BR04 - Comparison of Lime and Carbon Dioxide Methods of Bauxite Residue Neutralization

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Abstract

To promote bulk amount of bauxite residue (BR) utilization as industrial raw material, cost-effective and efficient reducing total alkali content ($\Sigma R_2O = Na_2O + K_2O$) below 1 mass % shall be achieved.

Following on from the RemovAl project the efficiency of carbon dioxide neutralization of BR was studied. Chemistry of the process was examined, and expert evaluation was performed to assess the availability of implementation of the carbon dioxide method under the process conditions of an alumina refinery. Some limitations were determined. Competitive abilities of carbon dioxide and lime BR neutralization methods were evaluated.

Keywords: Bauxite residue, lime neutralization, carbon dioxide treatment, carbon footprint.

1. State of the Problem

Bauxite residue (BR) can be used as industrial raw material only if a cost-effective and efficient technology is available for reducing the alkali content ($\Sigma R_2O = Na_2O + K_2O < 0.5$ mass %) and the moisture content ($W \approx 25 \div 30$ mass %) in BR. A traditional method of BR neutralization comprises processing BR with lime to recover the alkali and return it to the Bayer process. However recently a number of alternative methods have been studied on both laboratory and industrial scale which combined BR preparation for secondary use and reducing the carbon footprint from alumina production. These methods are discussed below.

1.1 Lime Neutralization

In the 1930s, a method of BR neutralization with lime was proposed that enabled to decompose desilication product (DSP) with alkali dissolution in form of NaOH [1]. The process is based on the reaction of DSP decomposition with lime:

$$Na_2O\cdot Al_2O_3\cdot 2SiO_2\cdot 2H_2O + 4Ca(OH)_2 = 2NaOH + 3CaO\cdot Al_2O_3\cdot mSiO_2\cdot (6\text{-}2m)H_2O + nCaO\cdot SiO_2\cdot xH_2 \quad (1)$$

Following lime regeneration BR is filtered on a filter press to separate the cake with a moisture content of ≤ 30 %; and the resulting caustic alkali solution is returned to the mud circuit of the alumina refinery [2]. A significant part of the lime regeneration costs is compensated due to the following:

- the return of caustic alkali to alumina production to compensate for losses;
- the sale of neutralized and dehydrated BR to customers;

- or reduction of environmental payments for disposing waste of a lower hazard class using ultra-dry storage technology, which increases the usable capacity of the bauxite residue disposal area.

However if neutralized and dehydrated bauxite residue cannot be used as industrial raw material, the extensive use of lime neutralization technology at alumina refineries is doubtful, since use of lime increases the carbon footprint of alumina production, which is on average equal to approx. 1.2 t CO_2 t/t Al_2O_3.

1.2 Acid Neutralization

Acid neutralization involves treating BR with sulphuric (in rare cases hydrochloric) acid with DSP decomposition and Na_2O dissolution in form of sodium sulphate Na_2SO_4. Spent sulphuric acid solution from chemical cleaning of the heating surfaces of heat exchangers and/or evaporators to remove scale formation is often used for this purpose. Acid reduces pH level of BR liquid phase from ≥ 13 to ≤ 8 and facilitates the dissolution of up to 85 % Na_2O in form of Na_2SO_4 [3]. In order to reduce acid consumption and to resolve the issue of disposal of the resulting sulphate solution CSIRO proposed to treat the sulphuric acid solution from BR neutralization using electrodialysis process. This method enables to return Na_2O to the Bayer mud circuit while feeding sulphuric acid to the beginning of the process to neutralize the fresh batch of bauxite residue [4]. This closed process of acid neutralization followed by electrodialysis has not been pilot tested, so no feasibility data of the process or actual implementation experience are available.

1.3 Cold CO_2 Treatment with Complexion

Complexion is a complex nitrogen containing organic substance making strong bonds with most cations [5]. Complexion treatment of DSP in the presence of CO_2 (required for pH regulation) results in DSP decomposition and dissolving salt of a complexione with aluminum (AlY), solution of sodium hidrocarbonate ($NaHCO_3$) and silica gel $Si(OH)_4$ as follows:

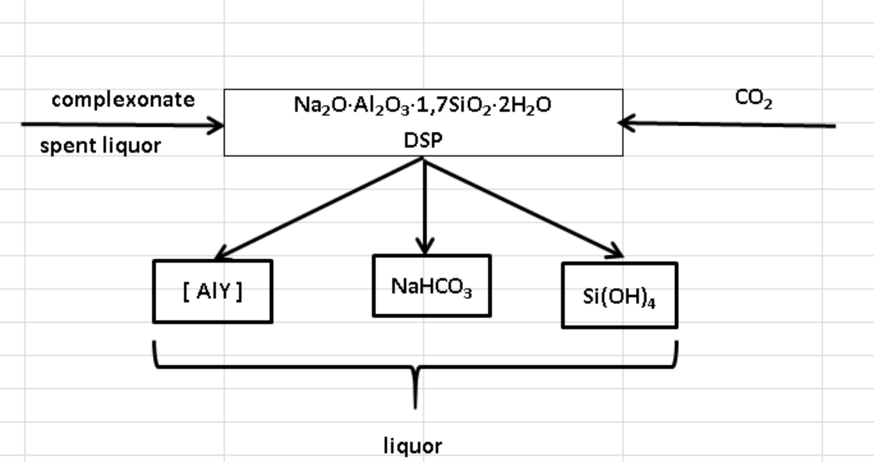


Figure 1. Cold CO_2 treatment with complexion for DSP decomposition.

