

Residues Recycling: Reducing Costs and Helping the Environment

Luis C.A. Venancio, José Antonio Silva Souza, Emanuel Negrão Macedo, João Nazareno N. Quaresma, and Antonio Ernandes M. Paiva

The aluminum production chain from bauxite to primary aluminum includes refining using the Bayer process, and smelting through electrolysis. This production chain produces two main solid residues, red mud at the refinery and spent pot lining at the smelter. The use of these residues as raw material for other industrial processes can save large amounts of energy, reduce the overall environmental impact, and even improve the emissions of other processes. This paper shows the results of ten years of co-processing of spent pot lining in the cement industry in Brazil and the efforts to develop technologies to reduce the reactivity and use the red mud as raw material for several different processes. This approach, although engineering intensive, can reduce CO₂ emissions and save huge amounts of wasted energy in transport and processing when compared with dedicated recycling or neutralizing processes.

INTRODUCTION

Aluminum production by electrolysis in Hall–Héroult cells generates a residue called spent pot lining. It is formed by the carbon and refractory lining of the cells after the useful life of around six years. This residue is considered a hazardous material and typically has small percentages of cyanide, lead, and chrome and large percentages of sodium, fluorides, silica, alumina, and carbon. The Alumar plant at São Luis-MA,¹ Brazil is completing ten years of co-processing this material at the cement plant Cimento Poty at Sobral-CE with very interesting environmental and economic results. The energy consumption was reduced at the furnace and at the clinker milling. The stack emissions improved on CO₂, NO_x, and SO_x due to the reduction of

the temperature in the furnace.

The production of millions of tonnes per year of alumina around the world generates 0.7 to 2 tonnes of residue known as red mud (RM) and 0.7 to 1.1 tonne of CO₂ per tonne of alumina.² The vast majority of the RM is stored in large sealed lakes. Due to its high reactivity and large volume it is considered dangerous and currently there

is no operating process capable of reusing all the RM material at any refinery. These lakes, after being filled with solid material, eventually have the surface revegetated.

This paper demonstrates that, by studying the main properties of this residue rich in silico-aluminates and oxides such as iron and sodium, that material could be utilized in the construction industry as building blocks and in the manufacture of synthetic aggregate. Residues such as RM have important physiochemical characteristics for the sintering of materials that feature higher mechanical strength than natural aggregates. Red mud residues can easily replace a part of the clay mined for red ceramic artifacts, a part of the aggregate used in paving roads, and all the material for the manufacture of synthetic aggregates to replace the aggregates extracted from nature and used in construction, thus avoiding the extraction of that material from natural reserves.

The use of the exhaust gases of the refineries to neutralize this residue may allow a double gain: opening a large array of new applications for the residue with the reduction of its reactivity and sequestering million of tonnes of CO₂ plus other gases like SO₂ and NO_x.

SPENT POT LINING FROM SMELTING

Hall–Héroult Smelting Process

In the aluminum smelting process the alumina produced at the refinery is reduced to primary aluminum through electrolysis (at approximately 950°C) in a cryolite bath (Na₃AlF₆). This process is called Hall–Héroult and takes place in electrolytic pots. These are essentially large steel shells lined with

How would you...

...describe the overall significance of this paper?

This paper shows that recycling residues can save money and reduce the overall impact of industrial processes, specifically in the aluminum industry. This approach, although engineering-intensive, can reduce CO₂ emissions and energy waste.

...describe this work to a materials science and engineering professional with no experience in your technical specialty?

Spent pot lining and red mud are the main residues of the primary aluminum industry. This paper shows the results of ten years of co-processing of spent pot lining in the cement industry in Brazil and efforts to develop technologies to reduce the reactivity and use the red mud as a raw material for several different processes.

...describe this work to a layperson?

Using residues of one industrial process as a raw material for other processes is not an easy task. This paper describes the co-processing of the two main residues of the aluminum industry. One example has been running for ten years at full scale. Several alternatives are under development for the other. This approach, although engineering-intensive, can reduce CO₂ emissions as well as energy waste.

