Production of High Purity Alumina and Utilization of Red Mud

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ABSTRACT

In this paper, a novel hydrometallurgical process for the production of high purity alumina is discussed. The process involves comminution, leaching, highly selective solvent extraction steps and precipitation to produce high purity alumina for a niche market. Application of red mud as a refining agent for the steel industry is also discussed. Characterization of the potential fluxing agents was performed using a combination of XRD, XRF, DTA, and TGA. Experiments were carried out to examine the potential of hot metal desulphurization with fluxes made from these residue materials in comparison with those obtained from processing of bauxite. To facilitate this comparative behavior of fluxes derived from different source materials, particular attention was given to the enhancing effects of controlled amounts of sodium oxide in contrast to the deleterious effects associated with the presence of silica and titanium dioxide on the desulphurization process.

Keywords: aluminum industry, red mud, hot metal desulphurization, steelmaking, bauxite, high purity alumina,

1. PRODUCTION OF HIGH PURITY ALUMINA

Chloride metallurgy is emerging as an alternative process for the production of base metals [1-10]. Chloride chemistry is complex and quite different from corresponding sulfate systems. The solubility of metal chlorides is generally higher than their corresponding sulphate salts. The solubility of $CuSO_4.5H_2O$ is about one fifth that of $CuCl_2.2H_2O$, while nickel and ferrous chlorides are also more soluble than their sulphate counterparts. This allows the use of more concentrated solutions [11]. Also, the activity of water is <<1 in concentrated magnesium chloride salt solutions, and the activity of the hydrogen ion, H^+ (or H_3O^+) increases rapidly with chloride concentration as shown in Figure 1 [12]. This enhances the leachability of minerals in mixed chloride solutions resulting in increased base metals recovery.

Process Research ORTECH Inc. (PRO) has been at the forefront of technological development of chloride metallurgy and PRO's patented mixed chloride technology has been applied to the recovery of several products including titanium dioxide from ilmenite ores, REE from alumino-silicate ores, base metals and PGM from sulfide ores, gold from refractory ores and base metals from laterite ores [13-26]. The application of PRO's mixed chloride technology for the production of high purity alumina from bauxite is described below.

1.1 PRO high purity alumina process

The process flowsheet as shown in Figure 2 involves novel leaching and solvent extraction separation steps and is efficient and environmentally friendly. The salient features of this innovative process are as follows:

I. **Leaching:** Leaching is conducted in mixed chloride media to bring Fe and Al in solution.
II. **Solvent Extraction:** Innovative solvent extraction steps are carried out for successive extraction and stripping of Fe, acid (optional) and Al to obtain high purity concentrated preg strip solutions of Fe and Al separately.

III. **Precipitation:** High purity alumina is produced from high purity concentrated preg strip solution of aluminum by crystallization or precipitation.

IV. **Pyrohydrolysis:** Fe_2O_3 is produced and HCl is regenerated by the pyrohydrolysis of the iron chloride rich preg strip solution. Pyrohydrolysis is a commercially proven process and pyrohydrolysis units can be designed by commercial vendors based on the preg strip analysis and planned plant output. PRO has developed a novel hydrothermal hydrolysis process that can be used to regenerate the hydrochloric acid and produce high purity iron oxide from the preg strip solution containing iron chloride. PRO's hydrothermal hydrolysis process is more economical than pyrohydrolysis process as hydrothermal hydrolysis process runs at a much lower temperature.

