Behaviour of Silica during Metal Recovery from Bauxite Residue by Acidic Leaching

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Abstract

Bauxite residue represents an interesting source for not only major elements such as aluminium, iron and titanium, but also for rare earths (REEs), while the residue after metal recovery can be used for low-carbon building materials and cementitious binders. Several methods based on direct acidic leaching for recovering metals from bauxite residue have been reported. The co-dissolution of iron represents a significant drawback for REEs recovery upon silica polymerization. The behaviour of silica has been studied during acidic leaching with concentrated mineral acid (H_2SO_4). The extraction of aluminium, iron and titanium is limited due to an insufficient amount of acidic solution for leaching caused by the polymerization of silica. Kinetic studies have demonstrated that at constant temperatures, silica dissolution increases with increasing acid concentration, but it decreases when the temperature is increased and the acid concentration is reduced. This is due to an enhancement in the solubility of monomeric silicic acid formed during acidic leaching. The control mechanisms of silica dissolution have been described according to the shrinking core model by a chemical reaction stage, i.e. silica polymerization, followed by a diffusion stage, because of the silica gel adsorbed on the surface of the particles that limits the metal extraction.

Key words: Dry digestion; silica; silicate; bauxite residue; red mud; rare earths.

1   Introduction

Bauxite residue (BR, also called red mud) represents an interesting source for major elements such as aluminium, iron and titanium, but also for rare-earth elements (REEs) [1]. Several methods based on direct leaching by acids have been reported for recovering valuable metals from bauxite residue [2–5]. The extraction efficiencies depend on the acid concentration with more extraction achieved at higher acid concentrations. Sulfuric acid leaching is considered to be the most versatile approach. However, higher acid concentrations also lower the silica solubility, which leads to a greater silicon supersaturation index (SSI). The SSI represents the ratio of dissolved silica with respect to the maximum silica solubility [6]. The increase of SSI is considered as the driving force for silica polymerization, also known as silica gel formation [7,8]. The formation mechanism of silica gel precipitation has been described in detail elsewhere [8–11].

Silica gel precipitation represents a serious drawback in the recovery of metals from ores and process residues by hydrometallurgical methods because the gel containing solutions can no

longer be filtered [12–14]. Additionally, this gelatinous precipitate may blind ore particles and reduce the leaching kinetics significantly.

Among others, quartz, sodalite and cancrinite are the most abundant silica bearing minerals in bauxite residue. Under standard conditions (1 atm, 25 °C), the solubility of quartz is about 6 mg L^{-1} whereas amorphous silica reaches a solubility of 100-120 mg L^{-1} under the same conditions. From this point of view, the contribution of soluble silica by quartz is negligible. The objective of this paper is to study the behavior of amorphous silica during leaching of bauxite residue with diluted H_2SO_4. Kinetic studies are performed at different concentrations and temperatures.

2   Material and Methods

The bauxite residue studied in this paper was kindly provided by Aluminium of Greece (Agios Nikolaos, Greece). It originates from a mixture of karst and lateritic bauxites. It was received from the alumina refinery after dewatering by filter pressing and drying at room temperature. Upon arrival in the lab, the sample was further dried at 105 ºC for 24 h. Chemical analysis of the major elements in bauxite residue was performed by wavelength dispersive X-ray fluorescence spectroscopy (WDXRF, Panalytical PW2400). The mineralogy of the samples was studied by X-ray powder diffraction (XRD, Bruker D2 Phaser). The obtained data were evaluated with EVA V.3.1 (Bruker AXS) and quantified with Topas-Academic V.5, using the Rietveld method.

Kinetics experiments were performed in a 150 mL glass reactor with H_2SO_4 (95-97 vol%, Sigma-Aldrich) solution of a fixed concentration (0.5 and 1.5 N). The experimental set-up consists of a hot-plate magnetic-stirrer device, a pH-electrode (Hamilton, VWR) and a thermocouple (Pt100, VWR). Within the reactor solid particles were mixed with 100 mL of the corresponding solution at a liquid-to-solid ratio (*L/S*) of 5:1. The entire experiment lasted for 60 min, in which aliquots of slurry were extracted from the glass reactor at specific time intervals. The mixtures were continuously agitated during the whole experiment in order to ensure a homogenous suspension. Each aliquot was filtered using a syringe and a 0.45 µm filter (CHROMAFIL PET-45/25 Polyester), and diluted with 2 vol% HNO_3 for Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, PerkinElmer Optima 8300) analysis for aluminium, iron, titanium and silicon. The experiments were conducted at different temperatures (25, 40, 60 and 80 °C). At the end of each experiment, the remaining reactor content was filtrated through a Buchner filter (VWR® Grade 413 Filter Paper, Qualitative, 5 µm retention), and the solid filter cake was dried (24 h, 105 °C) and stored for further XRD analysis.

3   Results and Discussion

3.1.   Characterization of the Bauxite Residue

The chemical analysis of the major elements present in bauxite residue is shown in Table 1. Bauxite residue is rich in iron oxide and alumina. Mineralogical analysis allowed the identification of several mineral phases (Table 2), rich in iron (hematite, goethite), aluminium (gibbsite, diaspore, bayerite), calcium (calcite, calcium silicates and calcium aluminosilicates), sodium (sodalite, cancrinite) and titanium (rutile).

