



A new process of continuous three-stage co-precipitation of arsenic with ferrous iron and lime



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ABSTRACT

Disposal of acid wastewater containing arsenic (As) from a metallurgical plant was systematically studied and a novel continuous three-stage treatment process was advanced based upon lime-ferrous flocculation technology. At first, the effect of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ dosage, temperature, reaction time and neutralization reagent on As removal efficiency was evaluated in a bench scale test. Then, the influence of oxidants (air and bleaching powder) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ dosage on As removal efficiency, was also tested in a pilot scale experiment. Finally, the removal of As from acid wastewater in industrial scale was evaluated based on the obtained optimized parameters from the bench and pilot scale tests. The results showed that the residual As in the final outflow water was less than 0.3 mg/L, which met the demands specified in *Emission Standard of Pollutants for the Sulfuric Acid Industry* issued by Ministry of Environmental Protection of China (GB26132-2010). The proposed strategy is efficient in utilizing a low cost and promising in industrial application.

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1. Introduction

Highly acid wastewater containing arsenic (As), known as dirty acid wastewater, is mainly produced in the non-ferrous metal-smelting or mineral-processing. The disposal of dirty acid wastewater is very difficult due to its high toxicity and complexity in components, especially for wastewater with high As concentrations. In addition, catastrophic damage will be caused to the environment and ecology if dirty acid wastewater is directly drained without proper treatment (Mandal and Suzuki, 2002).

Up till now, some classic technologies, including precipitation by lime treatment (Langmuir et al., 1999), adsorption (Harris, 2003; Masue et al., 2006), electrocoagulation (Kamala et al., 2005), membrane permeation (Gecol et al., 2004; Sato et al., 2002) and biological methods (Kamala et al., 2005; Loukidou et al., 2003), have been developed to remove As from dirty acid wastewater. Among these technologies, adsorption is one of the most common and effective methods (Hering et al., 1996; Nenov et al., 1994). It was reported that the combination of neutralization of acid wastewater with co-precipitation was one of the most available industrial options in the treatment of acid mineral-processing effluents (Hering et al., 1996; Nenov et al., 1994). To achieve the maximum As removal rate, experimental parameters have been optimized (Harris, 2000; Harris and Monette, 1988; Krause and Ettel, 1989). In general, co-precipitation with an Fe/As molar ratio greater than or equal to three

were shown to provide effective arsenic (V) removal up to mildly alkaline conditions (Krause and Ettel, 1989; Twidwell et al., 2005). However, a larger Fe/As molar ratio (Fe/As = 8–10) was necessary for high As concentrated wastewater (≥ 1 g/L). A case study was presented by Banerjee (2000) to illustrate the optimization and utilization of the 2-line ferrihydrite adsorption technology for the removal of arsenic from a groundwater in a northeastern U.S. industrial facility. The plant treated 550,000–750,000 L/day groundwater using an Fe/As weight ratio of 10 (mole ratio of 13). As is known to all, too low Fe/As molar ratio leads to arsenic emission over standard, and overtop Fe/As molar ratio increases the cost of the treatment and weight of solid wastes containing arsenic. From the viewpoint of optimization, it is very important to investigate the proper Fe/As molar ratio with the composition of dirty wastewater and the treatment conditions.

A few studies have already been related to the disposal of As-contained acid wastewater in the industrial scale (De Klerk et al., 2012; Jia et al., 2012). Herein, a novel continuous three-stage treatment process was proposed and As removal efficiency in industrial scale was evaluated by the advanced technology, based upon bench and pilot scale experiments (Fig. 1). The quality of the wastewater from a metallurgical plant was listed in Table 1. It can be seen that there are complex components in dirty acid wastewater which contain highly concentrated As (7.4–14.7 g/L), H_2SO_4 (6.5–13.2 g/L), as well as other metal cations such as Cu^{2+} , Zn^{2+} , Pb^{2+} and Cd^{2+} . The research aims to remove As and other hazardous materials by co-precipitation. After a one-year successful operation in the industrial scale, satisfactory results were obtained in the disposal of the dirty acid wastewater, indicating that

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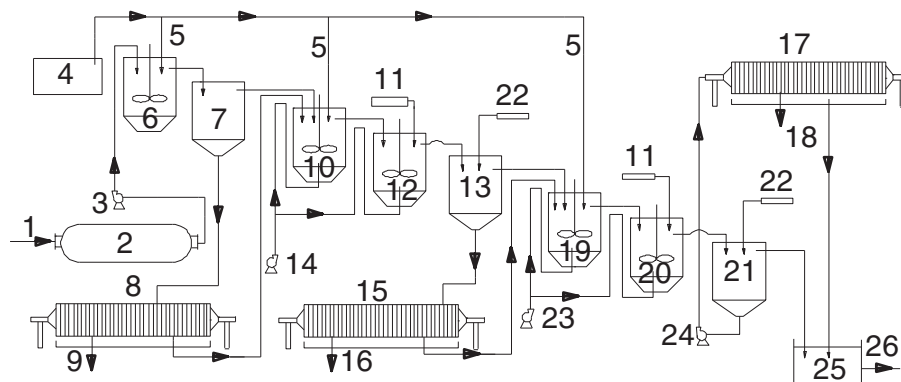