V. **Recycling:** HCl generated by pyrohydrolysis is recycled to leaching stage.

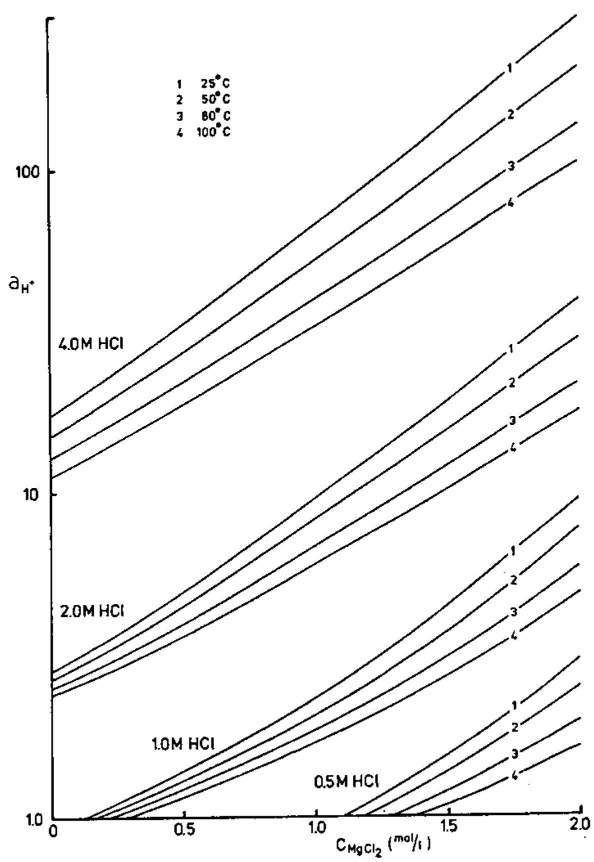

Figure 1: Effect of $MgCl_2$ Concentration on the Activity of H^+ in HCl Solutions [12]

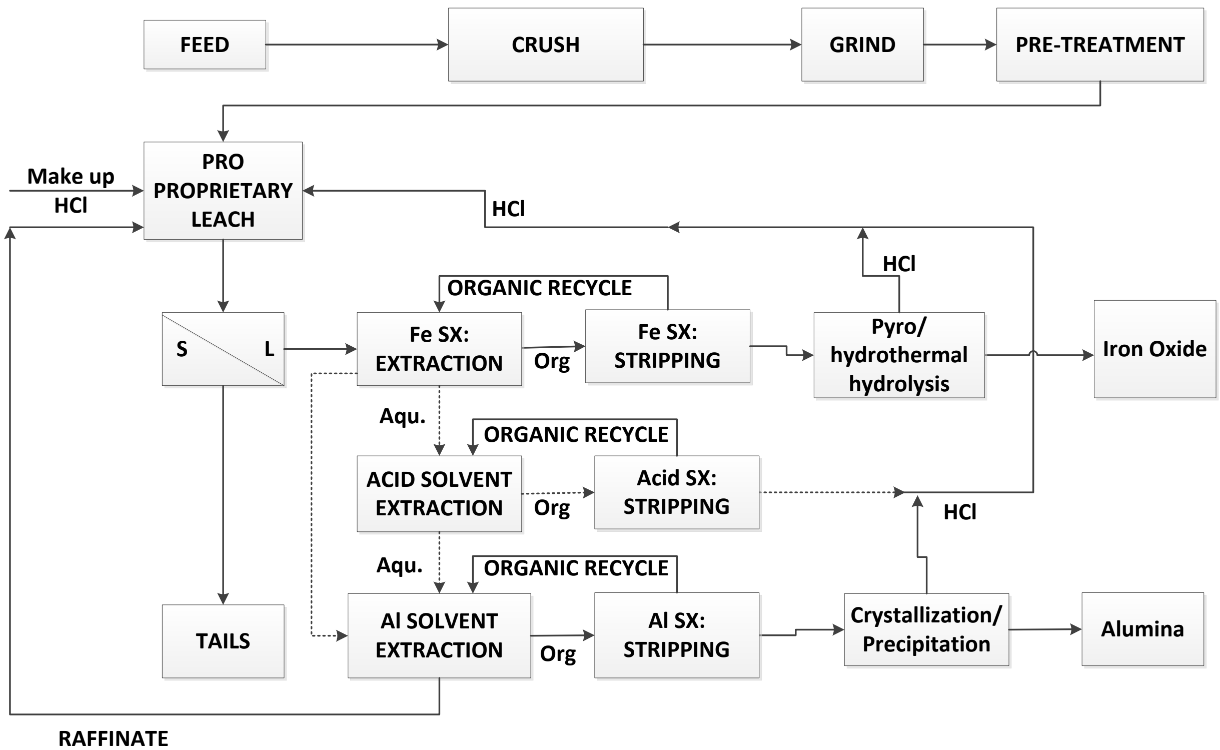

Figure 2: PRO process for production of high purity alumina

1.2 PRO Testwork

The composition of the ore used in the test work is shown in Table 1 on as-received basis as well as normalized basis after evaporation of moisture content.