Further processing successive steps include: separation (filtration) of silica gel; separating (filtration) dawsonite, i.e. sodium and aluminium hydrocarbonate $NaAlCO_3(OH)_2$. When heated to ≥ 600 °C dawsonite decomposes in two stages to sodium aluminate $NaAlO_2$ with a loss of crystalline hydrate moisture and CO_2 groups:

$$Na_2O\cdot Al_2O_3\cdot 2CO_3\cdot 2H_2O \rightarrow Na_2O\cdot Al_2O_3 + 2CO_2\uparrow + 2H_2O\uparrow \quad (2)$$

The obtained dawsonite or sodium aluminate is returned to alumina production. Active silicate (up to 80 % SiO_2) can be used as an active additive in the construction industry. Iron titanium concentrate (up to 75 % Fe_2O_3, ≥ 7 % TiO_2) is unlikely to be used in ferrous metallurgy, but it may be utilized as a Fe-containing additive for portland cement production. Use of carbon dioxide in BR complexonate decomposition reduces the carbon footprint of alumina production which makes this technology rather promising. However the bottleneck here is the lack of a cheap and effective way to recover Na_nY complexion from the spent liquor so that to return it to the beginning of the process for neutralization of the fresh batch of bauxite residue. Unless an effective solution to recover the complexion without generation of acidic tailings or significant increase of energy consumption, this method will not be implemented on a wide scale.

1.4 Use of Organic Acids

BR neutralization with formic acid and reducing carbon footprint. The technology involves the synthesis of a weak solution of formic acid H_2CO_2 (or HCOOH) using carbon dioxide from the exhaust gases of the alumina production at an ambient temperature using one of the currently developed technologies [6–8]. Then DSP and calcium hydrogarnets (HG) in BR are decomposed at nearly ambient temperature with the use of 10–15 % formic acid to generate formate salts (including aluminum, sodium, calcium, etc. formates), and iron-containing concentrate is filtered. The obtained solution of Na, Ca and Al formate salts is regenerated to obtain spent formic acid solution which is returned to neutralization of a fresh batch of bauxite residue, while sodium aluminate is returned to alumina production. This technology effectively solves the problem of reducing carbon footprint and does not generate additional tailings from production. The technology of formate salts regeneration is currently being developed and is not industrially implemented, cost-effective and efficient method of producing formic acid from exhaust gases with a low carbon dioxide content ($CO_2 \leq 8$ vol. %) is also under development.

1.5 BR Neutralization with Carbon Dioxide

In 2007 ALCOA developed and implemented a process for BR neutralization with the use of concentrated CO_2 at the Kwinana alumina refinery (Western Australia). This process allows reducing pH of the liquid phase and emissions of greenhouse gases (i.e. emissions of CO_2 into the atmosphere) [9]. The carbonization process has been implemented due to the availability of a low-cost source of CO_2 near the refinery. Use of CO_2 provides for partial BR neutralization and allows reducing pH of the BR slurry to some neutral level; besides, it also enables the utilization of greenhouse gases. The amount of CO_2 absorbed by BR liquid phase at the Kwinana refinery amounted to 1.4 kg/t of BR (as dry matter). In fact, due to partial sorption of carbon dioxide by the slurry, the ALCOA process requires 30÷35 kg of CO_2 per tonne of bauxite residue (dry weight). Accordingly, the actual CO_2 utilization is less than 5 % of the gas consumption for neutralizing the BR slurry.

The treatment of bauxite residue with carbon dioxide in an autoclave under pressure (P_{CO2} to 40 atm) and at a temperature of up to 80 °C was also studied [10]. As an advantage, it is indicated that up to 87 % alkali can be extracted from sodium hydroaluminosilicate. However, the additional anions contained in the sodium hydroaluminosilicate (SO_3 and Cl) are barely transferred to the solution, while the decrease in the amount of sodium hydroaluminosilicate is insignificant.

A side effect is that when bauxite residue is treated with CO_2 at ambient temperature; when pH value drops below 9.5, tricalcium hexahydroaluminate ($3CaO\times Al_2O_3\times 6H_2O$ or TCA) decomposes to calcite and X-ray amorphous aluminium hydroxide $Al(OH)_3$ [11] or agglomerates consisting of $Al(OH)_3$ and dawsonite [12]. The speed of this process increases as CO_2 pressure increases, but as pH value approaches to ~ 7, the rate of calcite formation decreases and mainly dawsonite is formed. This is due to the fact that as the partial pressure of P_{CO2} increases from ≤ 0.1 to ≥ 1, pH value of the liquid phase decreases from ≈ 10 to ≈ 7. This reduction in pH is caused by CO_2 sorption by aqueous solution. Under conditions of CO_2 high partial pressure, presence of H_2CO_3 in the solution and a low temperature ($T \approx 20 \pm 5$ °C), gibbsite is formed from aluminium released from TCA through pseudoboehmite, which is thermodynamically unstable under these conditions:

$$3CaO \cdot Al_2O_3 \cdot 6H_2O + 3CO_2 \rightarrow 3CaCO^{P}_3 + \times 2Al(OH)_3 + 3H_2O \qquad (3)$$

The authors [10] also believe that boehmite AlOOH contained in BR also passes into gibbsite $Al(OH)_3$.