The dissolution of silica from bauxite residue during acidic leaching is a very complex process controlled by a chemical reaction stage, i.e. silica gel formation as consequence of hydrolysis of silica, and a diffusion stage caused by the partial adsorption of this silica gel layer on the surface of the particles. However, the shrinking core model demonstrated limitations regarding the reproducibility of experimental data, because it does not consider aggregation of silica monomers formed during acidic leaching of bauxite residue.

5   Acknowledgements

6   References

1.   Koen Binnemans et al., Towards zero-waste valorisation of rare-earth-containing industrial process residues: a critical review, *Journal of Cleaner Production*, Vol. 99, (2015), 17–38.
2.   Chenna Rao Borra et al., Recovery of rare earths and other valuable metals from bauxite residue (red mud): a review, *J. Sustain. Metall*, Vol. 2, No. 4, (2016), 365–386.
3.   Na Zhang, Hong-Xu Li, and Xiao-Ming Liu, Recovery of scandium from bauxite residue—red mud: a review, *Rare Metals*, Vol. 35, No. 12, (2016), 887–900.
4.   Weiwei Wang, Yoko Pranolo, and Chu Yong Cheng, Metallurgical processes for scandium recovery from various resources: A review, *Hydrometallurgy*, Vol. 108, No. 1–2, (2011), 100–108.
5.   Zhaobo Liu and Hongxu Li, Metallurgical process for valuable elements recovery from red mud—A review, *Hydrometallurgy*, Vol. 155, (2015), 29–43.
6.   P. Kokhanenko, K. Brown, and M. Jermy, Silica aquasols of incipient instability: Synthesis, growth kinetics and long term stability, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, Vol. 493, (2016), 18–31.
7.   Dominique J. Tobler, Sam Shaw, and Liane G. Benning, Quantification of initial steps of nucleation and growth of silica nanoparticles: An in-situ SAXS and DLS study, *Geochimica et Cosmochimica Acta*, Vol. 73, No. 18, (2009), 5377–5393.
8.   Aly A. Hamouda and Hossien A. Akhlaghi Amiri, Factors affecting alkaline sodium silicate gelation for in-depth reservoir profile modification, *Energies*, Vol. 7, No. 2, (2014), 568–590.
9.   Jan Schlomach and Matthias Kind, Investigations on the semi-batch precipitation of silica, *Journal of Colloid and Interface Science*, Vol. 277, No. 2, (2004), 316–326.
10.   Sebastian Wilhelm and Matthias Kind, Influence of pH, temperature and sample size on natural and enforced syneresis of precipitated silica, *Polymers*, Vol. 7, No. 12, (2015), 2504–2521.
11.   D. Voßenkaul et al., Hydrometallurgical processing of eudialyte bearing concentrates to recover rare earth elements via low-temperature dry digestion to prevent the silica gel formation, *Journal of Sustainable Metallurgy*, Vol. 3, No. 1, (2017), 79–89.
12.   Yadong Zhang et al., Recovery of zinc from a low-grade zinc oxide ore with high silicon by sulfuric acid curing and water leaching, *Hydrometallurgy*, Vol. 166, (2016), 16–21.
13.   E. Abkhoshk et al., Review of the hydrometallurgical processing of non-sulfide zinc ores, *Hydrometallurgy*, Vol. 149, (2014), 153–167.
14.   Lina Shi et al., Desilication of low alumina to caustic liquor seeded with sodalite or cancrinite, *Hydrometallurgy*, Vol. 170, (2017), 5-15.
15.   T.W. Zerda, I. Artaki, and J. Jonas, Study of polymerization processes in acid and base

catalyzed silica sol-gels, *Journal of Non-Crystalline Solids*, Vol. 81, No. 3, (1986), 365–379.

16. Mary W. Colby, A. Osaka, and J.D. Mackenzie, Effects of Temperature on Formation of Silica Gel, *Journal of Non-Crystalline Solids*, Vol. 82, (1986), 37–41.

17. C.A. Milea, C. Bogatu, and A. Duta, The Influence of Parameters in Silica Sol-Gel Process, *Bulletin of Transilvania University of Brasov: Engineering Sciences*, Vol. 4, No. 1, (2011), 59–66.

18. Elizabeth A. Gorrepati et al., Silica precipitation in acidic solutions: Mechanism, pH effect, and salt effect, *Langmuir*, Vol. 26, No. 13, (2010), 10467–10474.

19. Fuqiang Zheng et al., Kinetics of Hydrochloric Acid Leaching of Titanium from Titanium-Bearing Electric Furnace Slag, *JOM*, Vol. 68, No. 5, (2016), 1476–1484.

20. Fathi Habashi, Principles of Extractive Metallurgy, General Principles, 2nd ed. (New York: Gordon and Breach Science Publishers, Inc.), 1969, pp. 111–169.

21. Hong Y. Sohn, Milton E. Wadsworth, Rate Processes of Extractive Metallurgy (New York: Plenum Press), 1979, pp. 135– 143.