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Selectively recovering scandium from high alkali Bayer red mud without impurities of iron, titanium and gallium

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Abstract: Experimental results here can give some new insights into the mechanism of selective recovery of scandium and sodium from high alkali Bayer red mud (RM) through sulfation-roasting-leaching process. Effects of roasting and leaching conditions including roasting time, roasting temperature, concentrated H_2SO_4 addition, leaching temperature, leaching time and liquid to RM solid ratio on the leaching rates of calcium, iron, aluminum, silicon, sodium, titanium, scandium and gallium were studied and analyzed, suggesting that roasting temperature and roasting time were the two primary constraints on selective recovery of Sc and Na. High leaching temperature also brought a negative effect on the iron leaching rate. Phase transitions and thermal behaviors of sulfated RM indicated that sodium had an inhibitory action on the liberation of SO_2 or SO_3 from metal sulfates, which should follow the decomposition order of $TiOSO_4 > Ga_2(SO_4)_3 > Fe_2(SO_4)_3 > NaFe(SO_4)_2 > NaAl(SO_4)_2 \sim Al_2(SO_4)_3 > Na_3Sc(SO_4)_3 > Na_2SO_4 > CaSO_4$. After water leaching, solid-liquid separation could be carried out extremely smoothly and >95 wt.% Na^+, ~60 wt.% Sc in $[Sc(H_2O)_x(SO_4)_n]^{3-2n}$ ($x \le 6$) with impurities of 0 wt.% Fe^{3+}, 0 wt.% Ti^{4+}, 0 wt.% Ga^{3+}, 7 wt.% Al^{3+}, ~29 wt.% Ca^{2+} and ~3 wt.% Si^{4+} could be leached into leachant under the optimized roasting and leaching conditions. The alkali-free residue obtained could then be employed as iron-making or building materials.

Keywords: $Na_3Sc(SO_4)_3$; scandium; selective; $NaFe(SO_4)_2$; titanium; gallium; rare earths

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Bauxite residue, commonly referred to as Bayer red mud (RM), is typically a kind of by-product of alumina production during the Bayer process and rich in some valuable elements in trace amount like scandium[1]. Its global yield in 2015 was 108.7~163.1 million tons estimated by the annual production of metallurgical grade alumina[1–3]. Poor handling of Bayer RM, such as stockpile, will not only occupy a vast tract of land but also result in the environmental pollution[4,5]. It is difficult to discharge this extremely fine solid waste with an average particle size <10 μm owing to its large amount and salt (Na) toxicity, as well as corrosivity with pH 10–12.5[6–8]. The high concentration of sodium, on the one side, could limit its application in using as iron-making material due to the circulation and lining erosion of low melting point alkali metals in the blast furnace, and also as construction materials thanks to the alkali-aggregate reaction that occurred in the concrete which weakens the intensity of building materials[3,9]. On the other side, considering the price of scandium ingot with purity of 99.9% as high as 134 $/g in 2015 and supply scarcity worldwide, the recovery of scandium from RM is of particular interest[10,11].

The effective methods for the removal of sodium include acid leaching, lime-hydrothermal treatment and lime-soda sintering accompanied with water leaching, etc.[12–14]. In case of scandium recovery from RM, the most widely researched and applied method is the direct acid leaching[11,15–18]. Despite the perfect leaching performance of Na and Sc, the "blindness" of leaching results is common for all the methods mentioned above. The subsequent process such as solvent extraction, back stripping and ion-exchange of Sc could be strongly affected by the co-leaching of impurities like iron[19]. Besides the effect of similar ionic radii between Fe^{3+} 64.5 pm (high spin) and Sc^{3+} 74.5 pm on the separation[15,19,20], the ferric ions are more likely to hydrolyze and form ferric hydroxide sol $Fe(OH)_3$ co-precipitating with other metal ions as compared with Na^+ or Al^{3+} [21].

Valuable elements could be easily leached out from RM nevertheless, is there an alternative to acid leaching for the selective and efficient recovery of scandium? Few literature data regarding leaching scandium or other valuable elements selectively are available[22–25]. Fulford et al. suggested that sulfur dioxide could be employed to selectively recover lanthanides, scandium and yttrium from RM by adjusting the pH among 1.8–3.2[23]. Recently, Davris et al. succeeded in using hydrophobic ionic liquid HbetTf2N for selective leaching of rare earth elements

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(≤45 wt.% Sc) against Fe, Ti and Si from RM[24]. Besides, selective recovery of rare earths by sulfation-roasting-leaching of low alkali RM was investigated by Borra et al.[22]. Leachate with ~60 wt.% scandium, >80% wt.% other rare earth elements and few of iron content (<1 wt.%), could be obtained by roasting the mixture of RM, concentrated H_2SO_4 and deionized water with mass ratio of 1:1:0.2~1 at 675 ºC for 2 h and subsequent water leaching at ambient temperature for 2 d with agitation or 7 d without. However, their results were only taken for the red mud containing small amounts of sodium, without considering the effects of a high content of sodium on the sulfation of red mud and decomposition of metal sulfates, and also the effects of leaching temperature on the leaching performance of objective elements. In the present study, we found that $NaFe(SO_4)_2$ and $NaAl(SO_4)_2$ are the primary metal sulfates during the roasting process, which is completely different from their results.