1.6 Calcification – Carbonation Method

This is a combined method of lime regeneration followed by carbon dioxide pressure treatment [13]. According to the proposed method overlapping of two processes occur: 1) lime regeneration for DSP decomposition to obtain TCA and caustic solution (see Formula (1)) and their separation; 2) processing with carbon dioxide for 2 hours at 120 °C to decompose TCA in order to obtain calcite and gibbsite (see Formula (3)) [14]. Then this calcified and carbonised BR is additionally leached with a diluted caustic solution (NaOH ≈ 100 g/dm^3) at a temperature of + 60 °C to dissolve aluminium from secondary gibbsite. The resulting low-alkaline and low-alumina residue is filtered and sent to the customers for cement production. The proposed method appears to be complicated, labour-intensive and costly. Moreover, its economic viability provokes some doubts.

1.7 Selection of Research Trend

Of the full range of discussed processes, the method of BR direct treating with carbon dioxide under pressure seems to be the most prospective both for neutralization of bauxite residue and reduction of carbon footprint from alumina production. Due to the high level of alkali dissolution (up to 87 %) from DSP, as specified in [10], the following was decided to be carried out:

- to study DSP behaviour mechanism when BR is pressure treated with carbon dioxide at different temperatures, and the actual extent of this process
- to assess the behaviour of tricalcium hydroaluminate (TCA) and calcium hydrogarnet (HG) during CO_2 treatment, i.e. to determine whether BR treatment with carbon dioxide enables to reduce the carbon footprint due to HG decomposition into calcite and/or calcium hydrocarboaluminate
- to evaluate the competitive performance of BR lime neutralization and carbon dioxide treatment.

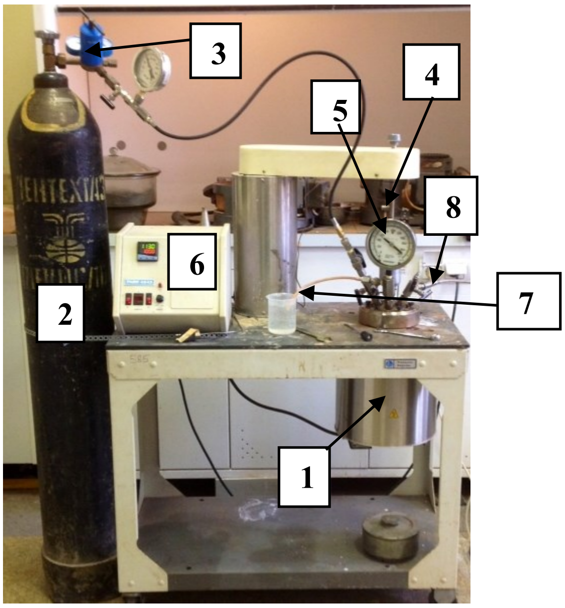
This paper discusses the obtained results.

2. Tests on BR Treatment with Carbon Dioxide

The present research was conducted using BR samples from the following refineries:

- Aughinish (Ireland) processes a mixture of Brazilian and Guinean gibbsite bauxite
- Ewarton (Jamaica) processes Jamaican gibbsitic bauxite
- Tulcea (Romania) processes a mixture of tropical gibbsite bauxite but mainly from Sierra Leone
- AoG (Greece) processes Greek diasporic bauxite.

BR slurry was treated with 100 % carbon dioxide under pressure at a specified temperature using Parr reactor unit (USA) (Figure 1).



1 — reactor, 2 l
2 — carbon dioxide container
3 — reducer
4 — stirrer (propeller)
5 — gas pressure gauge in the autoclave
6 — autoclave temperature control unit
7 — tube for continuous removal of CO_2 from the reactor
8 — sample point for slurry extraction during the experiment.

Figure 2. Unit for treating BR slurry with carbon dioxide under pressure.

The reactor was equipped with a mechanical stirring device (350 rpm). This speed made it possible to virtually eliminate the effect of CO_2 bubble coalescence under the stirrer and distribute the bubbles in the slurry. 100 % technical-grade carbon dioxide from 56 atm cylinder was used for gassing. The gas was fed through a reducer to the bottom of the reactor into the slurry under the propeller stirrer. The pressure in the carbon dioxide autoclave was ~ 40 atm. Carbon dioxide (CO_2) flow was measured using Mass View MV-104 electronic rotameter (Netherlands) and amounted to 0.43 ndm^3/min in all experiments. The slurry for gassing was prepared using distilled water. L/S ratio in the initial slurry was 5:1 (by mass) with account of the moisture content in BR, DSP, HG or their mixture. The gassing was carried out for 2 hours at 50 °C. After the slurry was prepared, pH was measured.

The obtained results on decreasing the amount of Na_2O_{total} in BR are shown in Figure 3.

