MECHANO-ACTIVATED BAUXITE BEHAVIOUR

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Abstract

Mechano-activation is often studied for various mineral industry applications, including in the alumina industry. Results found in the literature suggest potential alumina extraction improvement by mechano-activation, as well as an influence on reactive silica when lime is added during mechano-activation treatment. A bauxite sample was ground for 60 minutes in a laboratory scale attritor mill, with and without lime, a treatment known to produce important changes due to mechano-activation. Analytical results for gibbsite and boehmite contents in treated bauxite differed significantly from original bauxite, whereas kaolinite (reactive silica) and quartz were much less affected. Desilication and digestion behaviours were investigated, showing considerable differences between original and attritor milled bauxites.

Introduction

The extraction of alumina from bauxite in a low temperature Bayer circuit frequently involves a desilication step in which kaolinite, an aluminum silicate (reactive silica, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) dissolves and reprecipitates as sodalite ($3[Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O] \cdot Na_2X$), a caustic insoluble sodium alumino-silicate. This represents a net caustic soda loss, corresponding to ~1.17 g Na_2CO_3 per gram of SiO_2. Numerous studies over time have tried to minimise this soda loss, as NaOH consumption represents a significant cost for Bayer plants. Among the means that have been considered to minimise this bound caustic soda loss, several research groups around the world have considered mechanical activation of bauxite [1]. Others have studied the use of mechano-activation for potential alumina and soda recovery from residue (red mud) [2].

The utilisation of mechanical activation in hydrometallurgical processes was reviewed by Baláž in 2003, describing several examples in the mineral industry, mainly from sulfide ore processing [3]. This review also reports that the definition for mechanochemistry is accepted as "a branch of chemistry which is concerned with chemical and physicochemical transformations of substances in all states of aggregation produced by the effect of mechanical energy" [4]. This explains why the expression "mechanochemical activation" is widely used. In fact, the power of mechanochemical activation in materials chemistry is directly related to its ability to enable chemical reactions considered difficult or impossible using conventional routes.

It is known that the most significant drawbacks of mechanical activation treatments are contamination from grinding media and other mechanical parts, and energy consumption. To tackle these handicaps, work can be carried out quickly under gentle conditions, which is known as "soft-mechanochemical activation" [5].

Several types of mills can be used for mechanochemical treatment. Various effects are obtained, such as high surface area or disorder, depending on the type of mill. Agitated ball mills, or attritors, are known to produce very high surface area [3]. This type of apparatus was chosen for the present work, since a higher surface area is expected to be beneficial to bauxite reactivity.

Results in literature [6] suggest that bauxite attritor milling in water with lime addition reduces the amount of kaolinite reacting towards sodalite by forming an insoluble calcium-iron silica hydrogarnet (detected by X-ray Diffraction, (XRD), signals at $2\theta \approx$ 17°, 20°, 32°, 38.7°, 44.4° and 54.5°). These signals were not observed in our samples after attritor milling under similar conditions. Furthermore, it is worth mentioning that other research groups have also reported the absence of this insoluble hydrogarnet [1]. In our experiments, wet chemistry analyses for reactive silica at 150 °C after and before milling were almost identical.

Interesting features were observed, however, when digesting bauxite after dry attritor milling without additive. Available alumina under low-temperature digestion conditions was significantly increased, even though the opposite was suggested by XRD analysis and BQuant [7] software calculation based on XRF and LOM analyses. Various experiments were thus carried out to investigate the original and treated bauxite behaviour under various desilication and digestion conditions. These results are discussed in the present paper.

Experimental

A high monohydrate grade bauxite from a single deposit was analysed prior to and after attritor milling by usual instrumental or chemical techniques like X-ray fluorescence, (XRF), Loss of mass (LOM), XRD, Total organic carbon (TOC) as well as software calculations by BQuant [7] and XDB-Hungalu [8].

Mechano-activation was carried out at Union Process facilities in Akron, Ohio, USA. Attritor mill model 1-S was used. Milling time was 60 minutes at 280 rpm. Carbon steel grinding balls (27 kg) were used to treat 270 g of bauxite.

