Specifics of Alkali Recovery from Bauxite Residue of Different Alumina Refineries

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Abstract

To promote re-use of bulk amount of bauxite residue (BR) as an additive in Portland cement production the following two issues shall be solved: reducing total alkali content (Na_2O+K_2O) below 0.5 % and reducing moisture content below 25 %. Na_2O in BR of different refineries varies from 3.5 % to 8 %. BR contains alkali in three forms: up to 80 % of alkali is chemically bound in desilication product (DSP) - $Na_7[AlSiO_4]_6(OH,SO_4,CO_2)\times nH_2O$; up to 30 % of alkali can be sorbed on the surface of BR fine particles; up to 30 % of alkali is dissolved in the liquid phase. Upon completion of the laboratory tests, parameters to recover the alkali as NaOH and return it to the Bayer process have been established for three European refineries. Based on the experimental results, the design data for the construction of a mobile pilot plant have been developed.

Keywords: waste valorization, DSP, alkali removal.

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Figure 8. Logo of Horizon 2020.

2. Introduction

In the production of one tonne of alumina using the Bayer process, 0.65 to 2.5 tonnes of bauxite residue (depending on bauxite quality and process used) are deposited in the bauxite residue disposal area (BRDA). BR contains both useful, for other industries, components (SiO_2: 7 – 12%; Fe_2O_3: 40 - 52 %; TiO_2: 2 – 7 %; CaO: 4 – 9 %), and other components (Na_2O: 2.5 - 7%; K_2O: 0.1 – 1 %). Additionally, the liquid phase of bauxite residue contains alkaline aluminate liquor at pH ≥ 12.

To re-use bauxite residue (BR) in considerable amount as construction material (bedding of roads, filler in production of paving slabs), complex additive for production of Portland cement, it is necessary to solve two technical problems: to reduce Na_2O content to ≤ 0.5 % and humidity to ≤ 25 %.

In the slurry of bauxite residue sodium compounds are presented in three forms:

- bound in the structure of hydroaluminosilicate (up to 80%);
- sorbed on the surface of BR fine particles (up to 30%);
- component of sodium aluminate in a liquid phase (up to 30%).

To provide maximum extraction of sodium from BR slurry with minimum "disturbance" of alumina production process from bauxites and to reduce the impact on ecology, the option of processing the slurry with lime (milk of lime) was studied. Sodium aluminosilicate contained in bauxite residue is decomposed with formation of alkaline-earth compounds, such as $3CaO \times Al_2O_3 \times nH_2O$ and $2\ CaO \times SiO_2 \times mH_2O$ [1, 2].

Alkali from DSP as caustic alkali passes into solution by reaction:

$$Na_2O \times Al_2O_3 \times 2SiO_2 \times xH_2O + 7Ca(OH)_2 \rightarrow 3CaO \times Al_2O_3 \times nH_2O + \\ + 2(2CaO \times SiO_2\ mH_2O) + 2NaOH \quad (1)$$

If sodium aluminate is not available in the liquor in significant amount, an additional reaction occurs, and alumina contained in bauxite residue is precipitated:

$$2NaAlO_2aq + 3Ca(OH)_2 \rightarrow 3CaO \times Al_2O_3 \times nH_2O + 2NaOH \quad (2)$$

With addition of carbonate alkali such as sodium carbonate or potassium carbonate to the residue from these reactions, decomposition of alkaline-earth aluminates occurs by reaction:

$$3CaO \times Al_2O_3 \times nH_2O + 3Na_2CO_3 \rightarrow 3CaCO_3 + 2NaAlO_2 + 4NaOH + XH_2O \quad (3)$$

By combination of these two processes it is possible to extract alkali from bauxite residue into solution.

This method was tested on BR samples from European alumina refineries:

- Aughinish Alumina Ltd, Ireland (AAL);
- Aluminum of Greece, Greece (AOG);
- Alum Tulcea, Romania (Tulcea)

3. Experimental

To perform the laboratory work, a unit was mounted and prepared for tests enabling to resist required temperature condition over extended period at continuous mixing of slurry, to feed and select samples directly in the course of the experiment.

