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Preparation of high purity cadmium with micro-spherical architecture from zinc flue dust

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Abstract: This research has focused on the treatment of zinc flue dust by an acid leach process, combining an environmentally suitable impurity removal process to recover cadmium. Optimum conditions were found as follows: H_2SO_4 concentration 90 g/L, liquid/solid ratio 6:1, leaching temperature 60 °C and leaching time 1.0 h. Under these conditions, 95.8% cadmium was recovered. $FeAsO_4$ and $Fe(OH)_3$ precipitates with $FeCl_3$ are found to be highly effective to obtain a high degree of separation of heavy metals and the oxyanions of arsenic from the leachate. The overall separation of arsenic and other heavy metals and precipitate settling rates are optimum at n(Fe)/n(As) ratio of 3:1 and pH 6. The removal rates of Fe, Pb and Cu from the solution were greater than 98.9%, and As removal rate was 99.6%. A solvent extraction with P204 was used for the separation of zinc and cadmium. Optimum conditions are obtained as follows: 20% P204 (volume fraction) diluted with kerosene at room temperature, pH 3.0, and varying organic/aqueous (O/A) phase ratio 1:1. The extraction rate of zinc is 99.2% under these conditions. Spherical cadmium particles showing nearly uniform size were produced by hydrogen reduction at 310 °C and the crystal structure was cubic. In addition, the purity of the recovered cadmium powder is more than 99.99%.

Key words: zinc flue dust; impurity removal; micro-spherical; cadmium powder

1 Introduction

A part of cadmium is recovered from different secondary resources such as zinc ash, zinc dross, flue dust of roasting furnace and brass smelting, nickel−cadmium (Ni−Cd) batteries, which contain different levels of impurities depending on the sources [1]. The chemical nature of these dust particles is classified as hazardous waste. The disposal of such materials is now becoming expensive because of increasingly stringent environmental protection regulations [2−4]. Improved material management can lead to better utilization of refined materials, decreased use of primary materials and energy resources and a reduced need for landfill areas [5,6]. Zinc concentrate is roasted to remove the sulfur from the concentrate and produces impure zinc oxide [7−9]. Inevitably, zinc concentrate contains various contaminants such as cadmium, lead, copper, arsenic and sulfur. Furnace operation generates a hot off-gas containing fume and particulate matter [10]. These resulting gases and fumes are cooled and passed through a bag-house before discharging to atmosphere [11−13]. The roaster dust collected contains base metals, especially lead, cadmium and arsenic [14]. It is thus a toxic product and presents a problem for disposal in an environmentally acceptable way. However, the relatively high cadmium which is present as oxide phase provides a valuable resource. Currently, if the cadmium content of the dust reaches 12% (mass fraction) [15], the dust is mainly returned to the sintering operation for cadmium recovery. Flue dust of zinc smelter, which comes from sintering off-gases in bag-houses [16−18], is a serious problem in terms of pollution and storage because of its high content of hazardous materials such as cadmium, lead, copper, zinc and arsenic and its low apparent density [19,20].

Cadmium has many common industrial uses as it is a key component in battery production [21]. It is present in cadmium pigments and coatings, and is commonly used in electroplating [16,22]. High purity cadmium is widely used in making of II−VI type semiconductors, e.g., HgCdTe [23]. Certain impurities limit the electrical and optical performance in these devices. These may be bulk effects as in the case of γ-ray detectors and modulators or due to the migration of impurities from a

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substrate into an epitaxial layer eventually affecting detector performance [24]. High resistivity CdTe crystals with good crystalline quality and a low concentration of defects are needed for room temperature nuclear radiation detectors [25]. Hence, the main limiting factor in the performance of CdTe or CdHgTe is the purity of raw materials [26]. Such impurities at very low levels in high purity cadmium must be developed for the assessment of purity of the starting materials.