Table 1: Ore composition

	Al_2O_3	Fe_2O_3	K_2O	MgO	Na_2O	P_2O_5	SiO_2	TiO_2	LOI	Total
	%	%	%	%	%	%	%	%	%	%
As received	21.97	0.49	0.20	0.06	0.20	0.03	64.59	0.43	10.4	98.4
Normalized	24.97	0.56	0.23	0.07	0.23	0.03	73.42	0.49		100

Leaching tests were conducted under the following conditions: Lixiviant: PRO's proprietary Mixed Chloride Lixiviant (a mixture of $HCl+MgCl_2$); Temperature: 80 degree C; Time: 5 hours; Pulp density: 10 wt. % solids. Pregnant leach solution (PLS) contained ~0.5 gpL Fe and ~15 gpL Al. After solvent extraction of iron, the raffinate contained less than 5 ppm Fe and ~15 gpL Al. The raffinate from iron solvent extraction underwent solvent extraction for aluminum. Overall recovery of Al was ~98%, while the overall recovery of Fe was ~ 78%. After precipitation of alumina from aluminum rich preg strip and calcination of alumina precipitate, high purity alumina having the purity of ~99.95% was produced. Further testwork is being conducted to improve the purity of alumina.

2. UTILIZATION OF RED MUD

In order to produce one tonne of liquid steel, about 100-150 kg of slag will be produced in addition to that produced during the ironmaking process. Using hot metal low in sulphur and phosphorus contents will significantly reduce the flux consumption and waste slag disposal from the steelmaking process. In ferrous metallurgy, finding a flux with high refining capacity and low cost is of great interest. Traditionally, CaO-CaF_2 based fluxes are used as desulphurizing agents for hot metal pretreatment. However, it has been found that fluorine compounds can destroy ozone molecules. Also if fluorine compounds enter the water system, this can pose a problem to human health by weakening of the bones, inducing stomach problems or even bone cancer. As a result, metallurgical industries are seeking an alternative flux.

During the production of aluminum and alumina, several different types of waste materials are generated as by-products including red mud, white mud, and dross from electrolysis and casting. The storage of these waste residues constitutes a major environmental concern due to the sheer volume and causticity of the materials. The composition of the waste residues varies and often depends on the starting raw material and subsequent processing route.

The iron and steel industry could potentially utilize these materials as fluxes in refining operations, since the associated flux consumption is significantly higher than that of other industries. Preliminary research has shown that these waste materials are viable candidates to be used as refining agents in iron and steelmaking processes, since they are able to produce similar results as fluxes currently used by the industry. The resulting slag is inert, and will be safe to dispose after use for refining operations. The application of residues from the aluminum industry as a basis for metallurgical fluxes in the steel industry would be beneficial from both economical and environmental perspectives.

1.1 Red mud

Red mud is an iron-rich residue formed as a result of the extraction of alumina from bauxite. As shown in Figure 1, about 2-3 tonnes of red mud material are generated for the production of every tonne of alumina. Because of the size of this waste stream and its causticity, red mud is a major environmental concern. In most cases, the red mud is stored on location close to aluminum production establishments and a considerable amount of land is required for this purpose [1]. Development of potential applications for this bauxite residue would reduce its impact on the environment and is therefore an important consideration with respect to the management of waste materials and contaminated sites.

Currently, most alumina is produced from bauxite by three methods: the Bayer process, the Lime-Sintering process and the Combined process [2]. The choice of exact processing route largely depends on the specific composition of bauxite ores. There are four main types of bauxite in nature: gibbsite bauxite, boehmite bauxite, diasporic bauxite and combined bauxite [3]. In general, the digestion process is easier for gibbsite bauxite in comparison to boehmite bauxite and diasporic bauxite. Another important aspect that influences the quality of bauxite is the weight ratio between alumina and silica, expressed as the A/S ratio. The Bayer process usually requires gibbsite bauxite or boehmite bauxite with an A/S ratio greater than 7. On the other hand, the Lime-Sintering process is employed to cope with diasporic bauxite where the A/S ratio is often less than 7. Examples of the chemical composition of different waste materials generated during alumina and aluminum production processes are summarized in Table 1 where RM and WM refer to red and white muds respectively.