Table I. Comparing the Atmospheric Stack Emission Levels of the Blank Test, Several Measures with Co-processing, and the Legal Maximum Limits¹

Parameter	Blank Test	2000	2001	2002	Max Legal
Hydrochloric Acid (HCl)	0.34 kg/h	0.09 kg/h	0.020 kg/h	0.145 kg/h	1.8 kg/h
Hydrofluoric Acid (HF)	<0.03 mg/Nm ³	<0.04 mg/Nm ³	0.034 mg/Nm ³	0.058 mg/Nm ³	5.0 mg/Nm ³
CO	156 ppmv	<98.9 ppmv	95 ppmv	<08.9 ppmv	100 ppmv
Particulate	267 mg/Nm ³	35.3 mg/Nm ³	41.88 mg/Nm ³	25.16 mg/Nm ³	100 mg/Nm ³
THC (expressed as propane)	<0.1 ppmv	3.0 ppmv	0.01ppmv	2.31ppmv	20 ppmv
Mercury (Hg)	<0.002 mg/Nm ³	<0.001 mg/Nm ³	0.000061 mg/Nm ³	<0.001 mg/Nm ³	0.05 mg/Nm ³
Lead (Pb)	<0.005mg/Nm ³	<0.0019 mg/Nm ³	0.034 mg/Nm ³	0.011 mg/Nm ³	0.35 mg/Nm ³
Cadmium (Cd)	<0.035 mg/Nm ³	0.0019 mg/Nm ³	0.014 mg/Nm ³	0.035 mg/Nm ³	0.10 mg/Nm ³
Thallium (Tl)	<0.005 mg/Nm ³	<0.0019 mg/Nm ³	<00009 mg/Nm ³	0.0016 mg/Nm ³	0.10 mg/Nm ³
(As+Be+Co+Ni+Se+Te)	0.51 mg/Nm ³	0.02 mg/Nm ³	0.039 mg/Nm ³	<0.017 mg/Nm ³	1.4 mg/Nm ³
(As+Be+Co+Cr+Cu+Mn+Ni+Pb+Sb+Se+Sn+Te+Zn)	4.73 mg/Nm ³	0.150 mg/Nm ³	6.52 mg/Nm ³	0.345 mg/Nm ³	7.0 mg/Nm ³

refractory material at the bottom covered with carbon blocks to conduct the electricity. At the end of the life of this lining, it is removed and is called spent pot lining. Typically the composition is small percentages of cyanide, lead, and chrome and large percentages of sodium, fluoride, silica, alumina, and carbon. It is considered a hazardous material and is stored in paved and covered buildings.

The first step was a study with the Federal University of Pará to choose the processes which could benefit from the components and at the same time dissociate the cyanide and enclosure the metals. The first trials were conducted in the red ceramic industry, starting at the laboratory scale and later producing up to 33 million bricks and tiles. After some time, due to the complexity of managing the material handling at several ceramic industries, a decision

was made to shift the use to the cement industry.

At this point a crucial decision was made: Grind the material to be similar to the other raw materials and introduce it at the beginning of the furnace. This allows enough residence time to benefit from the fluor, which facilitates the formation of the alite crystals, forming the clinker at lower temperatures. The clinker is later ground and milled with gypsum and other additives to become the cement. This process benefits in several ways from the fluor and carbon.^{3,4} The temperature of the furnace was reduced by 80°C and the fuel consumption was reduced by 111 tonnes/month. This resulted in a proportional reduction of CO₂ and NO_x emissions. The average composition of the spent pot lining was (in wt.%) 19F-18.5C-17.9Na-14.6Al-2.5Fe-1.7Ca-0.6Mg-0.39P, with 0.2% cyanide and 1,200 kcal/Kg calorific power.¹

