



CR³ Communication: Red Mud – A Resource or a Waste?

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TMS has forged cooperative agreements with several carefully selected organizations that actively work to benefit the materials science community. In this occasional series, JOM will provide an update on the activities of these organizations. This installment, by the Center for Resource Recovery & Recycling (CR³), focuses on Bayer process residue. The CR³ is a research center established by Worcester Polytechnic Institute, Colorado School of Mines, and K.U. Leuven. Twenty-eight corporations and national laboratories along with support from the U.S. National Science Foundation's I/UCRC program are sponsors of the center.

“Waste is wasted if you waste it, otherwise it is a resource. Resource is wasted if you ignore it and do not conserve it with holistic best practices and reduce societal costs. Resource is for the transformation of people and society.”¹

Red mud, a byproduct of the Bayer Process, is a mixture of metallic oxides that has proven to be a major disposal problem due to its mass and toxicity. This disposal problem is compounded by the fact that for every kg of primary Al produced, 2.5 to 3.0 kg of red mud is generated. The global primary Al production is approximately 44 million tons.^{2,3} There are two current methods of storage. The first is to simply pump the red mud into holding ponds and the other is to store the mud after drying upon a special liner. In the latter case, once there is sufficient red mud, the dry stack is then covered with topsoil. Both methods create the issue of land use. Table I shows a typical compound analysis for red mud generated from Jamaican bauxite. As is evident, the presence of heavy metals such as lead, cadmium, and mercury, as well as the presence of soda, is a serious problem for groundwater.⁴

Limited application of red mud has been tried as a constituent in industrial construction aggregates, such as bricks, road surface material, and cement, in combination with other waste products such as flyash, and it has also been tried as a soil modifier. These applications do not add value but can serve as a valid route for waste utilization after metal(s) extraction. Careful consideration is required for addressing the vastness of the problem via construction material applications. The extraction of Fe, the main constituent in red mud, has been

the focus of several previous research efforts. One investigator suggests separating the red mud (in slurry form) using high intensity magnetic separation. The resulting magnetic product can be used as an ingredient for ironmaking or as a pigment for pottery making. The non-magnetic portion can be applied in building materials or supplemented back into the Bayer process. Recovery of the Fe is low.⁵ Another investigator reduces the Fe with chlorocarbons before magnetic separation and uses the resulting magnetic portion as feed for ironmaking.⁶ Another research suggests drying the red mud, blending with lime and ground coal and feeding the mixture into a machine that agglomerates it into 1/2-in. diameter balls. Subsequently, the balls are pre-reduced at high temperatures in a circular grate. The balls are then fed into a submerged-arc electric furnace for smelting and transported to a basic oxygen furnace, where high-quality steel is produced. The final product yields about 98–99% Fe.⁷ Another process entails mixing the red mud with Fe₂(SO₄)₃. This solution removes the Na from the mud, leaving

behind material eligible for ironmaking.⁸ Simultaneous recovery of Al and Na is performed by mixing the red mud with a solution of caustic soda and lime at 300°C at pressures of 4–9MPa. This solution is supplemented into the Bayer process for increased alumina recovery.⁹ One approach utilizes the amphoteric characteristics of Al by extracting it via treatment with sulfuric acid. It also attempts to extract the Al through biological leaching using sewage sludge bacteria.¹⁰

Another process that emphasizes Ti recovery converts the red mud into sodium-aluminum fluoride compounds. The red mud is mixed with hydrochloric and hydrofluoric acid to obtain silicic acid, which is then separated out. Evaporation leaves behind a material close to cryolite. The remaining material is mixed with the residual liquor, which dissolves the Fe and Al. The Ti-rich solid remaining can be further processed via chlorination.¹¹ Synchronous recovery of Al, Fe and Ti is investigated by a number of researchers. One method utilizes chlorination combined with fractional distillation to extract Fe and Ti from red mud. The red mud can be leached prior to this to retrieve Al.¹² A novel technique is being investigated where the red mud is carbothermally reduced in an electric-arc furnace to produce pig iron and a fiberized wool material from slag.¹³