3. PRODUCTION OF CALCIUM ALUMINATE REFINING FLUXES

The production of calcium aluminate fluxes can be classified based on the different sources of alumina: (1) from the by-products of alumina production, (2) from secondary dross of the high temperature dross treatment process, and (3) from bauxite.

3.1 From the by-products of alumina production

The iron oxide in red mud from the Bayer process can be recovered using smelting reduction, solid-state reduction or magnetic separation. In the smelting process, red mud is charged into the blast furnace or electric arc furnace with coke and lime or limestone. The iron oxide is reduced to generate pig iron that can be used in steel production, and the slag from the process can be used as refining flux or for construction materials after proper treatment. In the solid-state reduction process, the mud is mixed with a reducing agent or brought in contact with a reducing gas to produce metallic iron in a rotary kiln. The solid residue from this process can be used for making refining flux after adding a certain amount of lime and other additives. Magnetic separation is also an attractive option to recover iron from red mud. According to a study by Jamieson et al., [5] a wet high intensity magnetic separation (WHIMS) was employed to obtain a magnetic fraction containing around 56% Fe_2O_3 (mass percent) and a non-magnetic fraction of less than 4% Fe_2O_3 (mass percent). In China, Shandong Aluminum Company also used WHIMS to produce a concentrate containing 56%-76% Fe_2O_3 (mass percent). The recovery of Fe_2O_3 was 45%. Another method is to convert hematite or goethite in red mud to magnetite, followed by magnetic separation. Thus magnetic separation is becoming a more widely accepted approach for recovering iron from red mud, particularly in view of the increasing demand for iron ore throughout the world. Moreover, extracting iron from red mud also means lesser amounts of red mud will be stored in landfill. The residue after iron oxide recovery can be used to make calcium aluminate based flux by smelting or pelletizing with lime and other additives. Red mud from the Lime-Bayer process (RM3) or the Lime-Sintering process (RM2) contains higher lime and lower iron oxide contents. This material has a relatively low melting point and high basicity, which makes it suitable for hot metal pretreatment and steel refining. The iron oxide in the red mud can be controlled by addition of carbon and/or aluminum, or can be removed by calcination in a rotary kiln prior to its application. The compositions of RM2 and RM3 shown in Table 2, were calculated from Table 1 by removing the loss of ignition (LOI).

Table 2: Compositions of Calcium Aluminate Fluxes made from Different Sources (mass%)

	CaO	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2	Al_2O_3	SiO_2	Opt.B

B1	35.10	0.40	0	0.05	2.90	2.20	53.30	6.00	0.729
B2	33.80	0.70	0	0	2.30	2.60	52.40	7.20	0.725
D1	33.60	8.80	1.90	0	0.70	0.20	49.80	3.10	0.766
RM2	42.74	1.61	8.66	1.15	14.37	4.11	6.89	20.47	0.835
RM3	51.27	0.48	1.67	0.10	10.42	4.13	5.04	27.02	0.761
WM1	39.96	1.06	7.03	0.50	0.12	0.03	48.53	2.78	0.814
WM2	39.46	1.38	13.08	0.52	0.13	0.01	42.76	2.41	0.867
HN Flux	50.57	0	0.02	0	1.16	1.90	40.13	6.22	0.771

The white mud residues WM1 and WM2 from the Lime-Sintering process contain high lime, sodium oxide and low silica contents and therefore have a high basicity. They also have a relatively low melting point, and therefore should be an excellent base material for hot metal desulphurization.

4. CONCLUSION

An innovative process has been developed for the production of high purity alumina from a bauxite ore. This innovative process uses mixed chloride lixiviant ($HCl+MgCl_2$) to bring iron and aluminum in solution. The presence of $MgCl_2$ in the lixiviant makes the lixiviant very aggressive, which results in high recoveries of iron and aluminum. Additional advantage of using mixed chloride lixiviant is the opportunity to regenerate the hydrochloric acid by pyrohydrolysis, which can be recycled to leaching stage. Overall, the process flowsheet is efficient, environmentally friendly and economically attractive.

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