The decision to have a dedicated small crushing and grinding facility allowed the choice of the best addition point for the material at the cement plant. Some procedures for using the existing coke fuel grinding facility and introducing the material through the burner (which may be adequate for other residues) do not allow sufficient resident time to get the full benefits of the components and inhibit the burning process by introducing a low calorific power material. A facility to produce 1,000 tonnes a month is a very small one so the equipment should be carefully chosen to avoid overcapacity; on the other hand outsourcing this work

would add transport costs and environmental risk. The average particle size achieved was, for 325 mesh, 63.2 ± 13, for 250 mesh, 48.30 ± 11, and for 100 mesh, 18.31 ± 7.8.

The material initially was transported in big bags and later in bulk trucks and stored in closed silos, protected from the weather, with dust control and without contact with the employees.

As Table I verifies, some environmental control and emission result parameters were above the limits on the blank test and they were corrected with improved maintenance after the start of the co-processing.

One of the most important premises to obtain the co-processing license is the guarantee of the environmental control of the facility. With this objective it is very important to have the Environmental Protection Agency on board from the beginning of the process. To attend the legislation the Cimento Poty S.A. acquired a continuous gas analyzer for O₂, CO, NO_x, and THC. Transparency is a key factor in the relation be-



Figure 1. Spray of a suspension of RM and water on a reactor.

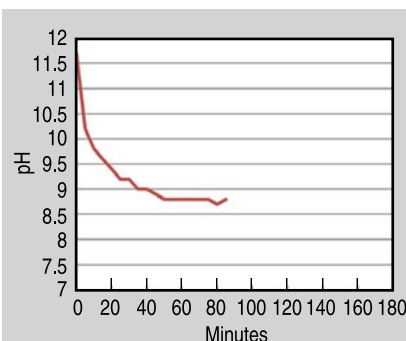


Figure 2. Reaction of RM with simulated exhaust gas.⁵

tween the generator of the material, the co-processor, and the environmental agency. The environmental emissions of the co-processor should be tightly controlled.

From an environmental aspect this process is saving energy versus spending energy on an alternative calcining process. A reduction of 300 tonnes per month of CO₂ resulted, plus a reduction from 850 to 550 ppm in the content of NO_x at the exhaust gases due to the lower temperature. A dedicated calcining process for the spent pot lining would consume a minimum of 500 kcal/kg to dissociate the cyanide.

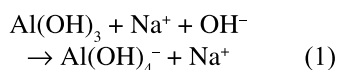
From an economic aspect the reduction of 80°C resulted in 111 tonnes of petroleum coke saved per month; additionally, the lower temperature allowed the use of cheaper coke with higher sulfur. This sulfur⁴ was incorporated into the clinker, improving its properties with no impact on the emissions. Milling energy for the clinker was also reduced.

RED MUD FROM ALUMINA PRODUCTION

The Bayer process to obtain alumina from bauxite can be divided into four steps:

Digestion – The minerals containing aluminum in the bauxite are selectively extracted from the nonsoluble components through the dissolution in sodium hydroxide.

Gibbsite:



Clarification – After the extraction the insoluble residue must be separated through a settling and filtering process. The aluminum-containing liquor is

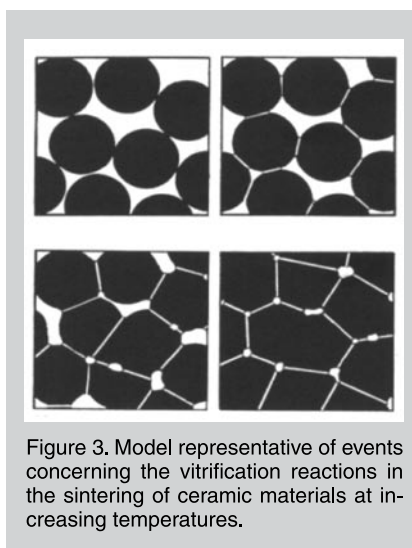
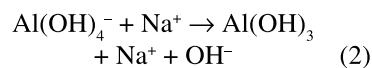


Figure 3. Model representative of events concerning the vitrification reactions in the sintering of ceramic materials at increasing temperatures.