Low (~245 g/L as Na_2CO_3) and high caustic (~350 g/L as Na_2CO_3) Bayer liquors were used for the desilication experiments. They were analysed by standard Metrohm potentiometric titration for

alumina, caustic and carbonate. Their organic contents are different in both amount and nature. They were also analysed for Si and Fe concentrations by induced coupled plasma (ICP). Two synthetic liquors were also prepared with compositions similar to the plant liquors, but without any organic content to try to evaluate the potential impact of the organics on desilication.

Laboratory desilication experiments were carried out in 45 mL Parr reactors, equipped with a cup containing dry bauxite. Three Monel balls (<8 mm) were also included to ensure proper agitation. Bayer liquor was pre-heated to target temperature, either 100°C or 145°C, in a stationary heating block. When temperature was reached, the reactor was manually agitated vigorously and inserted into a pre-heated Alcan ALExx rotating block heater for a period of time up to 4 hours. Parr reactors were removed from heater and cooled with water before being centrifuged. Samples for liquor analyses were syringe-filtered to 0.45 microns.

Similarly, laboratory digestion experiments were carried out in 45 mL Parr reactors containing three Monel (<8 mm) balls. A 250 g/L NaOH (331 g/L as Na_2CO_3) solution was used as pure liquor. Bauxite and liquor were mixed in the Parr reactor which was then inserted in the pre-heated ALExx rotating block heater for 25 minutes at four different temperatures : 75, 100, 125 and 150 °C. Targeted alumina to caustic (as Na_2CO_3) ratio (A/C) was 0.600, bauxite charge being based on bauxite analysis before attritor milling. After 25 minutes, Parr reactors were removed from heater and cooled with water before being centrifuged. Samples for liquor analyses were syringe-filtered to 0.45 microns.

Results and Discussion

Bauxite Composition

Original and treated bauxite samples were analysed by XRF and for LOM . The main elements are listed in Table I.

Table I. LOM and Main XRF Results
for Original and Treated Bauxite Samples

	Original Bauxite	Treated Bauxite
Al_2O_3[a]	70.6%	69.5%
SiO_2[a]	14.5%	13.9%
Fe_2O_3[a]	9.7%	11.4%
TiO_2[a]	4.5%	4.4%
LOM	24.8%	18.2%

[a] Values corrected based on LOM figures to bring concentrations on same basis.

XRF analyses, corrected for LOM, show that alumina, silica and titanium contents are similar in original and treated bauxite, within 1% difference. The iron content is however significantly increased, likely because of contamination by the equipment. This iron contamination suggests that about 0.015% (~4 g) of mild steel grinding balls was consumed when 270 g of bauxite was attritor milled for 60 minutes, with a 100:1 balls-to-bauxite weight ratio.

BQuant calculations were performed using LOM, XRF and TOC values. Bauxite samples were also analysed by XRD, which allowed for mineralogical composition calculations with the XDB-

Hungalu package. Results are listed in Table II. Unfortunately, XDB-Hungalu calculations were not conclusive for treated bauxite samples, likely because phases were amorphous.

Table II. Main BQuant and XDB-Hungalu Results
for Original and Treated Bauxite Samples.

Species	BQuant		XDB-Hungalu	
	Original	Treated	Original	Treated
Gibbsite (g.Al_2O_3)	37.9%	16.8%	39.7%	–
Boehmite (b.Al_2O_3)	9.4%	34.1%	8.4%	–
Kaolinite (k.SiO_2)	6.0%	6.3%	5.3%	–
Quartz (q.SiO_2)	4.8%	5.0%	5.5%	–

BQuant and XDB-Hungalu calculations are not fully consistent with each other for the original bauxite, but they remain rather close. The most important feature is that BQuant results suggest a significant increase of the boehmite proportion by attritor milling, while gibbsite is decreased. This is consistent with the LOM value that decreases from 24.8% to 18.2%, see Table I. We can thus assume that a significant amount of gibbsite ($Al_2O_3 \cdot 3H_2O$) is transformed into boehmite ($Al_2O_3 \cdot H_2O$) due most probably to localized high temperatures.

