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Physicochemical properties of arsenic-bearing lime−ferrate sludge and its leaching behaviors

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Abstract: Physicochemical properties and leaching behaviors of two typical arsenic-bearing lime−ferrate sludges (ABLFS), waste acid residue (WAR) and calcium arsenate residue (CAR), are comprehensively described. The chemical composition, morphological features, phase composition and arsenic occurrence state of WAR and CAR are analyzed by ICP−AES, SEM−EDS, XRD, XPS and chemical phase analysis. The toxicity leaching test and three-stage BCR sequential extraction procedure are utilized to investigate arsenic leaching behaviors. The results show that the contents of arsenic in WAR and CAR are 2.5% and 21.2% and mainly present in the phases of arsenate and arsenic oxides dispersed uniformly or agglomerated in amorphous particles. The leaching concentrations of arsenic excess 119 and 1063 times of TCLP standard regulatory level with leaching rates of 47.66% and 50.15% for WAR and CAR, respectively. About 90% of extracted arsenic is in the form of acid soluble and reducible, which is the reason of high arsenic leaching toxicity and environmental activity of ABLFS. This research provides comprehensive information on harmless disposal of ABLFS from industrial wastewater treatment of lime−ferrate process.

Key words: arsenic-bearing sludge; lime−ferrate sludge; physicochemical properties; leaching behavior; BCR sequential extraction

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1 Introduction

Arsenic pollution both in aqueous solutions [1−8] and contaminated soils [9−14] aroused a significant environmental concern. Various treatment processes such as coagulation, precipitation, ion exchange and adsorption were extensively employed for the removal of arsenic from water [15,16]. Lime−ferrate process is one of the most widely used methods for arsenic-containing wastewater treatment in practice of non-ferrous smelting industry because of its low cost and simple operation. However, this process generates a large amount of toxic arsenic-rich neutralization sludges, which are classified as a hazardous waste due to their high arsenic and other heavy metals contents [17]. The harm of arsenic-bearing lime−ferrate sludge (ABLFS) on health is mentioned by many researchers [18,19]. As one of the two most representative ABLFS, waste acid residue (WAR) is generated in traditional lime−ferrate process for the treatment of acidic wastewater from sulfuric acid production, while calcium arsenate residue (CAR) is from high arsenic wastewater treatment in less common and precious metal smelting, respectively. The huge quantities of these residues result in environmental pollution due to heavy metals leached out in disposal.

The physicochemical properties of sludge, including the chemical composition, structural feature and mineralogical phase composition, along with its leaching behaviors play a crucial role in treatment of solid wastes. In recent decades, various treatment techniques are developed to stabilize and recover heavy metals from solid waste, including direct extraction, roasting, crystallization and solidification based on its characteristics [20−23]. LI et al [24] determined the mineralogy characterizations of zinc leaching residue and provided information to develop new technology for separating iron and zinc from zinc leaching residue. MIN et al [25] accessed the environmental activity and potential ecological risks of heavy metals in zinc

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leaching residue by four different methods. CHAI et al [26] determined the behavior, transportation and distribution of arsenic during pyrometallurgical process in typical lead smelter. However, there is no detailed and complicated study on the characterization of ABLFS, which is an essential basis of proposing the most appropriate disposal method. Some critical mineralogy information about ABLFS is still unclear, especially phase composition, structural feature and grain morphology of arsenic in the sludge.

The transportation and transformation of heavy metals in environment were reported by many researchers. As an important accumulation of arsenic contaminant, arsenic-bearing solid waste becomes one of the hot issues on treatment and disposal. The potential for arsenic remobilization of arsenic-bearing solid wastes is assessed by TCLP, which is the current USEPA protocol for determining whether the waste is hazardous. PHENRAT et al [27] tested the leaching behaviors of arsenic-iron hydroxide sludge by TCLP. SHAW et al [28] studied the mobility of arsenic in arsenic-bearing solid residuals after stabilization by TCLP and CA-WET. However, it is well known that the TCLP poorly predicts the leaching of oxyanions, especially in arsenic species because the TCLP has a tendency to underestimate the leaching of arsenic from the residuals [29]. To efficiently evaluating various extraction methods, the standard sequential extraction method designed by BCR is used [30]. Such a sequential technique is also employed in several heavy metal and sediment-heavy metal studies [31−33]. Although the studies above are important to the pollution control and waste management, fewer relationships between physicochemical properties and leaching behaviors of ABLFS are clear. The lacking of basic knowledge on ABLFS can necessarily lead to difficulties in its treatment and disposal.

The objective of this work is to determine the relationship between physicochemical properties and arsenic leaching behaviors of ABLFS, and detect the reasons of its high leaching toxicity. Most significantly, the research will put forward reasonable proposals to minimize arsenic leaching concentration and provide information to develop appropriate technologies for the harmless treatment and disposal of this type of sludge.

2 Experimental

2.1 Materials and analysis

Two typical arsenic-bearing lime−ferrate sludges, waste acid residue (WAR) and calcium arsenate residue (CAR), were used as raw materials in this study. Both materials were generated from the process of arsenic-containing wastewater treatment by lime−ferrate process. WAR was supplied by a lead and zinc smelter in Chenzhou city, China and CAR was obtained from an antimony smelter in Huaihua city, China. All the samples were dried at 60 °C for 24 h and sieved below 0.15 mm.

The chemical composition of samples was detected firstly by inductively coupled plasma atomic emission spectrometry (ICP-AES, IRIS Intrepid II XSP), and then the main metal elements were analyzed by chemical analysis based on ICP-AES result. The main phases presented in ABLFS were detected by X-ray powder diffraction (Rigaku, TTR-III). The arsenic phase compositions were quantified by chemical analysis as described by ZHANG [34], and the analytical procedure is shown in Fig. 1. Morphological feature and micro-area chemical analysis of milled samples were observed by scanning electron microscope with energy spectrometer (SEM-EDS, Nova Nano SEM 230). The particle size distribution was determined by laser particle size analyzer (OMEC LS-POP VI). The grain morphology and mineralogical surface composition of WAR and

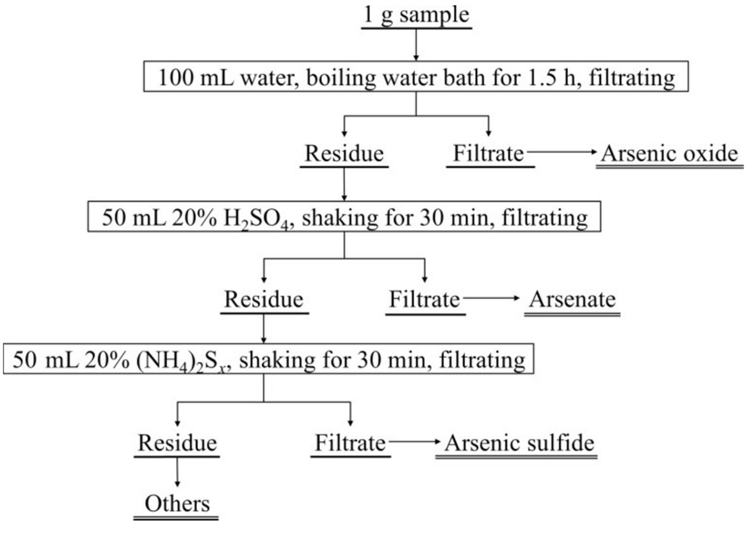

Fig. 1 Methodology used for chemical phase analysis of arsenic-bearing residues