The laboratory unit (Figure 1) comprises:

- reactor equipped with an external source of heating (thermostating);
- mixing device;
- submerged sampler (a tube for sampling).

Figure 1. Laboratory unit for simulation of the process of bauxite residue lime neutralization.

The test was developed to assess the parameters of the neutralization process which consisted of three main stages:

1. preparation of lime reagent (dosage of dry reagent / preparation of milk of lime);
2. BR treatment with lime reagent (mixing BR slurry streams and lime reagent with aging at reaction temperature and stirring);
3. phase separation on a vacuum filter with BR washing.

Control experiments will be conducted with a modified third stage. Filtration will be carried out on the press filter with wringing out and displacing the pore moisture (alkaline solution) with technical water.

Bauxite residue had the following phase composition:

Table 1. Phase composition of BR samples before and after testing.

Phase	Refinery					
	AAL		AoG		Tulcea	
	initial	neutralized	initial	neutralized	initial	neutralized
DSP	23.4	2.3	17.4	1.7	31.7	7.2*
TCA	2.0	35.0	0	31.6	2	37.6
Hematite + goethite	55.1	44.9	45.9	41.3	48.9	37.7
Anatase + Rutile	1.9	1.2	0.5	0.4	1	0.9
Diaspore + Boehmite	5.5	4.2	18.5	15.5	6.5	4.2
Perovskite	9.1	8.1	9.2	8.5	3.3	2.9

* - this value requires clarification, possibly this combination of DSP content in the BR and sorbed alkali.

4. Results

Lime reactant can be introduced into the process in the form of two products:

- Dry lime (Quick lime);
- Milk of Lime.

Feeding of dry lime enables to reduce production flows and equipment for BR neutralization, but it can lead to decrease in efficiency of the process.

To check this hypothesis, comparative experiments were performed with identical dosage of CaO and holding time of BR slurry, but various type of supplied calcium reactant.

Data obtained in processing BR of the Irish refinery are presented in Figure 2.

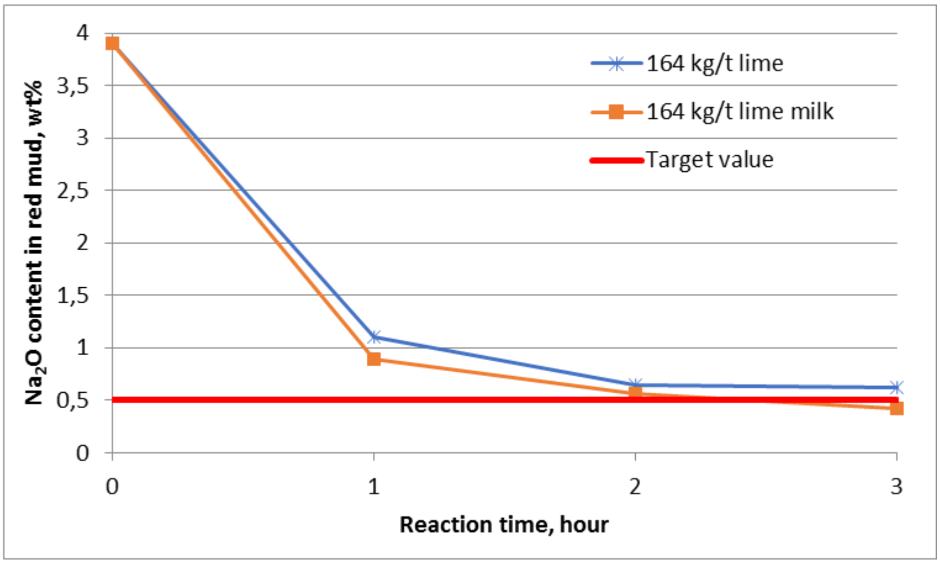


Figure 2. Results after processing AAL BR with quick lime and milk of lime.

As it is apparent from the curves presented in Figure 2 of Na_2O residual content in AAL BR the use of milk of lime as a reactant allows to reduce the residual content of Na_2O by extra 0.2% and to reach the target content of alkaline elements in the processed bauxite residue.