The sum of gibbsite and boehmite content is higher in treated bauxite only because of the LOM decrease: if LOM value is neglected, this sum is almost identical in original and treated bauxite. The effect of LOM decrease is the same on kaolinite and quartz values before and after attritor milling.

In order to confirm the BQuant results, the most intense gibbsite and boehmite signals were selected on the XRD spectra of original and treated bauxite. Using XRD data, relative values ("g/b ratio") were obtained by dividing gibbsite and boehmite peak heights at selected 2θ values. These ratios were compared before and after attritor milling. Results are listed in Table III. It is also noteworthy that these signals decrease significantly in treated bauxite sample indicating not well-defined crystals, which is consistent with the troubles experienced with the XDB-Hungalu calculation because of amorphous species.

Table III. Ratios of XRD Signals for Gibbsite and Boehmite
in Original and Treated Bauxite Samples

g.Al_2O_3 2θ	b.Al_2O_3 2θ	g / b ratio (original bxt)	g / b ratio (treated bxt)	$\frac{(g/b)_{treated}}{(g/b)_{original}}$
18.4°	14.6°	1.95	0.52	0.27
20.3°	14.6°	1.37	0.37	0.27
20.3°	38.4°	2.48	0.66	0.27
44.2°	38.4°	1.43	0.43	0.30
44.2°	49.0°	2.50	0.76	0.30
44.2°	49.3°	3.00	0.93	0.31

Results shown in Table III clearly demonstrate that the relative intensity of gibbsite signals decreases compared to boehmite signals for treated bauxite. Furthermore, this decrease is consistent for all of the selected signals, the ratio being rather similar, at ~0.3.

Because attritor milling likely affects diffracting properties, gibbsite's relative decrease could not be taken quantitatively. The trend is however consistent with BQuant results expressed in Table II.

Desilication Studies at 100 °C, for Original and Treated Bauxite

Even though reactive silica (kaolinite) concentration is not increased by attritor milling, according to BQuant calculation (Table II), silica extractability could nevertheless be significantly affected due to the very fine particle size provided by attritor milling. The particle median size after milling is about 12 microns. Detailed desilication studies were thus undertaken at temperatures of 100 and 145 °C in the two plant Bayer liquors (low and high caustic).

As expected, desilication at 100 °C is rather slow. Results in Figure 1 show that in low-caustic Bayer liquor, it takes about 4 hours to bring down the silica liquor concentration to the original SiO_2 concentration, i.e. 0.81 g/L. Original and treated bauxites, however, behave very differently: kaolinite in treated bauxite is extracted much faster, achieving SiO_2 concentrations of 5.6 g/L within 5 minutes.
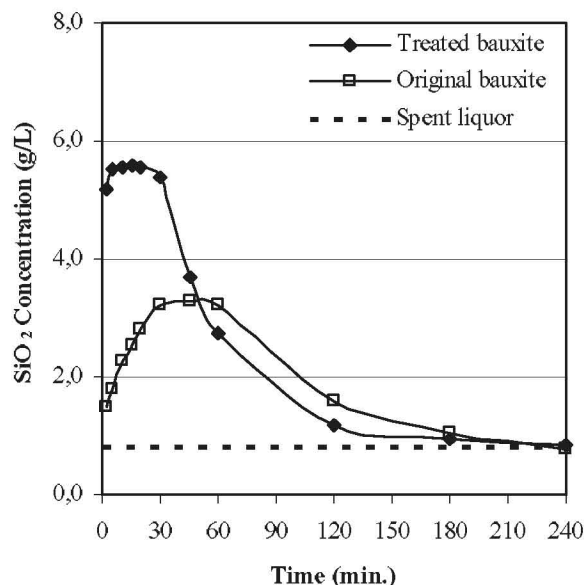

Figure 1. Silica in liquor behavior for original and milled bauxites at 100°C, in low-caustic Bayer plant liquor.