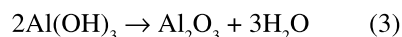
transferred to the precipitators.

Precipitation – Crystalline aluminum trihydroxide “hydrate” is precipitated from the liquor.



The hydrate is fed into the calcination kiln.

Calcination – The hydrate is calcined to form alumina through the separation of the water.



Bayer Process Residue—Red Mud and Exhaust Gases

Alumina production through the Bayer process generates from 0.7 to 2.0 tonnes of residue per tonne of alumina. It is usually called red mud (RM). The RM composition includes hematite and other iron oxides, quartz, and titanium oxides.

During the RM treatment only part of the sodium hydroxide is removed. The RM has a considerable amount

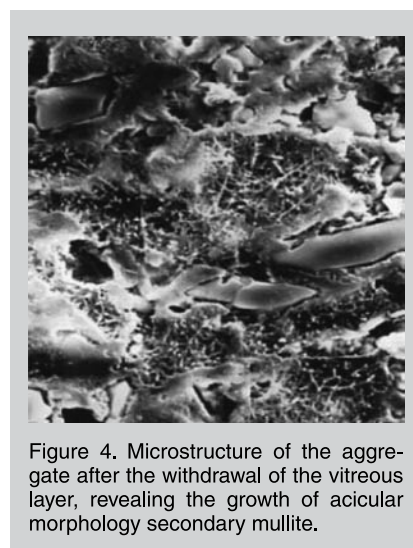


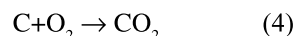
Figure 4. Microstructure of the aggregate after the withdrawal of the vitreous layer, revealing the growth of acicular morphology secondary mullite.

of sodium hydroxide and several concentrated ores. This represents a considerable resource waste of mineral resources. A chemical analysis of the RM from Alumina do Norte do Brasil S/A (ALUNORTE—Belém-PA-Brazil) found 34.9Fe₂O₃-22.6Al₂O₃-18.3SiO₂-9.31Na₂O-7.56PF-5.56TiO₂-1.32CaO-0.28V₂O₅-0.13K₂O-0.04MgO, and traces of V, Ga, P, Mn, Mg, Zn, Zr, Th, Cr, and Nb.

The generation of exhaust gases at the Bayer process occurs essentially at two points: the steam-generating boiler and the alumina calcinatory. The calcinators usually use fuel oil or natural gas.

The specific consumption is 0.18 tonnes of oil for each tonne of alumina.⁵

The composition of the exhaust gases can be estimated considering the oil to have 80% carbon in its composition and reacting with oxygen each atom of carbon with atomic weight 12 will meet two of oxygen with atomic weight 16.



Therefore each tonne of oil will generate 2.9 tonnes of CO₂.

Red Mud Carbonation—Amendment

The RM has around 5% of NaOH in its composition,⁵ in the presence of H₂O as a catalyzer:

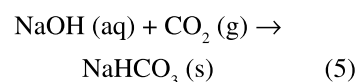


Table II. Ceramic Characteristics of the Test Specimens after Firing⁶

Samples	Temperature (°C)	RL (%)	TS (kgf/cm ²)	AA (%)	PA (%)	MEA (G/cm ³)
A-20	1,000	7.03	132.89	16.78	33.56	2.11
	1,050	7.78	136.90	15.90	31.40	2.12
	1,150	8.89	142.78	6.78	13.45	2.56
A-70	1,000	6.97	182.64	14.70	31.44	2.14
	1,050	14.23	310.33	4.48	11.95	2.67
	1,150	16.28	421.77	1.13	3.27	2.89
A-50	1,000	12.91	228.53	5.00	12.92	2.58
	1,050	13.29	240.14	3.49	9.11	2.60
	1,150	11.50	247.07	3.79	9.31	2.45

