



Dearsenization of caustic solution by synthetic hydrocalumite



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ABSTRACT

Arsenic is enriched in liquor during the processing of copper anode slime by alkali fusion-leaching. The conventional method of removing arsenic from caustic liquors requires the neutralization followed by the introduction of calcium oxide or calcium hydroxide. In this work, the hydrocalumite, $\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$, are proved for the first time to remove up to 91% arsenic from caustic solution. Hydrocalumite is a mineral anion exchanger belonging to the layered double hydroxides (LDHs) which was synthesized by co-precipitation of calcium chloride and aluminum chloride in sodium hydroxide solution. It was characterized by XRD, FESEM and TG-DSC. Experimental parameters affecting the dearsenization process, such as temperature, NaOH concentration, initial arsenic concentration and hydrocalumite dosage were investigated in detail. The main phases of dearsenization products formed from hydrocalumite at different temperature were identified as $\text{Ca}_6\text{Al}_3(\text{OH})_{18}(\text{H}_2\text{O})_6\text{-AsO}_4$ (flat hexagonal), $\text{Ca}_3\text{Al}_2(\text{OH})_6\text{-}(\text{AsO}_4)_2$ (cubic) and $\text{Ca}(\text{OH})_2$ (Octahedron-single). The apparent activation energy in dearsenization by hydrocalumite was estimated to be 12.43 kJ/mol over the range of 30–80 °C.

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1. Introduction

Caustic solution containing arsenic (As) is produced in the process of alkali-fusion leaching of copper anode slime (Li et al., 2015). It is of high alkalinity and high toxicity, which can't be directly drained without proper treatment. Before the recycling of alkali from caustic solutions, consideration has been given to the removal of arsenic firstly.

There are two typical ways of removing arsenic from caustic solution. The first way consists of the precipitation of arsenate by oxidizing As(III) to As(V), based on lower solubility of arsenate than arsenite in caustic solution (Guo et al., 2015; Tongamp et al., 2010; Li et al., 2011). This produces a decrease of arsenic concentration in the solution, but it is unavailable for processing of low arsenic content (e.g., <2 g/L) solution. The other way is to neutralize the caustic solution and then convert arsenic into some insoluble compounds by introducing chemicals, such as calcium oxide or calcium hydroxide into the solution (Cui et al., 2014; De Klerk et al., 2012; James and Paul, 1999). It is characterized with high efficiency (99%) and good applicability, but huge amount of acidic reagents consumption and salt production.

Layered double hydroxides (LDHs), known as anion-exchange clay materials, are widely used as promising absorbents for both inorganic (arsenate, chromate, selenite, bromide, phosphate, etc.) and organic anions (methyl orange, sodium dodecylsulphate, etc.) (Theiss et al., 2014; Qian et al., 2012; Zhang et al., 2012a, 2012b; Liu et al., 2010; Grover et al., 2009; Yang et al., 2005; Rousselot et al., 2002). Among

them, there is an interesting group of LDHs named as hydrocalumite ($\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$). It is formed in cements rich in tricalcium aluminate (Suryavanshi et al., 1996; Birnin-Yauri and Glasser, 1998). A net positive charge on the sheets originates from the partial replacement of Ca^{2+} with Al^{3+} ions, forming $[\text{Ca}_2\text{Al}(\text{OH})_6]^+$ layers. The distorted “brucite-like” layers were separated by interlayers of water molecules and Cl^- (Zhang et al., 2012b).

Hydrocalumite is a cost-efficient absorbent and has been reported to remove arsenic from different liquors including drinking water and industrial wastewater, but only investigated on acidic ones and a limited scale (<150 mg/L) (Grover et al., 2009, 2010). In this study, hydrocalumite was prepared by the reaction of mixed chlorides with sodium hydroxide and examined for its arsenate anion exchange capacity, using as a dearsenization agent in caustic solution for the first time. The experimental parameters affecting the dearsenization, such as temperature, NaOH concentration, the initial concentration of arsenic and hydrocalumite dosage, were investigated systematically.

2. Experimental

2.1. Experimental materials

The arsenic material (sodium arsenate, $\text{Na}_3\text{AsO}_4\cdot 10\text{H}_2\text{O}$), a product of 17.8% arsenic content, was from some leaching-crystallization experiment (Guo et al., 2015). All other chemical reagents used in the experiments were of analytical grade supplied by Sinopharm Chemical Reagent Co., Ltd., and were used without further purification. The water used in all experimental work was ultrapure water (conductivity <0.2 $\mu\text{S}/\text{cm}$) unless otherwise specified.

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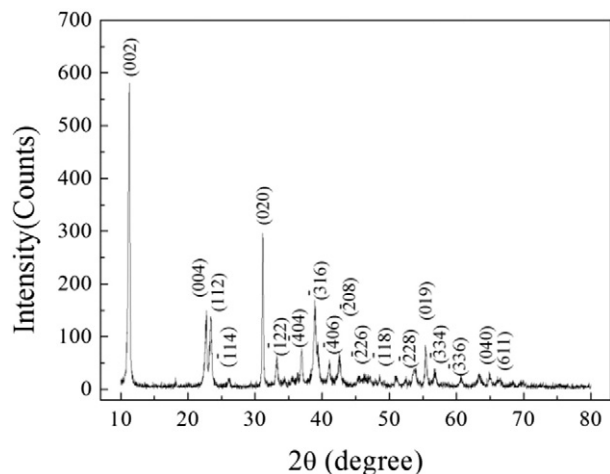


Fig. 1. XRD pattern of hydrocalumite.

2.2. Preparation and characterization of hydrocalumite

The experimental apparatus used was a 1 L round-bottomed flask with four necks which was baffled and equipped with a two-flat-blade turbine mixer and heated by thermostat water bath. The solution temperature was monitored by a thermocouple.

