Experimental Study on Hydrogen Reduction of Bauxite Residue Pellets Using H_2-H_2O Mixtures

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Abstract

The valorization of bauxite residue through hydrogen reduction followed by magnetic separation of iron and alkaline leaching of non-magnetic part for alumina recovery is a sustainable approach. In this research an experimental study was designed to investigate the effect of temperature and H_2-H_2O gas compositions on the reduction behaviour of iron oxides complex in Bauxite Residue (BR). Green pellets were made from a mixture of bauxite residue and $Ca(OH)_2$ powders, which were subsequently sintered at 1150 °C. The sintered oxide pellets were reduced in a vertical furnace using H_2-H_2O gas mixtures at elevated temperatures using gas compositions ranging from 0-25% H_2O. Total flow of the H_2-H_2O gas mixture was kept at 1 L/min to ensure comparative reduction potentials. X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) coupled with energy dispersive spectroscopy (EDS) were employed to characterize the reduced pellets. It was found that the iron oxides exist as complex Brownmillerite phase in the sintered pellets. Lower temperature and higher H_2O content of gas could inhibit reduction of Wüstite to metallic iron. Such behaviour was observed when H_2O gas composition is higher than specific compositions at different temperatures. Pellets reduced at higher temperatures were found to produce significantly smaller pore size but with comparable surface area to pellets reduced at lower temperatures which suggests notably different pore structures.

Keywords: Decarbonisation, Circular economy, Bauxite residue, Hydrogen reduction, Iron.

1. Introduction

1.1 Bayer Process and Bauxite Residue

The Bayer process was invented and patented by Carl Josef Bayer in 1888 and has since then been the leading process for alumina production in the world. The process consists of eight main stages: Milling, desilication, digestion, clarification, precipitation, evaporation, classification, and calcination. In the milling step, the bauxite ore is crushed down into finer particles. Additionally, limestone is added to create a pumpable slurry. After the milling step, the slurry moves through a process called desilication, which involves removing silica (SiO_2). The slurry is then digested using a NaOH solution, which dissolves the aluminum bearing minerals in the bauxite. These minerals include gibbsite ($Al(OH)_3$, boehmite (γ-$AlO(OH)$) and diaspore (α-$AlO(OH)$). When the solution is added, the following reactions takes place with gibbsite and boehmite/diaspore, given by Equation (1) and Equation (2) respectively [1][2].

$$Al(OH)_{3(s)} + NaOH_{(aq)} \rightarrow Al(OH)^{-}_{4(aq)} + Na^{+}_{(aq)} \tag{1}$$

$$AlO(OH)_{(s)} + NaOH_{(aq)} + H_2O_{(l)} \rightarrow Al(OH)^{-}_{4(aq)} + Na^{+}_{(aq)} \tag{2}$$

After the processing step, the slurry is cooled down using a series of flash tanks at 1 atm. The slurry is then prepared for clarification where the bauxite residue (BR) is separated away through sedimentation, where chemical additives assist in driving the BR to the bottom of the settling tanks. BR is transferred to washing tanks, where the goal is to recover the caustic soda used in the digestion step. The saturated liquid undergoes a series of filtration steps and BR is left in disposal areas. After clarification, alumina is recovered through crystallization during precipitation step. The precipitation reaction is shown in Equation (3) [1][2].

$$Al(OH)^{-}_{4(aq)} + Na^{+}_{(aq)} \rightarrow Al(OH)_{3(s)} + NaOH_{(aq)} \tag{3}$$

Evaporation of the liquid used during crystallization takes place in heat exchangers, where it is subsequently cooled down afterwards in flash tanks. The condensate that is created through this process is re-used for BR washing or as feed water. Recovered caustic soda is then re-added to the digestion step. The crystals are classified into size ranges, using cyclones and gravity classification tanks. For the coarse crystals, separation from liquid and calcination is performed. For the finer crystals, washing to remove organic impurities and re-addition to the precipitation step is performed. Calcination of the coarse crystals is done by roasting in calciners. The roasting process takes place at temperatures up to 1100 °C. This drives off moisture and water, which eventually creates alumina solids. The calcination reaction is shown in Equation (4) [1][2].

$$2Al(OH)_{3(s)} \rightarrow Al_2O_{3(s)} + 3H_2O_{(g)} \tag{4}$$

1.2 Bauxite Residue Valorization

Red mud, also known as bauxite residue (BR) in dewatered form, is the main by-product generated in the Bayer process. Typically, for each tonne of produced alumina from bauxite ore, about 1.5 tonnes of BR is produced [3]. The generated BR from the Bayer process is stored in large holding ponds, where only 1% to 2% is being recycled [4]. BR typically contains up to 50% of iron oxides. Other compounds found in BR includes silica oxides, titanium oxides, aluminum oxides and other oxides. It is also highly alkaline, with a pH level ranging from 12-13. Due to its high alkalinity, the BR that is stored away in holding ponds poses a great environmental threat to its surroundings. The main way of treating the alkaline BR, is to attempt neutralizing by adding acidic substances, such as HCl [4].

Several studies on BR valorization have been conducted within the past decade which mainly try to recover iron content in BR either in the form of magnetite [5], metallic iron [6] [7][8][9], or clinker [10]. BR reduction with H_2 at low temperature (480 °C) was able to produce magnetite with 87% conversion degree with insignificant metallic iron production [5]. Meanwhile BR reduction with H_2 at high temperature (1000 °C) was able to completely reduce Fe content in BR to metallic Fe [6][7]. However, recovery of Fe-containing phases from solid-state reduced BR remains an issue due to its physical nature which exists in miniscule spots with less than 20 µm in particle diameter [6][7].

Carbothermic reduction of BR beyond Fe melting point (>1538 °C) was able to reliably produce pig iron in its own separated phase [8][9]. The remaining issue was recovery of Al content from its slag where almost half of it was trapped in Gehlenite ($Al_2Ca_2O_7Si$) phase which is difficult to recover via hydrometallurgical means [8]. It is preferred for Al content in slag phase to form highly leachable Mayenite ($Al_{14}Ca_{12}O_{33}$) phase. CaO addition has shown to promote formation of Mayenite phase in reduced BR [8][9]. Another potential valorization of BR is in production of calciumsulfoaluminate-ferrite clinker for specific applications such as adhesive binder [10].

4. Conclusions

- Equilibrium condition for H_2 reduction of metallic Fe at 600 °C was observed at $H_2/H_2O \approx 19$ meanwhile at 800 °C it was observed at $H_2/H_2O \leq 5.7$.
- Iron oxides were the only oxides reduced during the reduction process in the experiments, all the other metal oxides were not reduced as confirmed by XRD analyses.
- Iron in sintered BR pellets exists largely as calcium ferrite in form of a Brownmillerite complex as confirmed by XRD and equilibrium calculation using thermodynamical software and database.
- Obtained experimental results are in accordance with calculated equilibrium conditions.
- More experiments with smaller steps of H_2/H_2O ratio need to be done to obtain more accurate figures on actual equilibrium condition.
- Sintering mechanism plays a major role in pore development during reduction process, higher reduction temperature causes more sintering and porosity loss.

5. References

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