As expected, since higher silica concentration is obtained with treated bauxite, desilication rate seems to be higher, likely due to the greater amount of sodalite seeds that are formed early in the process. On the other hand, it also slows down quickly and silica concentration stabilizes slightly above the initial silica concentration after four hours, whereas original bauxite solution gets to the initial SiO_2 concentration at about the same time.

A rather similar behavior is observed in high-caustic liquor: it takes about four hours for the treated bauxite solution to reach back the original SiO_2 concentration, i.e. 1.41 g/L, and kaolinite in treated bauxite is extracted much faster, achieving SiO_2

concentration of 6.7 g/L within five minutes. Original bauxite would likely desilicate to the initial silica concentration in about three hours whereas it took four hours for the treated bauxite. These results are shown in Figure 2.

It is noticeable that desilication rates are about the same for both bauxites (original and treated) despite the much higher silica concentration achieved very rapidly with the treated bauxite. Actually, a significantly faster desilication rate would be expected when SiO_2 concentration reaches 6.8 g/L, since a very large amount of sodalite seeds should form. This behavior is rather different from what was observed in low-caustic Bayer liquor (Figure 1) where the treated bauxite desilicates faster than the original bauxite, at least for the first 60 minutes. After this period, both desilication rates are similar. These results suggest that, at 100°C, the desilication pattern does not seem to be influenced by the caustic concentrations.
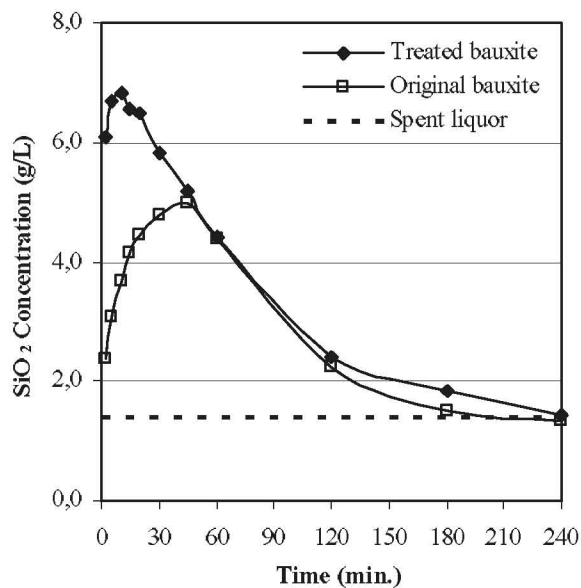

Figure 2. Silica in liquor behavior for original and milled bauxites at 100°C, in high-caustic Bayer plant liquor.

Desilication Studies at 145 °C, for Original and Treated Bauxite

At 145 °C, in low-caustic Bayer liquor, contradictory results were observed, as shown in Figure 3. A significantly higher silica concentration was again observed with treated bauxite very early, but desilication was overall slower than for original bauxite. In fact, desilication down to initial silica concentration was achieved after only 30 minutes for original bauxite, whereas more than 60 minutes were required to achieve this silica level with treated bauxite. This could be due to the higher alumina concentration obtained in solution when digesting treated bauxite (see Table IV).

In high-caustic Bayer liquor, at 145 °C, kaolinite dissolution is extremely fast for original and treated bauxite, as shown in Figure 4. Similarly to what was observed in low-caustic liquor (Figure 3), initial silica concentration was achieved after 30 minutes with original bauxite. Since potentiometric data indicate about 6%