Having confirmed the impact of type of calcium compound on the process of neutralization, further experiments were performed with milk of lime as it allows to reduce consumption of reactant and to reduce the time of neutralization process.

To determine the optimum dosage of milk of lime for neutralization of bauxite residue a series of experiments varying dosage from 100 to 210 kg CaO per 1 tonne of bauxite residue was performed. The results on BR from the Irish refinery are presented in Figure 3.

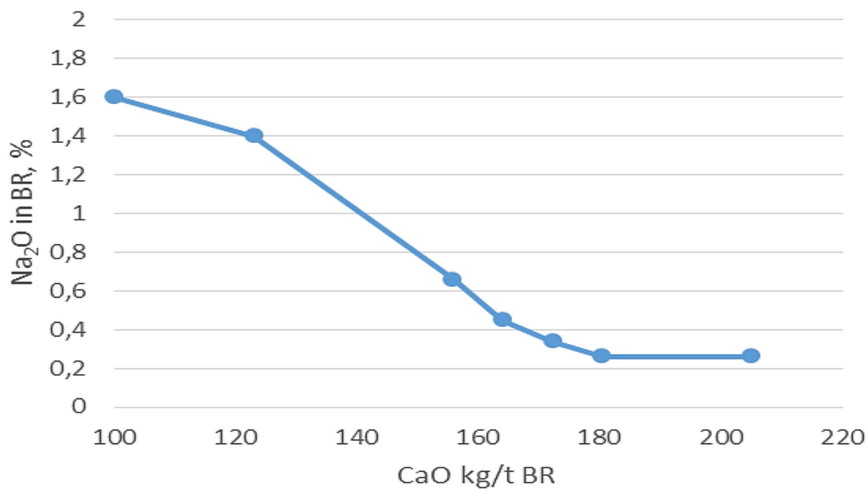


Figure 3. Results of experiments to determine optimum lime dosage for AAL BR.

The data allow to draw a conclusion that the dependence of residual content of alkaline metals in terms of Na_2O for this BR asymptotically approaches 0.26 mass %, and for sustainable production of BR with residual content of Na_2O below 0.5 % it is sufficient to provide lime (milk of lime) dosage in the process of alkali removal in amount of 160 - 170 kg/t BR.

For comparison, similar curves was obtained in a laboratory for BR of AoG (Figure 4) and Tulcea (Figure 5).

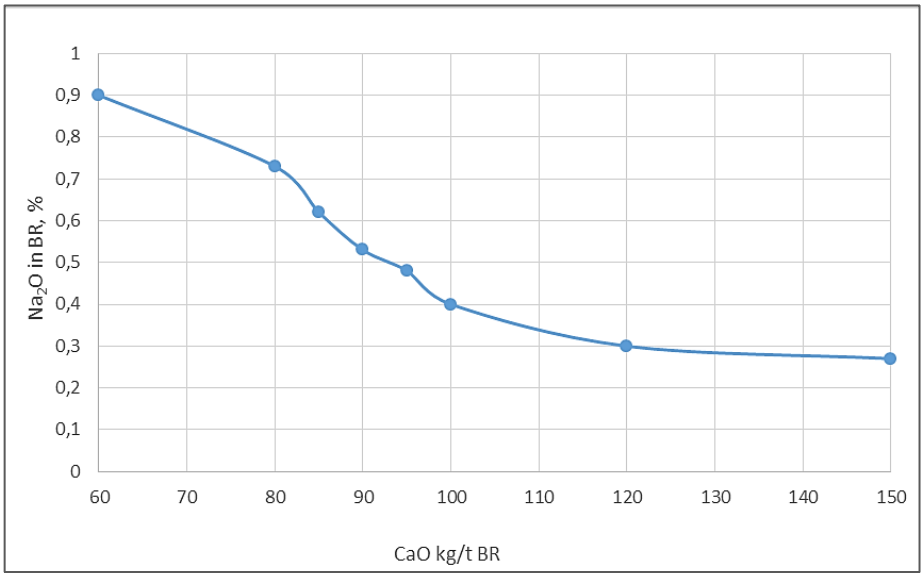


Figure 4. Results of experiments to determine optimum lime dosage for AoG BR.