As for the sulfation-roasting-leaching process, Inner Mongolia Baotou Steel Rare Earth Hi-tech Co., China launched the first commercial application on extraction of rare earth elements except Sc from Baotou rare earth concentrates and bastnasite in July 1988[26,27]. Performing this process on iron rich lateritic ores, nickel and cobalt could be extracted selectively[28,29]. Moreover, this method can be extended to other fields, for instance, recycling of NdFeB magnets and extracting alumina from coal fly ash[30,31]. But so far articles regarding selectively recovering scandium and sodium from high alkali red mud by sulfation-roasting-leaching methods have not been reported.

The purpose of present work was to investigate the leaching performance of various elements consisting of Sc, Na, Ga, Al, Fe, Ti, Ca and Si from high alkali red mud by sulfation-roasting-leaching process. The effects of roasting conditions including roasting temperature and time leaching conditions including leaching temperature, time and liquid to solid ratio as well as the addition of concentrated H_2SO_4 on the leaching performance were studied. Besides, the variation of leaching results and the mechanism of sulfation and roasting process based on the results of TG-DSC, XRD and SEM were also analyzed.

1 Experimental

1.1 Raw material

The Bayer RM used in the present work was provided by a subsidiary company of Chalco in Shandong province of China. X-ray fluorescence (XRF-1800, RIGAKU, Japan) was employed to determine the major chemical composition of dried RM. The minor components of scandium and gallium were determined by an inductively coupled plasma-optical emission spectrometer (ICP-OES, Optima 7000DV, PerkinElmer, USA). Prior to the ICP test, RM needed to be digested with HCl-HNO_3-HF-$HClO_4$ in a fluoropolymer beaker based on ASTM Standard E2941-14[32].

1.2 Methods

Thermal behaviors of RM and sulfated sample were carried out by thermogravimetric analysis-differential scanning calorimetry (TG-DSC, STA409C, Netzch, Germany) in argon atmosphere from room temperature to 1000 ºC at the heating rate of 10 ºC/min. Mineral phases of RM were conducted by powder X-ray diffraction (XRD, SmartLab, Rigaku, Japan) with a 2θ scan range of 10º–100º at 45 kV and 200 mA with Cu Kα radiation, a step size of 0.02º and a count time of 1 s. According to the Rietveld refinement method, quantitative X-ray diffraction (QXRD) technique was achieved by general structure analysis system (GSAS) software[33], adding CaF_2 (analytical reagent) to RM as the internal standard material[34]. Whereas the phases of other samples were investigated by a continuous mode with a 2θ scan range of 5º–90º and a speed of 10 (º)/min. The powder morphology was observed by field emission scanning electron microscopy (FE-SEM, JSM-6701F, JEOL, Japan). The powder samples were scattered over the conductive adhesive with cotton bud and coated with a thin gold film before the SEM observation.

The RM was first mixed with deionized water in a ratio of 1 g:1 mL in a corundum crucible and then with concentrated H_2SO_4 (analytical reagent) in a ratio of 1 g RM:1 mL H_2SO_4 unless otherwise stated. The addition of water makes the RM like newly produced. Besides, it is beneficial to the homogeneity of mixture and the absorption of SO_3 escaping from the roasting procedure. The well mixed materials were roasted at a planned temperature with a heating rate of 10 ºC/min for a period of time set in advance. After the roasting process, samples were cooled inside the furnace to <250 ºC. The leaching experiments were carried out by a magnetic heating stirrer (85-2A KEXI Instrument, China) under certain leaching conditions including leaching temperature, leaching time, liquid to initial RM solid ratio (L/S) and constant stirring speed of ~250 r/min. Leaching liquor and residue were separated by a vacuum suction filter with medium speed quantitative filter paper. Following the ICP-OES test, the leachate obtained was first filtered through a membrane filter with 0.45 μm pore size and then diluted with 1 vol.% HNO_3, if need be.

2 Results

2.1 Red mud characterization

The chemical composition of RM in the form of element is given in Table 1, indicative of Fe, Al, Si, Na ap-