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Preparation of magnesium hydroxide from leachate of dolomitic phosphate ore with dilute waste acid from titanium dioxide production

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ABSTRACT

A novel method for the removal of magnesium from dolomitic phosphate ores by using dilute waste acid (DWA) from titanium dioxide pigment production was experimentally studied in this work. The pH of liquid phase and particle size of granulized phosphate ore have been found to be crucial to the efficient removal of magnesium from phosphate ore. Operating under the optimum leaching conditions, a 98.31% removal of Mg with 0.02% P_2O_5 loss was obtained. It was demonstrated that dolomite can be selectively dissolved by H^+ in the DWA and the ability of H^+ to attack the apatite is inhibited by the strong interionic strength of DWA. By using the solubility differences of corresponding elements, a two-step precipitation process was presented to remove Fe selectively from Mg. A process for further purifying the synthetic leachate by a precipitation/leaching method and oxidation was also investigated. Subsequently, magnesium hydroxide ($Mg(OH)_2$) was prepared by precipitation from the refined solution with ammonia as the precipitant and sodium dodecyl sulfate (SDS) as the modifier. The phase structure and morphology of $Mg(OH)_2$ were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM), respectively. The prepared nanoparticles of $Mg(OH)_2$ were found to exhibit a column-shaped structure, demonstrating that the anions of DS^- adsorbed onto the surface of $Mg(OH)_2$ nucleus contribute to the stacking of $Mg(OH)_2$ regular-hexagon platelets along the c-axis perpendicular to the [001] plane. The adsorption of SDS on the surface of $Mg(OH)_2$ was supported by Fourier transform infrared spectroscopy (FTIR).

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1. Introduction

Magnesium in the form of dolomite constitutes a main impurity in sedimentary phosphate ores. Due to depletion of high-grade phosphate ore, the unexploited reserves of phosphate rock tend to contain less phosphate and more dolomitic carbonate (Zheng et al., 2001). The low-grade ores need beneficiation to be fit for subsequent processing. However, due to the physico-chemical similarity between dolomites and phosphates, it is usually difficult to remove the dolomites efficiently from such phosphate ores by conventional techniques such as flotation or physical separation methods (Abouzeid, 2008; Abouzeid et al., 2009; Feng and Aldrich, 2004). Several methods have been used to remove dolomites from phosphate rocks, namely, reactive flotation (El-Midany et al., 2011), magnetic separation (Blazy and Jdid, 1997), reverse flotation (Mohammadkhani et al., 2011), calcination (Zafar et al., 1995), and chemical dissolution (Ashraf et al., 2005; Economou and Vaimakis, 1997; Zafar et al., 2006). Nevertheless, these methods often involve complicated process conditions and vast consumption of thermal energy (Gharabaghi et al., 2010), or organic acids (Sengul et al., 2006), which

make them economically unfavorable for the removal of dolomite from phosphate rocks. A cheap and simple method for lowering the magnesium content in phosphate ores is thus urgently required.

Presently, disposal of the discharged diluted waste acid (DWA) in titanium dioxide pigment industry has become an international environmental issue, which is vital to the normal operation of existing plants (Braun et al., 1992). Typically, DWA contains a low concentration of H_2SO_4 (3.85 wt.%), which causes toxic metals to dissolve and also other elements such as Fe, Mn, Ca, and Ti (Table 1), and generally is neutralized by slaked lime slurry. The disposal of sludge generated through the active treatment is confronted with processing low-solid content suspensions, long-term instable operation and a requirement for large areas of land for disposal (Hove et al., 2007; Matlock et al., 2002). Moreover, the cost of DWA treatment leads to a large increase in the cost of thus manufactured titanium dioxide.

Herein, the DWA is used as a chemical dissolution reagent for enriching low-grade phosphate ores by selective dissolution of dolomites (Economou et al., 2002). In comparison with the methods cited previously, the new approach is more suitable for upgrading of the phosphate ores with a remarkable economic benefit because cost-free acid is used as a dissolution reagent (Gu, 2002). In addition, the utilization of DWA decreases the sulfuric acid consumption caused by the presence of free dolomite in the phosphate ores during the wet process

Table 1
Chemical analysis of raw DWA and leachates.

Samples	Concentration, mg/L							
	Mg^{2+}	Fe^{2+}	Mn^{2+}	Ti^{4+}	Ca^{2+}	SO_4^{2-}	PO_4^{3-}	F^-
Raw DWA	940.1	6200	320.1	299.0	22.7	52,000	1.8	7.0
Synthetic leachate	5800	6200	345.3	74.3	707.8	37,000	4.2	33.0
Leachate a	5200	564.2	184.1	3.7	749.3	23,500	BLD	16.8
Leachate b	30,500	4.5	900.3	BLD	392.9	124,100	BLD	37.0
Leachate c	32,300	BLD	0.64	BLD	428.6	133,300	BLD	60.1

BLD: Below detection limits.

production of phosphoric acid (Sengul et al., 2006; Zafar et al., 1995). This will simultaneously decrease the production cost of titanium dioxide pigment as well as phosphoric acid.

Removal of magnesium from phosphate ores with DWA leads to generation of highly contaminated leachate liquor. The recovery of magnesium from the leachate with the joint objectives of obtaining valuable products is one potential way to extend the use of phosphate ores, while maintaining an economy of sustainable development (Wei et al., 2005). Magnesium hydroxide is widely used due to its outstanding physical and chemical properties (Beall et al., 2013). Purified $Mg(OH)_2$ which is mainly synthesized via a wet precipitation method (Dong et al., 2010; Hsu and Nacu, 2005; Wang et al., 2011), has a remarkable commercial value. Methods for preparation of MH from nickel laterite leach liquors (Karidakis et al., 2005), boric magnesium fertilizer (Li et al., 2008), brine (Turek and Gnot, 1995), and dolomite (Amer, 1996) have been reported. However, the use of DWA leachate of phosphate ore as raw material has not been described.