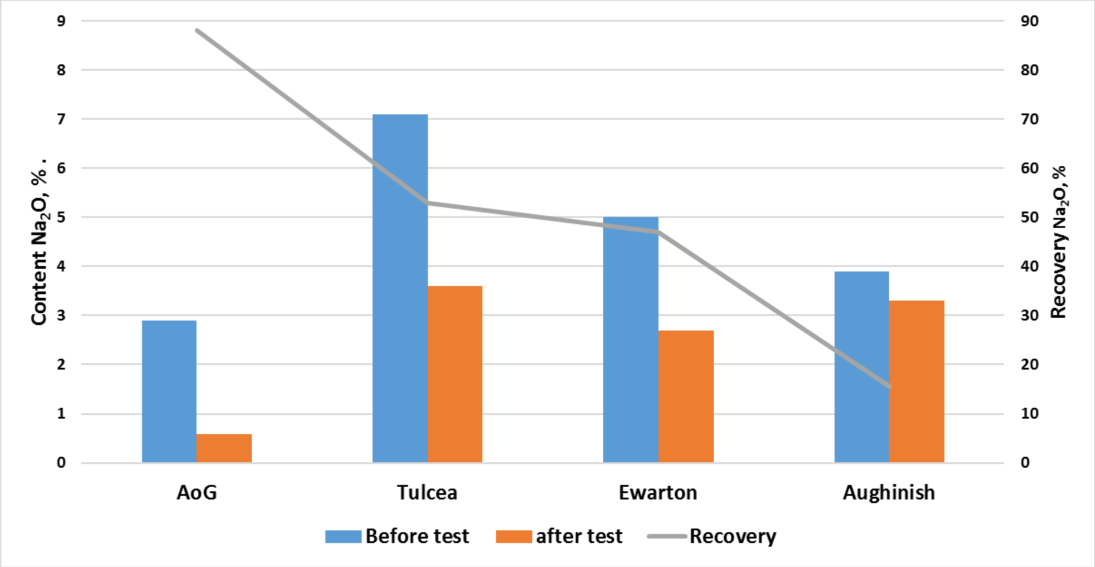


Figure 3. Results of tests on decreasing the amount of Na_2O_{total} in BR using the CO_2 gassing method.

Table 1. Semi-quantitative phase and mineral composition of bauxite residue (before and after gassing).

Refinery/ BR description	**Intensity of characteristic lines (d / I, Å / cps)**														
	Gibbsite, 4.85 Å	**Boehmite, 6.11 Å**	**Diaspore, 4.0 Å**	**Quartz, 3.35 Å**	**Al. Goethite, 4.18 Å**	**Hematite, 2.70 Å**	**Anatase, 3.52 Å**	**Rutile, 3.24 Å**	**Calcite, 3.01 Å**	**DSP, 6.30 Å**	**Hydrogarnet, 5.10 Å**	**Perovskite, 1.915 Å**	**Dawsonite, 5.67 Å**	**Chamosite 7.02 Å**	**Thermonatrite 2.76 Å**
AoG (Greece) initial BR	**150**	**60**	700	125	170	2700	100	60	**430**	**130**	**80**	130	-	45	-
AoG (Greece) BR after gassing	**120**	**100**	780	125	200	2730	100	50	**460**	**50**	**50**	110	**tr.**	54	**100**
Tulcea (Romania) initial BR	**175**	**20**	-	500	920	671	50	30	**350**	**350**	**70**	40	-	-	-
Tulcea (Romania) BR after gassing	**170**	**30**	-	490	990	670	44	30	**470**	**310**	**60**	40	-	-	-
Ewarton (Jamaica) initial BR	**330**	**160**	-	65	860	560	400	70	**350**	**230**	**tr.**	80	-	-	-
Ewarton (Jamaica) BR after gassing	**340**	**130**	-	50	850	530	400	60	**580**	**153**	**tr.**	40	-	-	-
Aughinish (Ireland) initial BR	**250**	**30**	20	200	790	1950	100	160	**-**	**245**	**300**	395	-	-	-
Aughinish (Ireland) BR after gassing	**230**	**45**	tr.	150	550	1750	100	180	**50**	**170**	**260**	550	-	-	-

The obtained data show that the conversion of Na_2O_{total} to the liquid phase for BR from different refineries varies widely, ranging from 15 % to 88 %, which can be attributed to the following reasons:

- different content of three alkali types, i.e. (1) washable; (2) sorbed; (3) chemically bound in BR
- presence of different DSP types (sodalite, noselite, cancrinite) formed during the pre-desilication, digestion, sweetening, thickening and washing. Their resistance to carbon dioxide treatment varies and depends on a number of factors
- conditions of carbon dioxide treatment including residence time and temperature. The paper [11] shows that at treatment temperatures of below 60 °C, released sodium remains in a solution in form of sodium carbonate Na_2CO_3 or sodium hydrocarbonate $NaHCO_3$. At a temperature of ≥ 80 °C, dawsonite $NaAlCO_3(OH)_2$ is formed, which precipitates and remains in bauxite residue thus reducing the effectiveness of neutralization.

Carbon dioxide treatment enables to significantly reduce the alkali content, but the Na_2O_{total} target value of ≤ 0.5 % has not been achieved.

