Carbothermic Reduction of Bauxite Residue for Iron Recovery and Subsequent Aluminium Recovery from Slag Leaching

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Abstract

Industrially and historically, alternative processes were developed to recover alumina from low-grade ores of non-bauxitic origin as well as for economic reasons. The Pedersen process from Norway was adapted towards high ferruginous and high silica containing bauxitic ores. This paper considers the adaptation of the Pedersen pyro-hydrometallurgical route of reductive smelting with lime and coke to recover iron and aluminium from bauxite residue (BR), which is the by-product of the Bayer process where aluminium is typically lost in complex desilication product matrices. Greek BR was firstly smelted in an Electric Arc Furnace (EAF) to recover pig iron (>95 %). The fluxing strategy entailed feeding lime to favour lower operating temperatures (1500–1550 °C) and slag viscosities, and to produce a slag containing calcium aluminate phases ($12CaO \cdot 7Al_2O_3$, $3CaO \cdot Al_2O_3$ and $CaO.Al_2O_3$). The calcium aluminates were identified as thermodynamically favourable in descending order to form $NaAlO_2$ when leached in Na_2CO_3 solution (ΔG_{rxn}^{298K} = -782, -188 and -68 kJ/mol, respectively). Leaching temperature, Na_2CO_3 concentrations, residence time and different particle sizes were varied to investigate the leachability of slags for aluminium recovery; up to 43 % aluminium was recovered with 95 % of silicon content remaining in leached residue. SEM studies also aided understanding of interstitial leaching mechanism.

Keywords: Bauxite residue, electric arc furnace, pig iron recovery, calcium aluminate, aluminium recovery.

1.   Introduction

The recovery of aluminium became a favourable production option largely because of the discovery of bauxitic ore that contained high aluminium-bearing components such as gibbsite (γ-Al(OH)$_3$), boehmite (γ-AlO(OH)) and diaspore (α-AlO(OH)). Hydrometallurgical Bayer processing has invariably outcompeted pyrometallurgical routes because of its economic viability in extracting alumina from high and several medium grade ores. However, the scarcity of bauxitic ores during and right after World War II became a crux of research initiatives that was driven to investigate alternative viable methods of production using lower-grade ores [1, 2]. One such method was the practice of a pyrometallurgical-based Pedersen process in Norway. The original Pedersen process focused on the smelting of bauxite, iron ore, lime and coke to recover low-silica calcium aluminate slag and metallic iron, followed with leaching of slag with sodium carbonate solution to achieve the formation and dissolution of sodium aluminate [2].

The plant in Høyanger, Norway (1928-1969) had an annual production of around 17,000 metric tons [3]. Hignett et al [2] reiterated the process in 1942 using clay as a raw aluminium source instead, in both laboratory scale and pilot plant level. The process was also adapted by Blake et al [3] during 1966 towards high-silica and titania bauxites of Pacific Northwest (U.S.A). Fly ashes were also proposed to be adapted towards the lime-sinter process [4]. In the past literature, it is important to note that lime-sinter process and smelting process are often used interchangeably as the formation of desirable calcium aluminates operate close to its eutectic point.

Miller and Irgens [1] sourced the bauxite from Greece, containing a high percentage of boehmite (58.5 wt% Al_2O_3). After the addition of limestone and coke, the molten slag was smelted continuously at 1500 °C, where it was tapped every 6 hours for pig iron and calcium aluminate slag. The slag was then cooled for four hours before crushing and leaching. 5 metric tons of slag added to 200 m^3 of lye (15 gpl total alkaline). The first leaching step was completed after 5 ½ hours at 40 °C until the lye reaches 13-14 gpl Al_2O. The mixture was then emptied into a clarifier, where underflow was treated in the second leaching step. Saturated liquor was next sent to the precipitation section.

Using clay and limestone as the raw materials, Hignett et al [2] achieved about 90 to 95 % of "soluble" alumina content from total alumina in slag (operational temperature range: 1360-1400 °C). Laboratory-scale results showed maximum extractions was achieved in the temperature range of 45 °C to 65 °C, residence time of 15 to 30 min, and > 1.6 moles Na_2CO_3 per mole of alumina (20 g sinters/200 mL of 3 % sodium carbonate). Higher silica (Si) content of the raw material was found to influence co-leaching of Si element into leachate.

