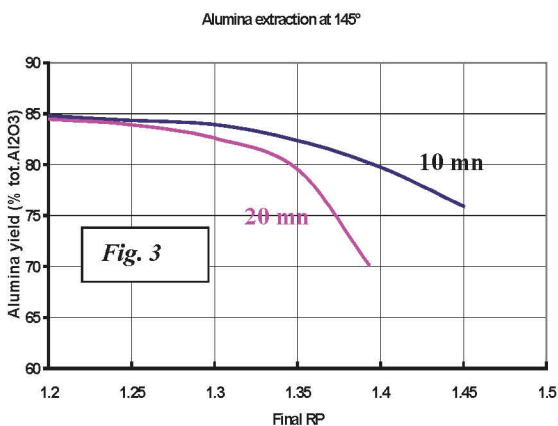
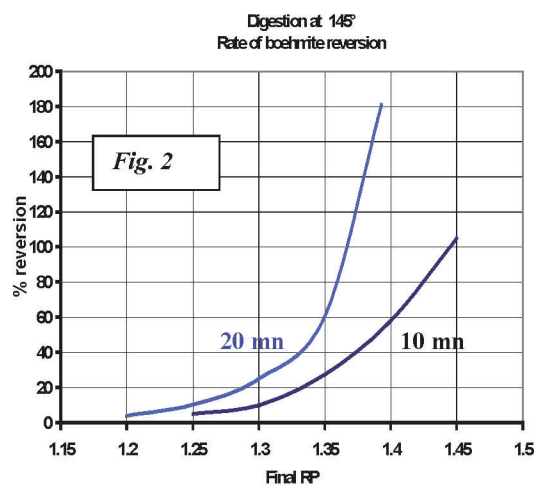
The bauxite mass had been calculated to target several RPs between 1.1 and 1.6 as if no reversion would occur. RPs really obtained were more or less lowered because of boehmite reversion.

Two temperatures (145° and 155°) and two durations (10 and 20 mn) have been tested.

Next figures show the correlation between targeted RP and final RP, and yields for alumina digestion.

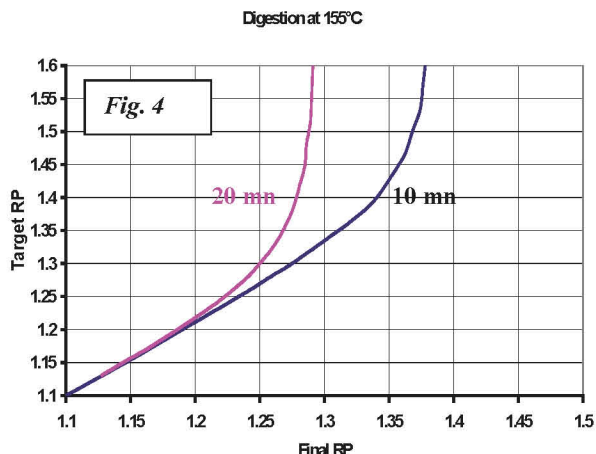


In next figure, % reversion is defined as the ratio: (additional boehmite from reversion/initial boehmite)*100



We can see that the shift between targeted and final RP is low up to RP=1.2 but it then increases rapidly, especially for the highest temperatures of digestion.

For 20mn at 155°, RP=1.3 will never be obtained whatever ratio bauxite/liquor is imposed.

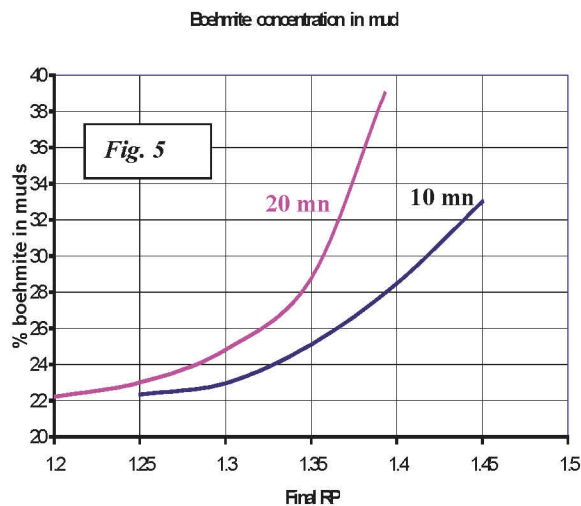


For a given RP, boehmite supersaturation is higher at 145° than at 155°, but the kinetic is slower because of the dominant influence of temperature on the activation term.