The data from laboratory tests demonstrated that to achieve alkali content below 0.5% for BR of Greek refinery the dosage of lime in amount of 100 kg/t BR is sufficient.

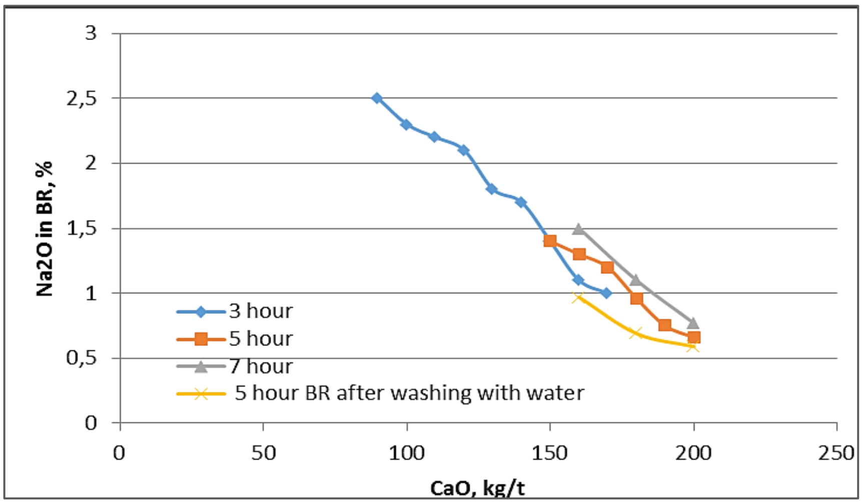


Figure 5. Results of experiments to determine optimum lime dosage for Tulcea BR.

Laboratory test results have shown that using this technology, achieving of alkali content of less than 0.5% for the sludge of the Romanian Tulcea plant is not possible without carrying out additional processing.

5. Discussion

Decrease in a consumption of lime for Greek BR was expected since the content of alkali in the initial BR is lower than in the Irish one by 1.5%.

The curve of decrease in residual alkali in BR is non-linear character and dependences were plotted of amount (kg) of recovered Na_2O versus addition of CaO (kg) for the entire range of dosages. The obtained calculated data are presented in Figure 6.

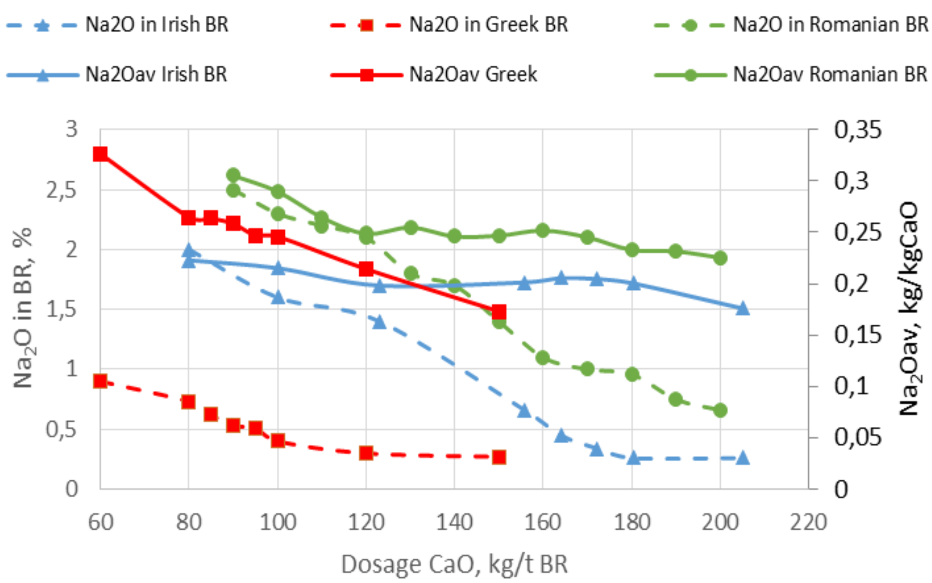


Figure 6. Results of calculation and experimental data.