A review of all these past and current efforts highlight certain limitations that must be overcome before red mud can be converted into useful metals. These are:

1. Red mud is generated and currently stored where processing for alumina recovery from bauxite ore (Bayer's process) is done. Any

Table I. Composition of Dried North Coast Jamaican Bauxite and the Generated Red Mud

Compound	Bauxite (%)	Red Mud (%)
Al ₂ O ₃	56.4	14.7
SiO ₂	0.7	2.6
CaO	1.2	8.8
TiO ₂	4.3	7.2
Fe ₂ O ₃	35.1	60.7
Na ₂ O	0.0	1.6
Others (P, S, Cr, Mn, Hg, Pb, Zn, Cd, RE, Mg)	2.3	4.4

recovery process from red mud that would require the transport of red mud (fine material with 20–30% water) to far distances, e.g. ironmaking operations, will likely be cost prohibitive. Thus, any conversion scheme that is adopted needs to be located near the bauxite processing facility. Whether an electric arc furnace or a rotary hearth type of process is used, it must be collocated.

2. Solid-state carbothermic reduction of red mud to recover Fe and its separation from the remaining oxides via any physical means is difficult due to the mineralogy of red mud where fine iron oxide is intimately associated with other oxides and does not allow the separation of reduced Fe in a concentrated form. This is a major limitation which forces the carbothermic smelting of red mud. A solid Fe-rich product, such as direct reduced Fe, is unlikely. However, a solid product with reduced metallic Fe amenable to steelmaking remains a possibility.
3. Injection of red mud, with or without pre-reduction, into a blast furnace through the tuyeres, is an interesting concept. However, the high alumina content is a problem for the slag fluidity and volume in the blast furnace and the high alkali content is not compatible with the refractory and alkali accumulation. While lime, silica and titania additions from red mud are acceptable to the blast furnace, alumina and alkali oxides must be removed before any injection. This concept will also require transportation adding to commercialization challenges.
4. Removal of alumina via soda-ash roast and water leaching can produce a liquor that can be reverted back to the Bayer process, thus generating a residue that will be very low in alumina and alkali metals—a material now suitable for Fe production by any viable process. Alumina can be a recoverable commodity at this stage.
5. Once alumina and alkali metals are removed by soda-ash roast and Fe is reduced by carbon, the

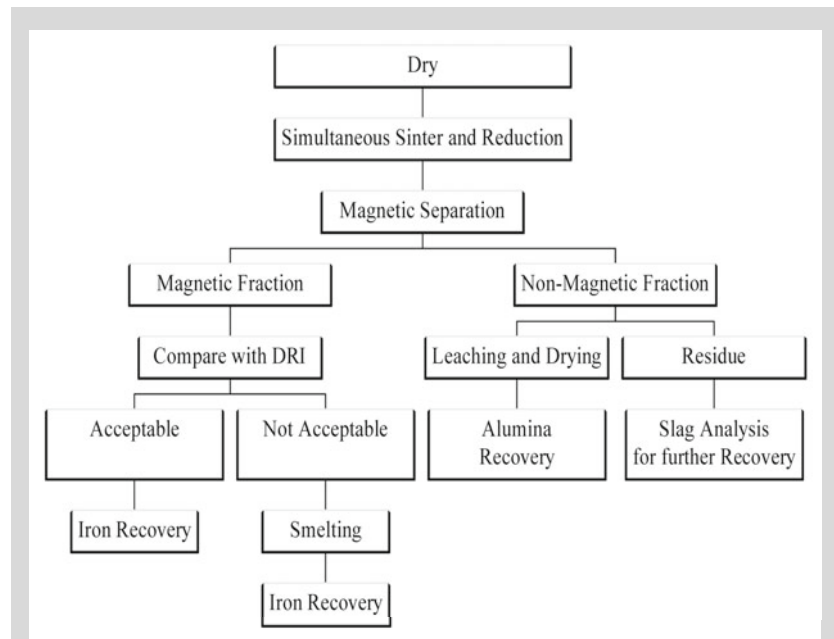


Figure 1. A potential flow sheet for full red mud utilization under investigation in CR³.