The semi-quantitative phase and mineral analysis of bauxite residue (Table 1) before and after gassing showed that the following phases have undergone major changes:

- DSP amount decreased
- the amount of calcium hydrogarnet (HG) decreased
- the amount of calcite increased.

The content of gibbsite and boehmite in BR before and after treatment did not show any significant change.

To promote better understanding of the behaviour patterns of DSP and HG it was decided to carry out CO_2 pressure gassing tests using synthesized phases.

3. Tests on DSP Treatment with Carbon Dioxide

DSP synthesis. DSP synthesis was conducted as similar as possible to actual DSP generation in BR during the bauxite digestion. The synthesis was carried out using enriched kaolinite from the Troshkovskoe kaolinite deposit which consisted of 97 % kaolinite $Al_2Si_2O_5\times(OH)_4$ and 3 % alpha-quartz.

The conditions of DSP synthesis were taken from the previous studies [15]:

- the ratio of kaolinite (as dry matter) to synthetic spent liquor L/S = 10:1 (by mass);
- synthesis temperature: + 230 °C;
- synthesis time: 90 minutes at reaction temperature.

The chemical composition of synthesized DSP is shown in Table 2.

Table 2. Composition of synthesized DSP.

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	CaO	MgO	Na_2O	K_2O	SO_3	LOI
Init. DSP	33.3	29.8	0.92	0.37	<0.02	0.4	0.3	20.3	<0.15	0.8	16.2

Phase composition of synthesized DSP as per XRF data was as follows:

calcium cancrinite $3.8Na_2O\cdot0.1CaO\cdot3Al_2O_3\cdot6SiO_2\cdot2CO_3\cdot2.2H_2O$	79 %;
noselite $4Na_2O\cdot2.5Al_2O_3\cdot0.5Fe_2O_3\cdot0.5TiO_2\cdot5SiO_2\cdot SO_3\cdot5H_2O$	9 %;
sodalite $4Na_2O\cdot3Al_2O_3\cdot6SiO_2\cdot Cl_2\cdot H_2O$	9 %.

Average estimated DSP formula is as follows:

$$3.7Na_2O\cdot2.87Al_2O_3\cdot0.079CaO\cdot5.79SiO_2\cdot1.58CO_3\cdot0.04Fe_2O_3\cdot0.045TiO_2\cdot0.09SO_3\cdot0.09Cl_2\cdot2{,}3H_2O.$$

In fact, BR always contains a mixture of different forms of DSP, as they are synthesized under different process conditions, including the following:

- pre-desilication of the raw slurry at 90–100 °C
- digestion at ≥ 210 °C
- "sweetening" in the separation circuit at ~ 130–175 °C
- post-desilication of the digested slurry at ~ 105 °C
- thickening and washing at 80÷95 °C.

Therefore, we assume that the obtained DSP mixture represents the BR composition and can be used for further research.

DSP pressure treatment with carbon dioxide was carried out using the same equipment and the same procedure as BR treatment (see section 2). Wet synthetic DSP was dissolved in an aqueous solution containing 5.0 g/dm^3 of sodium carbonate Na_2CO_3. L/S ratio in the initial slurry was 10:1 (by mass) with account of DSP moisture content.

pH value of the initial slurry after DSP reslurrying (before the test) amounted to 13.1 (at + 21.6 °C).

During gassing tests slurry samples were taken directly from the reaction zone using a special sampler (Figure 1, item 8). The volume of samples taken was approximately 50 cm^3. Immediately after the sampling the precipitate was filtered and pH in the liquid phase was measured. The resulting precipitate was dried on a filter press and washed with 100 cm^3 of distilled water at a temperature of 60÷70 °C. The dried precipitate was analyzed for chemical and phase composition and particle size distribution.

Table 3 shows the chemical and phase composition of the obtained precipitate. Gassing lead to changes in DSP composition due to reduction of Na_2O content from 20 % to 15–17 %.

Table 3. DSP composition treated with carbon dioxide (moles).