Table III. Properties of Conventional Aggregates Compared to the Synthetic Aggregate

Aggregate	Specific Gravity (G/cm ³)	Porosity	Strength Resistance (MPa)
Sand	2.71	6.89	35
Round Pebble	2.62	1.98	25
Gravel	2.79	1.09	40
Synthetic Aggregate M-20 / 1,200°C	2.76	1.78	42
Synthetic Aggregate M-20 / 1,250°C	1.59	2.56	26
Synthetic Aggregate M-20 / 1,300°C	1.11	9.51	15

Since the molecular weight of the NaOH is 40.0 g/mol and the CO₂ is 44.01, to neutralize one tonne of RM with 5% of NaOH with a recovery of 80% we need around 69 kg of CO₂. Since we have only 415 at the calciners we have excess gas for the neutralization (Figures 1 and 2).

Properties of the Clay–Red Mud Mix after Firing

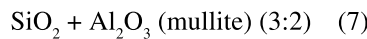
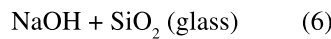
Tensile Strength

The mean values in kgf/cm² for the tensile strength (TS) are shown by the specimens after sintering. The test specimens A-7 (clay with 70% red mud) and A-5 (clay with 50% red mud) have increasing values of TS. It is worth mentioning that the TS values submitted by test specimens A-5 and A-7 are above the limits recommended by standards for red ceramics (Table II).

Solid State Reactions and Properties of the Mixture after Sintering

Most authors^{7,8} combine the necessary conditions for the sintering of ceramic materials (pore closure) along with the increase in strength with the efficiency of solid-state reactions, which occur within the material responsible for the formation of mullite and for the amorphous phase (glass). These transformations can be controlled in four ways, namely: by the composition of the mixture, the particle size of the raw material, the firing temperature, and the time of exposure to this temperature. The material can also produce pyro-expansion; that is, in the firing temperature, the expansion of this synthetic material produces a cellular structure, which is essential for the manufacture of high-quality lightweight aggregate with density <1.5 g/

cm³. The material in the sintering must have sufficient glass content in low viscosity at the temperature of formation in order to fill the majority of the pores and retain the gases that formed; the presence of NaOH in the red mud is responsible for most of the glassy phase formed through the reactions of vitrification (formation of amorphous phase) and subsequent nucleation and growth of secondary acicular mullite.⁷



The vitrification reactions are responsible for the reduction of pores in the structure of ceramic materials. This stage of phase transformation in these materials is directly influenced^{7,8} by the reduction in the viscosity of the glassy phase, which is favored by the presence of alkali metals such as sodium and potassium. Figure 3 illustrates a representative model of the sintering



Figure 5. Rupture of the specimen outside the structure of the aggregate.

Table IV. Average Properties of Ceramics Obtained for the RM Aggregate

Sample	Area in (mm ²)	Load (kN)	Rupture (MPa)
M-10	7,853.9	132.38	21.72
M-20		222.61	39.26
M-30		107.87	15.49

stages with the formation of the vitreous phase and consequent reduction in its viscosity, which is responsible for the occupation of the void in the structure, thus causing a reduction in porosity and consequently an increase in material strength.

The microstructure of the material after the removal of the vitreous layer is shown in Figure 4, which shows the formation of a large amount of vitreous phase, especially for temperatures above 1,200°C, showing the dependence of mechanical strength with the viscosity of the vitreous phase and likely nucleation of the secondary mullite of the acicular morphology,^{7,8} which can be observed after removal of the vitreous layer with HF attack on the surface.

Strength of the Synthetic Aggregate Produced from Red Mud on Compression

Table III shows the results obtained for the synthetic aggregate M-20 (20% silica by weight) for three different temperatures, compared to conventional aggregate used in civil construction in Brazil.