resulting material may be smelted to produce pig-iron and a slag now rich in calcium titanate. Titanium could be considered a product from this slag stream. However, the process suitable for Ti recovery is the Sulfation Method developed by the U.S. Bureau of Mines.¹⁴ The Kroll process is unsuitable due to the high lime content of the slag.

Based on these considerations, Figure 1 shows the flow sheet that CR³ is attempting to improve upon. There appear to be more valuable materials in red mud than the Fe and Al, such as Ti and rare earth elements. Preliminary analyses indicate the levels are relatively high. Further investigation is needed on four main parts of the previous research: a complete elemental, mineralogical and particle size analysis; solid state reductions for magnetic separation feasibility tests; smelting reduction feasibility work for metal slag separation; and slag analysis for further recovery of metals.

References

1. R. Boily, "Twenty Cases of Red Hazard, An Inventory of Ecological Problems Caused by Bauxite Residue from Alumina Production" (Laval, Quebec, Canada: Inforex, 2012), www.orbitealumine.com/media/upload/filings/Twenty_Cases_of_Red_Hazard_-_PublicVF.pdf.
2. "Aluminum," *U.S. Geological Survey, Mineral Commodity Summaries* (Washington, D.C.: USGS,

2012), minerals.usgs.gov/minerals/pubs/commodity/aluminum/mcs-2012-alumi.pdf.

3. A.K. Staley, "An Investigation into the Pyrometallurgical and Electrometallurgical Extraction of Iron from Red Mud Generated in the Processing of Bauxite Ores," Thesis No. T 5668 (Golden, CO: Colorado School of Mines, 2002).

4. D. Gura, "Toxic Red Sludge Spill from Hungarian Aluminum Plant—An Ecological Disaster" (October 5, 2010), www.npr.org/blogs/thetwo-way/2010/10/05/130351938/red-sludge-from-hungarian-aluminum-plant-spill-an-ecological-disaster.

5. J. Fursman, J.E. Mauser, M.O. Butler, and W.A. Stickney, "Utilization of Red Mud Residues From Alumina Production", *U.S. Bureau of Mines Report of Investigations 7454* (1970).

6. R. Piga, F. Pochetti, and L. Stoppa, *JOM*, 45 (11) (1993), pp. 55–59.

7. W. Braithwait, GB patent 2078211-A (January 1982).

8. Agency of Ind. Sci. Tech., J. patent 52152896-A (December 1977).

9. S. Guccione, *Eng. Min. J.*, 172 (9) (1971), pp. 136–138.

10. N. Dakatos, M. Miskei, and J. Szolnoki, DE patent 2,747,436 (May 1978).

11. M. Cresswell, and D.J. Milne, AU patent 88102 (September 1981).

12. R. Vachon, R. Tyagi; J.-C. Auclair, and K.J. Wilkinson, *Environ. Sci. Technol.*, 28 (1) (1994), pp. 26–30.

13. E. Balomenos, I. Gianopoulou, D. Panias, and I. Paspaliaris, "A Novel Red Mud Treatment Process" (Paper presented at the 3rd Intl. Conf. on Industrial & Hazardous Waste Management, Crete, Greece, 2012).

14. B. Mishra, A. Staley, and D. Kirkpatrick, *Recycling and Waste Treatment in Mineral and Metal Processing: Technical & Economic Aspects: Vol. 2*, ed. B. Björkman, C. Samuelsson, and J.-O. Wikström (Warrendale, PA: TMS, 2002), pp. 567–576.

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