T, °C	Time	Chemical composition, mass%				Mole fraction				DSP composition*
		Na_2O	Al_2O_3	SiO_2	LOI	Na_2O	Al_2O_3	SiO_2	LOI	
Initial DSP		**20.3**	**29.8**	**33.3**	**16.2**	**1**	**1**	**1.9**	**3.1**	**$Na_2O \times Al_2O_3 \times 1.9\ SiO_2 \times 3.1\ H_2O$**
20	1	**16.5**	35.5	30.3	15.1	**0.76**	1	1.45	2.4	$0.76Na_2O \times Al_2O_3 \times 1.45SiO_2 \times 2.4\ H_2O$
	2	**16.3**	35.5	30.5	15.4	**0.76**	1	1.46	2.46	$0.76Na_2O \times Al_2O_3 \times 1.46SiO_2 \times 2.46\ H_2O$
	3	**16.1**	35.3	30.2	15.6	**0.75**	1	1.45	2.5	$0.75Na_2O \times Al_2O_3 \times 1.45SiO_2 \times 2.5\ H_2O$
	4	**15.8**	35.7	30.8	15.2	**0.73**	1	1.47	2.4	$0.73Na_2O \times Al_2O_3 \times 1.47SiO_2 \times 2.4\ H_2O$
80	1	**17.5**	34.3	29.5	15.4	**0.84**	1	1.5	2.5	$0.84Na_2O \times Al_2O_3 \times 1.5SiO_2 \times 2.5\ H_2O$
	2	**19.0**	32.5	28.4	17.2	**0.96**	1	1.49	3.0	$0.96Na_2O \times Al_2O_3 \times 1.49SiO_2 \times 3.0\ H_2O$
	3	**19.4**	32.1	28.9	17.8	**0.99**	1	1.53	3.1	$0.99Na_2O \times Al_2O_3 \times 1.53SiO_2 \times 3.1\ H_2O$
100	1	**17.4**	34.8	30.7	13.5	**0.8**	1	1.5	2.2	$0.8\ Na_2O \times Al_2O_3 \times 1.5\ SiO_2 \times 2.2\ H_2O$
	2	**17.3**	34.6	30.5	13.5	**0.82**	1	1.5	2.2	$0.82\ Na_2O \times Al_2O_3 \times 1.5\ SiO_2 \times 2.2\ H_2O$
	3	**17.5**	34.7	31.0	13.4	**0.83**	1	1.5	2.2	$0.82\ Na_2O \times Al_2O_3 \times 1.5\ SiO_2 \times 2.2\ H_2O$
	4	**17.8**	34.3	30.7	13.2	**0.85**	1	1.5	2.2	$0.85\ Na_2O \times Al_2O_3 \times 1.5\ SiO_2 \times 2.2\ H_2O$

Note:* DSP composition was calculated based on Al_2O_3 content equal to one.

The analysis of the obtained results showed that the following processes occurred in the slurry during the gassing process:

- part of Na_2O from DSP dissolved into solution, which caused increase of Na_2O_{total} concentration from 3 to 13–20 g/dm^3, i.e. by 4÷7 times. Therefore, from 17 to 27 % of Na_2O can be extracted from DSP
- as a result of sorption, 80–85 % sodium carbonate passes into sodium bicarbonate leading to reduction of pH of the liquid phase from ≥ 12 to ~ 8.2
- when the process is carried out at 20 ºC, sodium content in the product decreases after gassing while alumina content is maintained, and, consequently, the molar ratio Na_2O: Al_2O_3 in DSP decreases from 1 to ~ 0.75.

X-ray diffraction analysis shows that the following changes occur in the bauxite residue:

- substitution of NaOH embedded in DSP crystalline structure as an additional anionic group for CO_2. This is probably one of the reasons for decrease of sodium content in the product after gassing, and therefore the resulting decrease of $Na_2O:Al_2O_3$ ratio from 1 to ~ 0.75
- during the gassing at a temperature of 20 °C there was a small amount of gibbsite in the BR, and at a temperature of + 80 °C there were trace amounts of dawsonite due to DSP partial decomposition.

The residence time at a temperature of ~ 20 °C shall be ~ 1 hour. At a temperature of above 20 °C and residence time of more than 1 hour there is not any significant increase in the alkali amount dissolving from DSP to the solution.

4. Tests on TCA Treatment with Carbon Dioxide

Synthesis of TCA. In order to study the behaviour of tricalcium hexahydroaluminate treated with carbon dioxide under pressure, TCA was synthesized. The conditions of TCA synthesis were taken from the previous studies [16].

TCA was obtained by reaction of the aluminate liquor with lime. Reactive lime CaO of CP grade with an activity rate of 86.1 % was used as lime. The dosage of lime in the aluminate liquor was calculated based by obtaning a ratio of $CaO_{act}/Al_2O_3 = 1.5$ (by mass) in the reaction slurry.

The obtained synthetic TCA was analyzed for moisture content, while the chemical and phase compositions were analyzed using XRS and XRF methods (Table 4 and Figure 3).

Table 4. Chemical composition of synthesized TCA (%).

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	CaO	MgO	Na_2O	K_2O	V_2O_5	Cr_2O_3	MnO	SO_3	LOI
<0.06	25.7	0.21	<0.05	<0.02	45.3	0.35	<0.15	<0.15	<0.015	<0.02	<0.01	0.05	29.3