This paper describes a laboratory-scale study of a method for producing a high purity cadmium powder based on leaching and precipitation of arsenic in the presence of iron at a pH of 5.5, leaving a residue of metals together with ferric hydroxide. Separation of zinc from the solution is treated by solvent extraction with the acidic extractant di(2-ethylhexyl) phosphoric acid (D2EHPA). Then, the cadmium containing in the solution precipitates with sodium hydroxide. This paper presents an experimental study on the preparation of cadmium powder by reduction of $Cd(OH)_2$ with hydrogen in a tube furnace. In our experiments, reaction zone temperature is considered the key process variable for the control of particle size and product composition.

2 Experimental

2.1 Materials and analysis methods

The roaster dust was from Yuguang Gold and Lead Group Co., Ltd., Henan, China. The content of impurities was analyzed by inductively coupled plasma optical emission spectroscopy (ICP, IRIS intrepid XSP, Thermo Electron Corporation). The products of cadmium powder were characterized by X-ray diffraction (XRD, Rint−2000, Rigaku). The morphology was measured by scanning electron microscope (JEOL, JEM−5600LV) with an accelerating voltage of 20 kV. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using Perkin−Elmer TGA and DTA system on well ground samples in flowing nitrogen atmosphere at a heating rate of 5 °C/min.

2.2 Experimental procedure

2.2.1 Sulfuric acid leaching

Leaching of the dried powder was carried out in a three-necked glass reactor (500 mL). A thermometer was fitted to one of the openings. The reactor was heated in a mantle to the required temperature and controlled at the desired temperature. The temperature during the leaching experiments could be controlled to be ± 2 °C. The reactor was filled with H_2SO_4 and the sample was added to a preheated acid solution. The stirring speed was kept constant at 400 r/min throughout all the experiments. The operating variables of acid concentration (30, 70, 90 and 110 g/L), temperature (25, 40, 50, 60 and 70 °C) and liquid/solid ratio (4:1, 5:1, 6:1, 7:1 and 8:1) were investigated. At the end of each leaching experiment, the solutions were filtered. The cadmium and other impurities in the solution were determined using an inductively coupled plasma. The leaching residue was dried in an oven at 105 °C for 12 h, subjected to X-ray diffraction.

2.2.2 Purification

After the leaching process, the purification experiments were taken for the leaching solution. A typical treatment procedure involved addition of 30% H_2O_2 (mass per volume) to the solution. The mixture was stirred to oxidize the As (III). At this point, $FeCl_3$ was added and the solution was further stirred. The pH was adjusted with NaOH solution (6 mol/L) and the final step involved filtering off the solid ferric arsenate using nylon membrane filters. The filtered samples were analyzed for the residual arsenic, iron and other impurities concentrations using an inductively coupled plasma (ICP) emission spectrometer.

2.2.3 Solvent extraction

The extractant D2EHPA was used to separate zinc from the solution. The reactive component $(C_8H_{17}O)_2PO_2H$ is di(2-ethylhexyl)phosphoric acid. The relative molecular mass is 322 and the density at 20 °C is 0.974 g/cm^3. The extractant was used without further purification. In all experiments, aviation kerosene was used as organic diluent. All experiments were conducted in a 500 mL three-necked round bottomed reactor in a heating jacket, which was fitted with a stirrer, a thermometer and a pH electrode. The organic phase and aqueous phase were contacted for 10 min by stirring and the pH was controlled by small addition of 4 mol/L H_2SO_4. The solvent extraction separation was carried out in a separation funnel of 150 mL. After each extraction stage, the mixture was left to stand still for 20 min, permitting the complete separation of the phases. Then, a sample of the solution was withdrawn to measure the zinc and cadmium contents by ICP.

2.2.4 Hydrogen reduction

A tube furnace was used to conduct hydrogen reducing experiments. 10 g $Cd(OH)_2$ powder was put in a ceramic boat and pushed forward to the reaction zone of the tube furnace. The samples were heated to different temperatures for different durations in a quartz tube. During the heating process, nitrogen gas was introduced to the quartz tube and mixed with hydrogen when the given temperature was reached. Gases were supplied from a gas tank at a flow rate of about 1.0 L/min and room temperature. At the end of each batch reducing, the residues in the boat were collected for XRD analysis.