The use of ferruginous bauxites by Blake et al [3] was divided into two samples in the research investigation, high silica and low silica bauxites (13.5 and 4.5 wt% SiO_2 respectively). Extra lime was added in the system to promote the formation of perovskite ($CaTiO_3$). Samples were then smelted at 1750 °C and the slag was left to cool slowly in the furnace overnight. Both sample types were tested in a range of leaching time and temperatures while keeping Na_2CO_3 concentration and solid-to-liquid ratio constant (15 g slag/ 250 mL liquor at 11 gpl Na_2CO_3 concentration). Alumina from high silica slag was best leached for 16 hours at 25 °C (70 % Al_2O_3 extraction), whereas low silica slag achieved maximum leachability (88 % Al_2O_3 extraction) at the same temperature in 8-10 hours.

Bauxite residue contains typically 13-25 % of alumina content from Bayer processing. Silica is a very important impurity that affects alumina product quality and causes chemical soda losses due to the formation of desilication products (DSP) such as Bayer cancrinites and hydrogrossular phases [5]. DSP also builds up in scales in evaporators, retarding the heat transfer. Currently, bauxite residue estimates are ever increasing with 150 million tonnes produced per annum globally [6]. Current research initiatives are focused on exploring bauxite residue as a part of a zero-waste approach. Being the host of leftover products and complex matrices, enriched bauxite residue contains a considerable amount of value in the form of titanium containing compounds and rare earths.

The main incentive for smelting bauxite residue is to recover iron, however, iron recovery on its own is not sufficient to justify the smelting of bauxite residue since bauxite residue is an inferior source of iron compared to primary iron ores. Current researches on bauxite residue smelting is experiencing a shift towards complete valorisation of bauxite residue, such as Balomenos et al [7] that conducted semi-industrial scale tests on the recovery of pig iron and viscous slag using an Electric Arc Furnace operating at 1540 °C. The slag was subsequently transformed into mineral wool. Borra et al [8] recovered pig iron at 1500-1600 °C, with the aim to enrich leftover slag for acid leaching of rare earths downstream. In another work, Borra et al [9] also removed

Raman data indicate that calcite was deposited on the surface of the slag. SEM elemental mapping also indicates Na was found in higher levels at the surface of the slag. Again, in the Figure 4 (e) previously, it was noted that finer particle sizes of below 90 μm show slight improvement in Al recovery compared to particle sizes of 90 μm to 125 μm. All observations indicate that the leaching of the slag is surface driven. An insoluble layer of calcite build-up inhibits the dissolution of alumina from calcium aluminates in the core particle. We can also hypothesise that because of mayenite leaching that is surface driven on the slag particle, complete leaching of Al species is diffusion dependent that may require higher residence time in Na_2CO_3 solution at low temperatures.

4. Conclusion

The combined recovery of iron and aluminium from bauxite residue through the adaptation of the Pedersen process has been demonstrated successfully for the former and to be focus on improvements on the latter. The smelting of bauxite residue was undertaken at 1500 °C using lignite coke as reductant under lime fluxing, achieving high iron recoveries. The combination of highly reducing conditions during smelting and high CaO slag (54 wt% CaO) favoured desulfurization of the pig iron product. Furthermore, low sodium content was reported in the slag. The aluminium was mainly found in the mayenite and tricalcium aluminate minerals in the slag. It is recommended that the presence of these species is best confirmed through a combination effort of XRD, SEM Quantitative analysis and Raman spectroscopy.

Low aluminium recoveries were achieved for the slag leaching testwork. This is in contradiction with reported Al recoveries for calcium aluminate slags, as these slags are reported to be readily leachable under low temperature Na_2CO_3 leaching. Leaching of calcium aluminates are best done at low temperatures of below 40 °C as they are exothermic in nature. In terms of Na_2CO_3 concentration of low temperature leaching, the preferred concentrations lean towards 150 gpl Na_2CO_3 and below as higher concentration has the tendency to draw out silica into leachate. The cooling rate of slag influences the crystallization path and the formation of leachable calcium aluminate minerals and should be investigated in the future work. Leaching of calcium aluminate slag is surface driven and once again, the correct leachable crystallinity of mayenite mineral phase formation during cooling of smelting process is crucial to allow better aluminium recoveries.

5. Acknowledgement

6. References

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