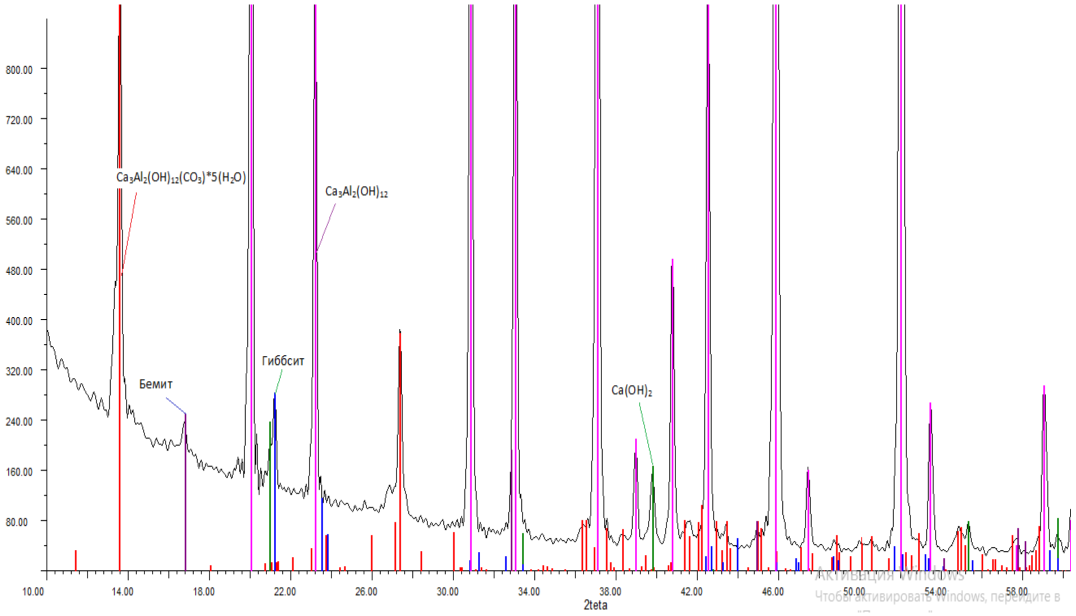


Figure 3. X-ray graph of the initial synthesized TCA.

The main phase of the obtained product is tricalcium aluminate of a katoite structure. Calcium hydrocarboaluminate $Ca_4Al_2(OH)_{12}CO_3 \times 5H_2O$ (CHCA) is present as an impurity in the amount of ~ 15÷20.

TCA was *treated with carbon dioxide under pressure* using the same equipment and the same procedure as BR treatment (see item 2)**.** Wet synthetic TCA could dissolve in an aqueous solution containing 5.0 g/dm^3 of sodium carbonate Na_2CO_3. L/S ratio in the initial slurry was 10:1 (by mass) with account of TCA moisture.

TCA was treated with carbon dioxide at two temperature modes: + 20 and + 80 °C. The duration of gassing varied from 1 to 4 hours. Intermediate sampling while stirring was carried out via a special sampler (Figure 2 item 8). Sample of ~ 50 cm^3 was taken every hour. The samples were filtered, washed with 200 cm^3 distilled water and pH of the liquid phase was determined. The solid phase was analyzed for phase and chemical composition.

Table 5 presents results of the tests.

Table 5. Conditions of tests on TCA treatment with carbon dioxide and composition of the obtained filtrates.

$T_{gas.}$ (°C)	Gassing time (h)	Filtrate			
		pH	Na_2O_{total}, (g/dm$^{3)}$	including Na_2O carbon dioxide	including Na_2O bcb
80	1	7.35	6.03	none	**6.03**
	2	7.28	6.06	none	**6.06**
	3	7.02	6.1	none	**6.1**
	4	7.19	5.71	none	**5.71**
20	1	7.08	6.15	none	**6.15**
	2	7.32	6.14	none	**6.14**
	3	6.82	5.97	none	**5.97**
	4*	**11.01**	2.98	1.93	**1.05**

Note: * The solution contains A_2O_3 = 2.86 g/dm^3.

1. When synthetic TCA is gassed with carbon dioxide under pressure, a two-stage process occurs:

- calcium hydrocarboaluminate reacts with CO_2 to form various calcium carbonates (calcite, vaterite, aragonite) and bayerite:

$$Ca_4Al_2(OH)_{12}CO_3 \cdot 5H_2O + 3CO_2 = 4CaCO_3 + 2Al(OH)_3 + 8H_2O$$

This process also generates a certain quantity of portlandite $Ca(OH)_2$.

- TCA reacts with CO_2 and portlandite in an aqueous solution to form CHCA:

$$Ca_3Al_2(OH)_{12} + CO_2 + Ca(OH)_2 = Ca_4Al_2(OH)_{12}CO_3 \cdot 5H_2O$$

Table 6 shows the phase composition of TCA gassing products.

Table 6. Results of the semi-quantitative X-ray phase analysis of TCA treated with CO_2 under pressure.

Temperature, °C	**Time/h**	**Intensity of the characteristic lines (imp/cps)**							
		TCA, 2.3 Å	**$CaCO_3$ calcite, 3.03 Å**	**CHCA, 7.54 Å**	**AlOOH boehmite, 6.11Å**	**$Al(OH)_3$ bayerite, 4.75 Å**	**$Ca(OH)_2$ portlandite, 2.63 Å**	**$CaCO_3$ vaterite, 3.71 Å**	**$CaCO_3$, aragonite, 3.4 Å**
	init. TCA*	3250	-	800	85	160	127	-	-
20	1 h	2330	1400	65	-	70	-	**50**	-
	2 h	2300	2000	60	65	66	50	**52**	-
	3 h	2300	1400	70	50	75	50	**50**	-
	4 h	**850**	**2020**	**1250**	55	70	-	**70**	-
80	1 h	2000	2100	-	60	80	30	30	**130**
	2 h	1730	2000	40	-	40	30	40	**100**
	3 h	**1750**	**2200**	**70**	-	30	20	30	**140**
	4 h	**1700**	**2700**	30	-	40	20	50	**160**

Note: * the composition of the initial TCA: TCA (katoite) - 80 % in form of $Ca_4Al_2(OH)_{12}CO_3 \times 5H_2O$, CHCA - 20 % in form of $Ca_4Al_2(OH)_{12}CO_3 \times 5H_2O$.