Preparation experiments were conducted by preheating 300 mL mixed solution (0.5 mol/L CaCl_2 + 0.25 mol/L AlCl_3) to 50 °C and adding an equal volume of 1.5 mol/L NaOH at a rate of 2 mL/min using a peristaltic pump, whilst stirring at 300 rpm. When the addition was completed, stirring continued for 1 h. The precipitate was then collected, filtered off, and washed with ultrapure water to remove residual ions before it was finally dried at 50 °C overnight.

For phase characterization, X-ray diffraction (XRD) patterns were detected on a D/Max-2550 X-ray diffractometer (maker: JEOL, Japan) using $\text{CuK}\alpha$ radiation. Field emission scanning electron microscope (FESEM) images were obtained with a Nova NanoSEM230 spectrometer (maker: FEI, USA). Thermo-gravimetric and differential scanning calorimetry (DSC-TGA) analyses (maker: TA, USA) were conducted on the synthesized samples.

2.3. Dearsenization experiments and analytical methods

Dearsenization experiments were also conducted in the same flask reactor. Dry samples were added into 500 mL sodium arsenate solution which was heated to a given temperature. Samples of 5 mL were taken

at prescribed times and filtered (0.45 μm) immediately. The liquor was analyzed for arsenic by an AFS-2202E atomic fluorescence spectrometry (AFS, maker: Haiguang Corp., China) coupled with a hydride generator. The residues were filtered, washed with ultrapure water, dried at 50 °C for about 10 h and analyzed by XRD and scanning electron microscope (SEM) with a JSM-6360LV spectrometer (maker: Rigaku, Japan).

3. Results and discussion

3.1. Characterization of synthesized hydrocalumite

Hydrocalumite samples were characterized by XRD, FESEM and DSC-TGA. Fig. 1 shows the XRD pattern which was sharp and in good agreement with the hydrocalumite literature values (JCPDS 31-0245). Whilst Fig. 2 shows FESEM images of flat and fine crystal of 1 μm average size with some serious agglomeration, Thermal analysis data is shown in Fig. 3 with the DSC and TGA traces recorded simultaneously under 100 mL/min N_2 . A double endotherm centered at 132 °C and 303 °C was matched by two well-resolved weight loss steps. Loss at 132 °C is due to the removal of interlayer water giving a product with reduced crystallinity with a determined composition of $3\text{Ca}(\text{OH})_2 \cdot 2\text{Al}(\text{OH})_3 \cdot \text{CaCl}_2$. With further heating, this phase persists up to 303 °C at which dehydroxylation occurred, followed by exothermally recrystallization at 600 °C, yielding mainly calcium chloroaluminate, $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaCl}_2$ (Birmin-Yauri and Glasser, 1998).

3.2. Dearsenization tests in sodium aluminate solution

3.2.1. Effect of dearsenization temperature

Fig. 4 plots the arsenic concentration as a function of dearsenization time and dearsenization temperature and shows both extent and rate of dearsenization were enhanced with increasing temperature. Typically for the different temperatures, the arsenic concentration decreased rapidly from its initial value of 2 g/L and then rather slowly with prolonged time. It can be found obviously that with high temperature (90 °C), the arsenic concentration decreased rapidly in the initial 30 min and then reached equilibrium.

As presented in Fig. 5, the structure of the dearsenization products formed from hydrocalumite at different temperatures was examined by XRD. It was found that arsenate form of $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ ($\text{Ca}_3\text{Al}_2(\text{OH})_6(\text{AsO}_4)_2$) and $\text{Ca}(\text{OH})_2$ are the main phases in dearsenization products at 30 °C, and arsenate form of hydrocalumite ($\text{Ca}_6\text{Al}_3(\text{OH})_{18}(\text{H}_2\text{O})_6\text{-AsO}_4$) is dominant in dearsenization products at 50 °C. When the temperature is increased from 70 °C to 90 °C, the $\text{Ca}_6\text{Al}_3(\text{OH})_{18}(\text{H}_2\text{O})_6\text{-AsO}_4$ diffraction peaks are gradually weakened and almost completely disappear at 90 °C. Simultaneously, diffraction

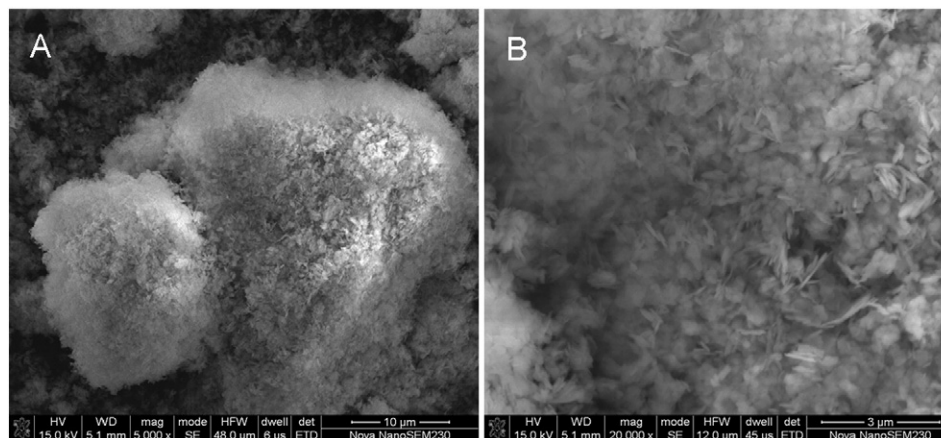


Fig. 2. FESEM images of hydrocalumite at two magnifications. (A: 5000 \times ; B: 20,000 \times).

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