2-Settling tests

Settling tests have been performed after digestion of the desiccated bauxite with the same procedure and same apparatus as above.

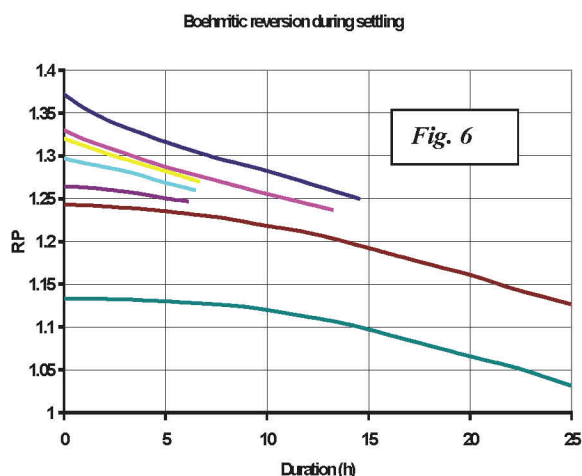
Only one type of digestion was selected, i.e. 145°- 10 mn. But several final RPs have been tested, so that the decantations have started between RP = 1.13 and RP= 1.37. Because of these different RPs, the initial percentage of boehmite in the muds before settling was somewhat variable (see next figure)



The bombs were not opened at the end of the digestion and their temperature was regulated at 105°C during the decantation in vertical position without agitation.

This procedure avoids any pollution by gibbsite germs, so there could not be gibbsite reversion.

Figure number 6 shows the evolution of RP in time.



If its initial value is >1.3, the reversion seems to start immediately and it is rather fast. But at RP=1.25 or lower, rather little reversion is observed during the first five hours.

INDUSTRIAL APPLICATION

Upper data can be used to optimize the process. A possible choice can be:

Targeted RP after digestion at 145°	:	1.35
Real RP after digestion	:	1.28
RP to decantation, after trim liquor addition	:	1.218
RP after settling	:	1.205

In practice the parameters are adjusted taking into account the bottlenecks of the plant and the residence time of digestion and decantation.

An important point is the balance between the two digestions. According to the respective flows and to the bauxite quality, it can be useful to adjust the boehmite reversion via the final first digestion's RP.

For example bauxites with higher boehmite content may incite to lower this RP

CONCLUSIONS

In order to assess boehmite reversion risks in Bayer process unit operations such as predessiccation, medium temperature digestion and mud settling, the predictable effects of temperature, supersaturation and seed content are not sufficient.

They should be combined with experimental data related to seed poisoning, boehmite nucleation and the effective seed surface area.

Industrial know-how acquired in Gardanne with Boké bauxite allows Péchiney to evaluate behavior and performance of any kind of bauxite in double digestion process with a limited set of laboratory tests.

REFERENCES

1. D.PANIAS, P.ASIMIDIS, and I.PASPALIARIS "Solubility of boehmite in concentrated sodium hydroxide solutions: model development and assessment", Hydrometallurgy, 2001, vol. 59, N1, Jan, 15-29
2. C.DILLISENGER, "Experimental modelisation of AL and Fe oxo-hydroxides dissolution in a 5 M NaOH solution, at 200 and 250 degree C. Industrial application to the Bayer bauxite processing", (Ph.D Thesis at Université d' Orléans-France, 1995)
3. S.I.KUZNETSOV, V.M.NOVOZHENOV, and T.A.RYBAKOVA, "Décomposition des solutions sursaturées d'aluminates de 100 à 160°", Zh.Prikl.Khim., 1973, vol. 46, Nr 7.
4. J.LEPETIT, "Etude de la rétrogradation des liqueurs Bayer en présence de boues rouges", (Report C854, Aluminium Pechiney, Gardanne Laboratory, 1985)
5. K.YAMADA, "Autoprecipitation of gibbsite and boehmite in settler for red mud separation", J.of Jap.inst. of Light.Metals, vol.31, jan. 1981, 43-48.
6. J.M.LAMERANT, "Process for the treatment of bauxites containing a mixture of alumina trihydrate and alumina monohydrate", European Patent, EP 0 652 181 B1, 1977