2. The proposed scheme of reactions of TCA, CO_2 and CHCA, water and other intermediate reaction products is undoubtedly of a more complex and multi-stage nature. Obviously, there is a dynamic balance between the reaction products. The proposed chemical properties can be accepted as an operational process diagram.

3. The presence of small amounts of calcium hydroxide in form of portlandite in all the samples proves the possibility of its use in the process of DSP lime neutralization. Better BR neutralization can be attributed to the overlaying of these processes.

The combined processing of DSP and TCA mixture with carbon dioxide will be tested as part of future research on this subject.

5. Comparison of Lime and Carbon Dioxide Neutralization Parameters of Bauxite Residue

Table 7 presents main parameters of BR neutralization technologies.

Table 7. Comparison of main parameters of neutralization technology.

Parameter/property	UoM	Lime method	Carbon dioxide method			
Main reagent		lime	carbon dioxide			
Implementation		tanks	autoclave\reactor			
Process temperature	ºC	95-98	20			
Process time	h	3-5	1			
Na_2O residual content in BR	mass %	<0.5	0.6-3.5			
			AoG	Tulcea	Ewarton	AAL
			0.6	3.6	2.7	3,3
Na_2O form in the filtrate returned to alumina production		Caustic	Carbonate			
Requirement for filtrate treatment		no	yes, lime			

The data in the Table prove that carbon dioxide method to remove alkali from the bauxite residue by gassing BR with carbon dioxide in the reactor to obtain the material that is close to required target parameters can be used for processing AoG bauxite residue only (out of BR samples analyzed in this paper).

6. Conclusions

1. Treatment of BR samples from various alumina refineries with carbon dioxide under pressure makes it possible to dissolve from 17 to 88 % of alkali into the solution by following reactions:

- The removal of sorbed alkali from the surface due to the destruction of the solvate shells around DSP during the transformation of NaOH into Na_2CO_3 and then into $NaHCO_3$
- Partial substitution of NaOH embedded into DSP crystalline structure as an additional anionic group for CO_2
- Partial DSP decomposition (this value ranges from 10 to ~ 20 %).

2. The temperature of above 20 °C and gassing time of more than 1-2 hours do not cause any significant increase in the alkali amount dissolving from DSP to the solution.
3. The reaction of treating BR and DSP with carbon dioxide should be carried out at a temperature close to 20–25 °C which is associated with the presence of a secondary reaction of the released

amorphous alumina with sodium bicarbonate to form dawsonite $NaAl(CO_3)(OH)_2$. At a temperature of around 20 °C, dawsonite is not formed and aluminium remains in the form of amorphous aluminium trihydrate so the neutralization process is more effective.

4. When tricalcium hydroaluminate containing calcium hydrocarboaluminate is treated with carbon dioxide under pressure the process occurs in two stages:

- calcium hydrocarboaluminate reacts with CO_2 to form various calcium carbonates (calcite, vaterite, aragonite) and bayerite resulting in increased CO_2 binding and reduced carbon footprint
- TCA reacts with CO_2 and portlandite in an aqueous solution to form calcium hydrocarboaluminate, that later reacts with CO_2, sodium bicarbonate and decomposes to form various calcium carbonates.

The proposed scheme of reactions of TCA, CO_2 and CHCA, water and other intermediate reaction products is undoubtedly of a more complex and multi-stage nature. Obviously, there is a dynamic balance between the reaction products. The proposed chemical properties can be accepted as an operational process diagram.

5. Treatment of BR samples from alumina refineries with carbon dioxide under pressure provides for a partial reduction of alkali content, but this process does not allow producing BR with the required application properties ($Na_2O_{total} \leq 0.5$ mass %). The best results in terms of achieving the target alkali content were obtained for AoG bauxite residue (0.6 mass %).

6. When treating BR with carbon dioxide an issue arises regarding the conversion of all alkali into a mixture of Na_2CO_3 and $NaHCO_3$ which will require lime treatment up to 2.2 mole of CaO per mole of $Na_2O$for for its causticisation to NaOH which will affect the carbon footprint. However, lime consumption will be less as compared with purely lime regeneration.

7. The results discussed in this pater do not allow determining gas consumption; besides parameters of carbon dioxide BR neutralization can be improved by some additional research activities. At this stage the advantages of the carbon dioxide method seem to be disputable due to incomplete reaction for a majority of BR samples (except for AoG) and due to high capital costs for the equipment (autoclave\reactors) and requirement to have gases with relatively high content of CO_2.

7. Acknowledgement

This research was funded by the European Union as part of Horizon 2020 research programme, grant under contract No. 776469.

European Commission | Horizon 2020
European Union funding
for Research & Innovation

The authors would like to acknowledge Anna Damaskina, Tatyana Shalkova, Lidiya Fyodorova, Tatyana Golovanova, Tatyana Mukina, Yulia Maksimova and Yulia Chernyshova — employees of the Engineering and Technology Department of LLC RUSAL ETC in St. Petersburg, who made a great contribution to this work.

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