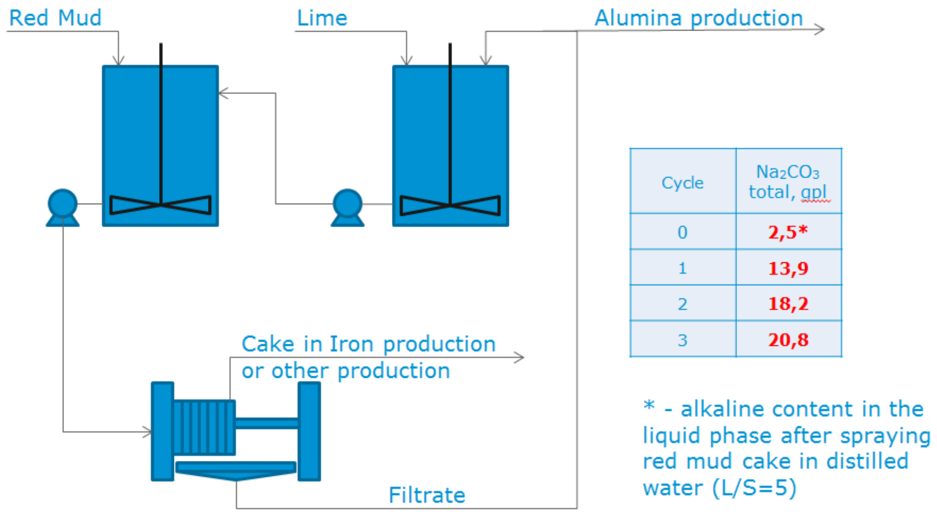
The data demonstrates that for AoG BR plant specific alkali recycling to alumina production per 1 kg of CaO is higher than for Irish BR (to achieve the target value for residual alkali) at 0.25 kg/kg for AoG versus 0.2 kg/kg for Irish BR. This is also higher compared to Romanian BR in the areas investigated.

The resulted curve knee of residual alkali content in BR is confirmed by decrease in specific extraction of Na_2O kg/kg CaO.

After achieving the target value of residual alkali content ($Na_2O \leq 0{,}5$ %) cyclic experiments were conducted to recover milk of lime from filtrate after extraction of neutralized BR. The cyclic data demonstrate that reuse of a filtrate allows to increase concentration of caustic alkali (NaOH) in the liquid phase recycled to alumina production. This method recovers alkali and to some extent alumina and avoid fresh water consumption for preparation of milk of lime.

As a result of DSP destruction two phases are formed: cubic calcium hydroaluminate and dicalcium silicate hydrate. These phases in the course of production of Portland cement clinker even at a temperature ≥ 500 °C directly form ready phases of Portland cement: celite ($3CaO \times Al_2O_3$) and belite ($2CaO \times SiO_2$).

Principal flowsheet of BR neutralization with filtrate recycling to produce alumina is presented in Figure 7.



Cycle	Na_2CO_3 total, gpl
0	2,5*
1	13,9
2	18,2
3	20,8

Figure 7. Principal flowsheet of BR neutralization.

6. Conclusions

The main task of this work was achievement of residual content of alkali in BR below 0.5% that will allow to use considerable amount of bauxite residue as construction material (bedding of roads, filler in production of paving slabs), complex additive for production of Portland cement.

Laboratory tests confirmed that for two tested samples of BR (Irish and Greek) the required decrease in residual alkali to the value below 0.5% is achievable without digestion (agitation) processing of BR slurry with lime reactant. Significant destruction of DSP structure occurs and decrease the content of alkali to the target value.

Based on the data calculation of material flows of BR neutralization unit was determined and development of mobile pilot plant has started to produce large-scale batches of neutralized bauxite residue from the two alumina refineries.

7. References

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