Fig. 1. Flow diagram for acid wastewater with arsenic treatment process, (1) inflow wastewater, (2) wastewater storage tank, (3) pump, (4) liming storage tank, (5) lime milk, (6) neutralizing tank, (7) settling tank, (8) frame filter, (9) non-hazardous waste (calcium sulfate), (10) causticizing tank, (11) ferrous sulfate, (12) neutralizing tank, (13) settling tank, (14) blast engine, (15) frame filter, (16) solid waste with arsenic, (17) frame filter, (18) solid waste with arsenic, (19) causticizing tank, (20) neutralizing tank, (21) settling tank, (22) anionic polyacrylamide flocculant (APAM), (23) blast engine, (24) pump, (25) clean water reservoir, (26) outflow.

this strategy is promising in the treatment of industrial dirty acid wastewater.

2. Materials and methods

2.1. Materials and analytical methods

Lime (CaO, 85 wt.%), hydrated ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 90 wt.%), sodium hydroxide (NaOH, 96 wt.%) and bleaching powder (active chlorine ingredient of more than 30 wt.%) were utilized in the experiments.

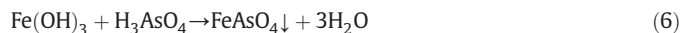
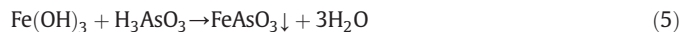
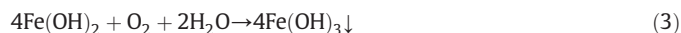
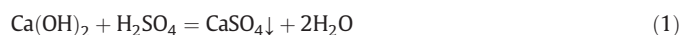
The dirty acid wastewater was received from a sulfuric acid production workshop in a non-ferrous metal plant located in Hubei, China's central province. The wastewater was about 600 m³ per day. The concentration of As in original wastewater was 7.4–14.7 g/L and the initial pH value of wastewater was less than 1. Obviously, the dirty acid wastewater was characterized as high acidity and complexity in the components. The major chemicals in wastewater were As, Cd, F, Pb and Zn, most of which are hazardous waste pollutants listed in the first category.

The concentrations of As, Cd, Zn, Cu and Pb listed in Table 1 were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Varian, US). It must be noted that the concentration of As was also determined by an atomic absorption spectrophotometer equipped with an HIG-1 hydride generator (AAS, Shimadzu 6300, Japan) if it was in low concentration (≤ 0.1 mg/L).

2.2. Flow diagram of the three-stage co-precipitation process

The flow diagram of the present technology was depicted in Fig. 1. In the 1st stage, dirty acid wastewater in Storage Tank 2 was pumped into Neutralizing Tank 6. Next, lime slurry was added to Neutralizing Reactor 6 and stirred until the solution pH value was about 2 (Eq. (1)). The

resulting mixture was then poured into Settling Tank 7 for separation. After separating sediment in Settling Tank 7 for 60 min, the filtrate was poured into Neutralizing Tank 10 in the 2nd stage, while the formed sediment was poured through Frame Filter 8 to produce insoluble CaSO_4 (Eq. (1)). In the 2nd stage, the filtrate was poured into Causticizing Tank 10, by lime to pH 5, FeSO_4 solution with Fe to As mole ratio (Fe/As) of 4, was simultaneously added to remove As in Neutralizing Tank 12, under aerated bubbling (Eqs. (2)–(6)). Then the subsequent mixture was poured into Settling Tank 13, which was followed by the addition of anionic polyacrylamide flocculant (APAM) for separation. The filtrate from Settling Tank 13 entered Causticizing Tank 19 (3rd stage), while the underflow went to Frame Filter 16 for dewatering. Similarly, the filtrate in Causticizing Tank 19 was neutralized to pH 9, which was followed by the addition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Fe/As = 4) and flocculating agent APAM. At last, the effluent was discharged into a clean water reservoir or pumped into the emergency tank for retreatment in accordance with the quality of the water.



The 1st stage was designed to remove most of the sulfate acid by forming insoluble CaSO_4 , in the presence of lime slurry (neutralization reagent). The 2nd stage was used to remove As and other metal ions from wastewater by forming solid wastes. During the 2nd stage, H_3AsO_4 or H_3AsO_3 reacted with a variety of metal ions such as Fe, Cd, Cu, Pb and Zn, and formed insoluble arsenate or arsenite (Table 2, (Lide, 2003–2004)). These insoluble arsenates or arsenites could be removed during the co-precipitation process. At the same time, some of the arsenic could also be removed by adsorption of $\text{Fe}(\text{OH})_3$ or $\text{Fe}(\text{OH})_2$. During the 3rd stage, lime was mainly used for pH adjustment to meet the discharge limit of pH 6–9.

Table 1
Components in dirty acid wastewater for experiments (unit: mg/L).

Averaged components (mg/L)	Bench-scale and pilot-scale	Industrial-scale	
		Case I	Case II
As	10,100	7400	14,740
Cd	115	120	140
H_2SO_4	6130	6500	13,200
F	60.5	63.2	40.5
Cu	70.1	87.3	90.1
Pb	20.3	25.6	10.4
Zn	60.4	55.2	84.8
Suspended sediment	905	913	880

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