higher alumina concentration in solution from treated bauxite digestion, it is likely that the higher final silica concentration is due to the higher alumina concentration (Table IV), thus higher sodalite solubility [9] and lower driving force for desilication. As it was observed at 100°C, the caustic concentration does not seem to impact on the desilication trend at 145°C.
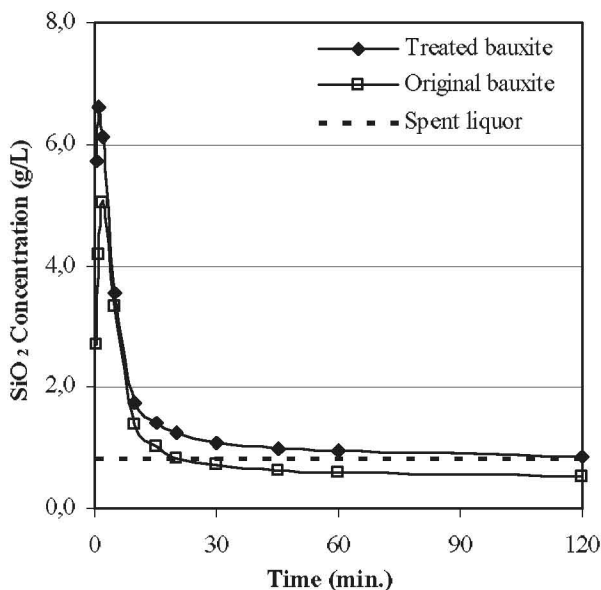

Figure 3. Silica in liquor behavior of original and milled bauxites at 145 °C, in low-caustic Bayer plant liquor.
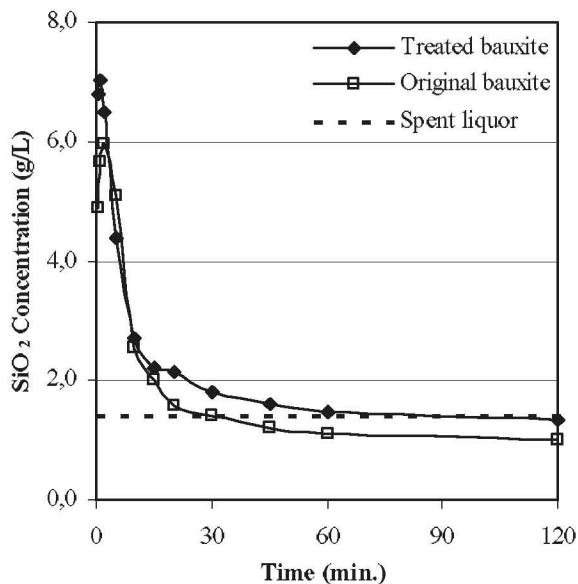

Figure 4. Silica in liquor behavior of original and milled bauxites at 145 °C, in high-caustic Bayer plant liquor.

Desilication Studies in Synthetic Bayer Liquor

In order to evaluate the effect of organic impurities in Bayer liquor on the desilication rate, similar studies were carried out in synthetic Bayer liquor. These liquors were prepared to match the main constituents concentrations (Al_2O_3, SiO_2, NaOH, Na_2CO_3, Na_2SO_4, NaCl) of the corresponding plant liquors. No organic matter was included in the synthetic liquors.

Table IV. Final Alumina Concentration in Desilication Experiments, Analysed by Potentiometric Titration

	Time (min.)	T (°C)	Original Bauxite Al_2O_3 (g/L)	Treated Bauxite Al_2O_3 (g/L)
Low caustic plant liquor	240	100	132.1	137.4
	120	145	131.7	137.4
High caustic plant liquor	240	100	165.1	179.2
	120	145	168.5	179.8
Low caustic synthetic liquor	240	100	133.3	_[a]
	120	145	133.2	_[a]
High caustic synthetic liquor	240	100	168.7	175.6
	120	145	170.0	177.9

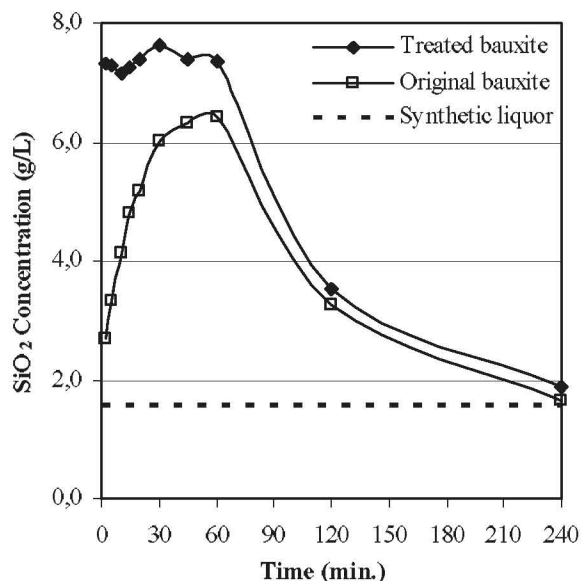[a] These experiments were not carried out due to experimental difficulties

Figure 5. Silica in liquor behavior of original and milled bauxites at 100 °C, in high-caustic synthetic Bayer liquor.