The compressive strength of concrete was obtained when the test specimens reached the age of 28 days and was conducted according to the guidelines of the NBR 5739.⁹ The results of the compressive strength values for the concrete produced with selected aggregates are presented in Table IV.

The average of the test specimens of sample M-20 reached the expected dosage resistance at 28 days, around 39 MPa. Among the concretes with the aggregates of samples M-10 and M30, the differences were significant. The porosity of sample M-20 (sample made up of 80% red mud and 20% silica), when synthesized at 1,200°C, showed relatively low porosity, around 1.78%, making cement/aggregate adherence difficult. This contributed to

the rupture propagating preferentially outside the aggregate (there was no rupture of the aggregate), as shown in Figure 5, in spite of the compressive strength remaining high.

In the samples M-10 and M-30, with the increase of silica in the composition of the aggregate, porosity was reduced due to the increase of the vitreous layer that formed, causing a very weak interface in the concrete formed between the aggregate and cement. Although the compression test of the test specimens also cause disruption, preferably in the cement, the aggregate suffered some kind of crack due to having lower tensile strength. That interface without adherence may also be responsible for the low compressive strength of the test specimens.

CONCLUSION

The use of residues from other processes as raw materials can save large

amounts of energy compared to exclusive treating facilities. Additionally large amounts of energy that would be spent in transportation are saved. In some cases, due to the large volumes, this is the only option economically viable for recycling. It is an engineering-intensive process and needs to have a partnership and transparent relationship between the generator, the environmental agency, and the recycler in order to have an environmental impact.

References

1. Valerio A. Gomes et al., "Co-processing Spent Pot Lining at the Cement Industry," Published as part of the Environmental Licensing Process (2003).
2. Luis C. Venancio, "Bauxite Residue Neutralization with Carbon Sequestration" (Paper presented at the TMS 2010 Annual Meeting, Seattle, Washington, 14–18 February 2010).
3. M.S. Surana and S.N. Joshi, *Use of Mineralizers and Fluxes for Improved Clinkerization and Conservation of Energy*, vol. 1 (Wiesbaden, German: Zement-Kalk-Gips, 1990).
4. Sérgio Luiz Centurione et al., "Evaluation of Mineralization Degree of Portland Clinker" (Paper

presented at the 5th Brazilian Conference on Portland Cement, Sao Paulo, Brazil, 1999).

5. Luis C.A. Venancio, "Process of Neutralizing Bauxite Residue with Carbon Sequestration" (Paper presented at IFET-MA 2010, Connepi, Belém, PA, Brazil, 2009).
6. E.A. Hildebrando, J.A.S. Souza, and R.F. Neves, "Aplicação do Rejeito do Processo Bayer (Lama Vermelha) como Matéria-Prima na Indústria de Cerâmica Estrutural," in: *Anais do 43º Congresso Brasileiro de Cerâmica* (Sao Paulo, Brazil: Brazilian Ceramic Association, 1999), pp. 28101–28111.
7. H.J. Oel, "Sintering of Crystalline Ceramics," *Fortschritte der Mineralogie*, 63, Supplement 1 (1985), p. 167.
8. H. Mortel and K. Heimstadt, "Ceramics," *Werkstoffe und Korrosion-Materials and Corrosion*, 45 (1994), pp. 128–136.
9. "NBR 5739: Ensaio de Compressão de Corpos de Prova Cilíndricos de Concreto - Método de Ensaio" (Rio de Janeiro: ABNT – Associação Brasileira De Normas Técnicas, 1994).

Luis C.A. Venancio, José Antonio Silva Souza, Emanuel Negrão Macedo, and João Nazareno N. Quaresma are at Federal University of Pará—Amazon Natural Resources Engineering Development Program—PRODERNA. Rua Augusto Correia 01, Guamá, Belém, Pará, CEP 66075-110, Brazil; Antonio Ernandes M. Paiva is at the Federal Institute for Education, Science and Technology-IFMA, PPGEM. Luis Venancio can be reached at luisvenancio@terra.com.br.