In this paper, an integrated process is proposed, which is suitable to treat high magnesium content phosphate ores and recover the magnesium element as $Mg(OH)_2$ both efficiently and economically. The operating conditions for different stages of the process were experimentally studied in detail. The research work is reported in four parts: (1) leaching of phosphate ores by DWA and investigation regarding the mechanism of leaching process; (2) evaluation of the precipitation rate of ions in a synthetic solution with a chemical composition similar to the real leachate (Table 1) and developing of a two-step selective precipitation process to remove Fe from Mg; (3) purification leachate liquor via a precipitation/leaching method followed by oxidation; and (4) preparation of $Mg(OH)_2$ using ammonia as the precipitant and sodium dodecyl sulfate (SDS) as a modifier as well as the subsequent characterization of MH product.

2. Materials and methods

2.1. Materials

Untreated dilute waste acid (DWA) was collected from the effluent treatment unit of the titanium dioxide production plant of Sichuan Lomon Corporation in Mianzhu (China) and sealed in high-density polyethylene bottles. The dilute waste acid was firstly filtered to remove debris and suspended solids before being used in chemical beneficiation experiments of phosphate rock. Phosphate rock and lime milk (available calcium, 10 wt.%) were supplied by Sichuan Lomon Corporation. Prior to beneficiation experiments, phosphate rock was dried at 110 °C overnight, and then ground to the required granularity.

Technical grade ammonia ($NH_3 \geq 99.64$ wt.%) and brucite powder ($Mg(OH)_2$, 78.35 wt.%) were purchased from Sichuan Hongfu Chemical Company and Dandong Talc Factory, respectively. Sulfuric acid, ammonium persulfate and ammonia solution (NH_3, 25–28 wt.%) were all of analytical grade and provided by CUICR, while chemically pure sodium dodecyl sulfate was supplied by Jiangsu Yonghua Fine Chemical Company. All chemical reagents were used without further purification.

2.2. Characterization

2.2.1. Characterization of phosphate rock

The mineralogical analysis of the phosphate ore was carried out by X-ray diffraction (XRD), using Cu Kα ($\lambda = 1.54056$ Å) radiation on a X-ray diffractometer (X'Pert PRO, PANalytical, Netherlands) at a scan rate of 0.05°/s ranging from 5° to 80°. Phase identification was conducted with the aid of the computer software X'Pert HighScore Plus and PDF-2004 cards. Microstructural characteristics of solid samples were surveyed by the scanning electron microscopic image (SEM, JSM-6390A, JEOL, Japan). The ore particle size distribution was determined by using a laser particle size analyzer (HYDRO 2000, Malvern Instruments, UK).

The contents of P_2O_5, SO_3 were gravimetrically determined, while the contents of MgO, CaO, Al_2O_3, and Fe_2O_3 were measured by titration. The content of F was detected using an ion-selective electrode. The TiO_2 content was determined by means of an X-ray fluorescence spectrometer (XRF, Axios max, PANalytical, Netherlands). Loss on ignition (LOI) was defined as the decrease in weight of the sample in a temperature range between 110 °C and 950 °C. The amount of CO_2 in the sample was defined as the weight loss between 550 °C to 950 °C (Ashraf et al., 2005).

2.2.2. Determination of ion contents

The concentrations of Mg^{2+}, Mn^{2+} and Ca^{2+} in all aqueous samples were analyzed using an atomic absorption spectrometer (AAS, TAS-990, PGENRAL, China). The contents of Fe^{2+}, Ti^{4+}, and PO_4^{3-} were spectrophotomerically determined, while the content of F^- was detected using an ion-selective electrode.

2.2.3. Characterization of $Mg(OH)_2$ products

The phase structural identification and morphology of the as-product were characterized by the XRD and the SEM, respectively. Fourier transform infrared spectroscopy (FT-IR) spectrum was performed with a spectrometer (Nicolet iS10, Thermo Scientific, USA) by employing the KBr pellet method.

2.3. Experimental

2.3.1. Magnesium removal from phosphate

Ground phosphate rock and deionized water were added into a stirred vessel which was immersed in a thermostat bath. The phosphate and water were previously weighed so as to form a slurry of 65 wt.% solid after mixing in the stirred vessel. The temperature was kept constant at 45 °C. The dilute waste acid was continuously fed into the stirred vessel with a peristaltic pump to keep a certain reaction pH. The slurry was agitated continuously to keep the solid particles in suspension. Total duration for every batch of acidification experiments was about 2 h. After acidification, the phosphate suspension was filtered to separate the treated phosphate ore from the leachate liquor, while the filter cake was washed with deionized water several times to remove the residual soluble ions, such as Mg^{2+} and PO_4^{3-}. The washed filter cake was then dried at 95 °C until no more weight loss was observed. Dilute sulfuric acid was also used in control test. The percentage for the removal of Mg and loss of P_2O_5 was calculated as follows, respectively:

$$\% \, Mg\,removal = \left[1 - \frac{M_{solid,i} \times C_{Mg,i}}{M_{solid,o} \times C_{Mg,o}} \right] \times 100 \qquad (1)$$

$$\% \, P_2O_5\,loss = \left[\frac{M_{liquid} \times f}{M_{solid} \times C_{P_2O_5,o}} \right] \times 100 \qquad (2)$$

where $M_{solid,o}$ and $M_{solid,i}$ are the mass of the raw material and treated solid, $C_{Mg,o}$ and $C_{Mg,i}$ represent the contents of Mg in the raw material and treated solid, respectively; M_{liquid} is the mass of the leachate solution,