In high caustic liquor, the most striking difference between synthetic and plant liquor is the breakpoint, defined as the time when the silica liquor concentration starts decreasing. It takes a significantly longer time to reach this breakpoint in synthetic liquor, than in plant liquor, as can be seen by comparing Figure 2 with Figure 5, and Figure 4 with Figure 6. Since the major difference is the liquor organic content, these results suggest that the organic molecules present in this plant liquor would favor sodalite nucleation. Further studies would be required, however, to confirm these preliminary results.

On the other hand, in low caustic liquor, the breakpoint is similar in both plant (Figures 1 and 3) and synthetic liquor (Figure 7). It is likely that the amount and the nature of the organics present in this plant liquor do not affect the desilication at all.
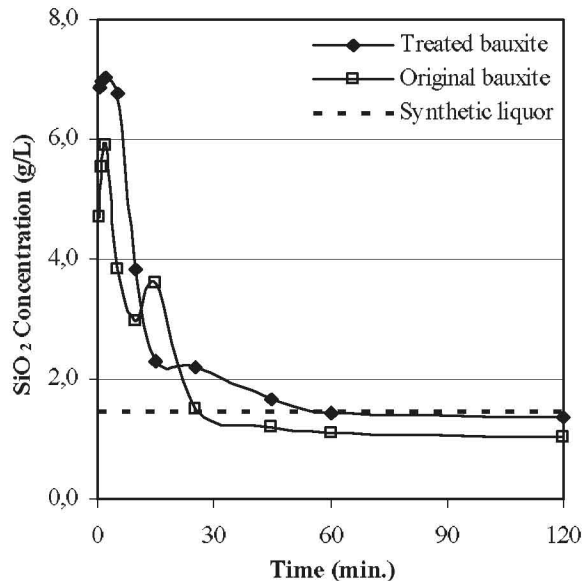

Figure 6. Silica in liquor behavior of original and milled bauxites at 145 °C, in high-caustic synthetic Bayer liquor.
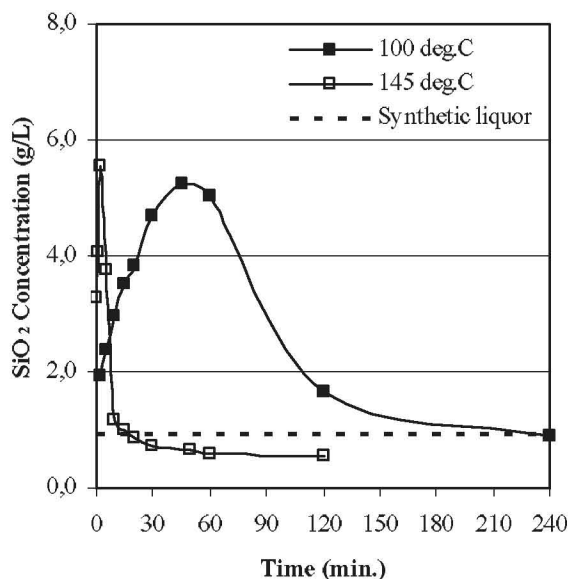

Figure 7. Silica in liquor behavior of original bauxite at 100 and 145 °C, in low-caustic synthetic Bayer liquor.

Digestion of Original and Treated Bauxite

Original and treated bauxites were digested for 25 minutes in pure 250 g/L NaOH solution, at four different temperatures namely 75,

100, 125 and 150°C in order to evaluate if atmospheric digestion could be considered for treated bauxite. Identical bauxite charges were introduced in the 45 mL Parr reactors, targeting a 0.600 A/C ratio based on the original bauxite gibbsitic content. Results are shown in Figure 8.

It is obvious that alumina extraction from treated bauxite is much easier at any temperature, the difference being most significant at 75 °C. Actually, achieved A/C ratio is above the 0.600 target for all of the tested temperatures with treated bauxite, whereas it is always slightly below target with the original bauxite. The Al_2O_3 concentration decrease between 100 and 125 °C is mainly due to sodalite formation, since SiO_2 concentration is also significantly decreasing between these two temperatures for the same digestion time (see Table V).

The alumina concentration achieved with treated bauxite suggests that atmospheric digestion at 100 °C could be considered for treated bauxite. Nevertheless, a long residence time would be required (results in Figure 2 suggest four hours) in order to achieve an acceptable silica concentration in the blow-off liquor.
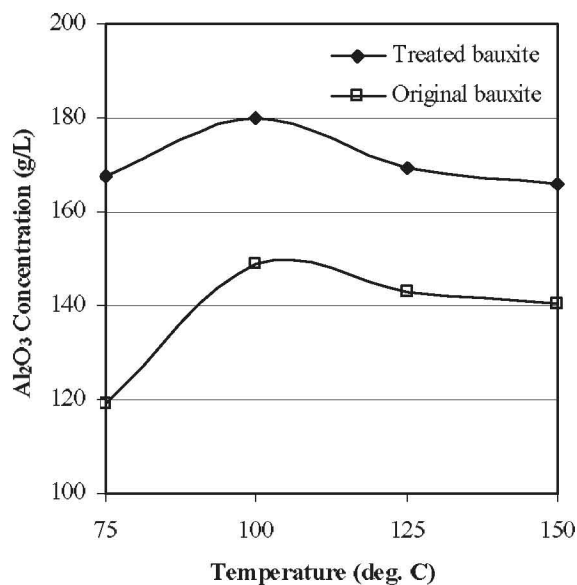

Figure 8. Alumina concentration at various temperatures, for original and treated bauxites in pure caustic liquor

Table V. Alumina and silica concentrations in digestion experiments (after 25 minutes, including pre-heating up to digest temperature).

T	Original bauxite		Treated bauxite	
(°C)	Al_2O_3 (g/L)	SiO_2 (g/L)	Al_2O_3 (g/L)	SiO_2 (g/L)
75	119.2	4.2	167.6	11.6
100	148.8	3.2	179.8	6.6
125	143.0	0.96	169.3	0.6
150	140.5	0.93	166.1	1.12

Conclusion

Based on the XRD data, the expected insoluble calcium hydrogarnet was not observed in our bauxite samples attritor-milled with lime. Accordingly, kaolinite content is about the same in original and treated bauxite samples. This result is not consistent with studies reported by other groups [6], and eliminates, for the studied bauxite, one interesting feature expected from mechano-activation, i.e. the potential reduction of caustic consumption.

An impact of attritor milling on desilication behavior was however observed. Kaolinite dissolution is always faster with treated bauxite, as one would expect with such a fine grind. On the other hand, desilication rates are not faster, which is rather surprising since a very high active surface of sodalite is likely to be formed with the high silica concentrations observed after the kaolinite dissolution step. This behavior can be partially explained by the fact that higher alumina concentration were achieved with treated bauxite. As a result, the sodalite solubility is higher [9] and the sodalite precipitation rate is reduced. But this does not explain all, so further investigations will be required. The two caustic concentrations studied gave similar results although the impact of organics is less clear and more testwork is needed.

Alumina species are significantly affected by attritor milling. It was shown by BQuant and XRD that a large proportion of the original gibbsite content is transformed into boehmite. This newly formed monohydrate, as well as a large portion of the treated original boehmite, is however digested under moderate digestion conditions (100-150 °C). A long residence time (~4 hours) is nevertheless required, since complete desilication is not faster with treated bauxite.

Acknowledgement

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