Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 15503–15514

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Utilization of alum sludge for producing aluminum hydroxide and layered double hydroxide

Ling Yun Wang[a], Dong Shen Tong[a], Li Zhi Zhao[a], Feng Guo Liu[a], Ning An[a], Wei Hua Yu[a], Chun Hui Zhou[a,b,*]

[a]Research Group for Advanced Materials & Sustainable Catalysis (AMSC), Research Center for Clay Minerals, Breeding Base of State Key Laboratory of Green Chemistry Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032, China

[b]The Institute for Agriculture and the Environment, University of Southern Queensland, Toowoomba, Queensland 4350, Australia

Received 17 May 2014; received in revised form 22 June 2014; accepted 2 July 2014
Available online 10 July 2014

Abstract

The present work dealt with the utilization of alum sludge, which acted as an aluminum source, for producing aluminum hydroxide ($Al(OH)_3$) and layered double hydroxide (LDH). The effects of the acid treatment and the neutralization with an aqueous sodium bicarbonate ($NaHCO_3$) solution or with CO_2 gas on the $Al(OH)_3$ products were investigated. The $Al(OH)_3$ samples were characterized by powder X-ray diffraction, Fourier transform-infrared spectroscopy, thermal analysis, scanning electron microscopy, X-ray energy dispersive spectroscopy and N_2 adsorption–desorption. A maximum 87.23% yield of $Al(OH)_3$ was achieved under conditions as follows: the treatment of 10 g of alum sludge with 15 ml of sulfuric acid (16 mol/L) at 170 °C for 1 h, followed by the separation of $Fe(OH)_3$ and $Al(OH)_3$. Depending upon the conditions of extraction and precipitation, the $Al(OH)_3$ products appeared to be in the form of boehmite and bayerite or their mixture. Varying neutralization influenced the purity, yield, morphology, and texture of the $Al(OH)_3$ products. Amorphous $Al(OH)_3$ was obtained by using CO_2 gas for the neutralization, whereas fiber-like crystalline $Al(OH)_3$ was obtained by using an aqueous $NaHCO_3$ solution for the neutralization. With addition of an external magnesium source, the resultant $Al(OH)_3$ can then be converted into crystalline layered double hydroxide (LDH) by a coprecipitation and hydrothermal method. The results indicated that crystalline and amorphous $Al(OH)_3$ can both undergo decomposition and subsequent reassembly with Mg species to form crystalline LDH.

Keywords: Alum sludge; Aluminum hydroxide; Layered double hydroxide; Alunite; Sodium bicarbonate

1. Introduction

Alum, with a formula of $AlK(SO_4)_2 \cdot 12H_2O$, is widely used in food [1], flame retardant [2], the treatment of poultry litter [3] and water [4], medicine [5] and composite materials [6]. It is usually produced from alunite minerals. Alunite is calcined and then the resultant solid is exposed to humid air for a considerable time so that it falls into powder via deliquesce and efflorescence. The powder is then lixiviated with hot water. In this way, the alum was dissolved in water. After press filtration, the filtrate and the insoluble solid filter residue are obtained. The filtrate is used for recrystallization, yielding the crystalline alum product. The insoluble solid filter residue, usually called alum sludge, is usually discarded as a solid waste [7].

Chemical analyses show that alum sludge consists of aluminum compounds, SiO_2 and Fe_2O_3 [8]. Namely, alum sludge proved to be an aluminum-rich solid. Over the past decades, many attempts have been made to utilize alum sludge technologically and economically [9–13]. For example, alum sludge is thought to be used as adsorbent for the removal of phosphorus [9], Pb(II), Cr(III), Cr(VI) [10], As(III) and As(V)

*Corresponding author at: Research Group for Advanced Materials & Sustainable Catalysis (AMSC), Research Center for Clay Minerals, Breeding Base of State Key Laboratory of Green Chemistry Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032, China.

E-mail addresses: clay@zjut.edu.cn, Chun.Zhou@usq.edu.au (C.H. Zhou).

http://dx.doi.org/10.1016/j.ceramint.2014.07.012
0272-8842/

[11] from wastewater. It is also suggested that alum sludge can be used for constructing a wetland system [12]. In addition, some researchers reported that alum sludge can be added to a nutrient-deficient soil to improve cereal productivity on it [13].

In contrast to above-mentioned uses, using alum sludge as an aluminum source for producing value-added products such as aluminum hydroxide $Al(OH)_3$ and layered double hydroxide is more attractive. Usually, $Al(OH)_3$ is produced from bauxite ores in industry [14,15]. $Al(OH)_3$ can then be used to produce to alumina (Al_2O_3). Both $Al(OH)_3$ and Al_2O have many applications in ceramics [16,17], catalyst supports [18,19], adsorbents [20] and functional fillers in polymeric materials [21]. Undoubtedly, to produce $Al(OH)_3$ from alum sludge is of much value and such a product has existing large marketplace.

It is also worth noting that aluminum-containing compounds are indispensable starting sources for the production of layered double hydroxide (LDH) [26,27], which has a general formula of $M^{II}_{1-y}M^{III}_{y}(OH)_2(X^{n-})_{y/n}\cdot mH_2O$, where M^{II}, M^{III}, and X^{n-} denote divalent metal cation, trivalent metal cation and interlayer anion, respectively [22], and y is in the range of 0.2–0.33 [23]. For example, $Mg_3Al(OH)_8(CO_3^{2-})_{0.5}\cdot mH_2O$ (MgAl–LDH) can be prepared from an Al source and a Mg source. Because of its peculiar layered structure, anion exchangeability and tunable chemical composition, LDH has many practical and potential applications in the fields of ceramics [24,25], catalysts [26–29], adsorbents [30–32], drug delivery [33–36], polymer fillers [37,38], supercapacitors [39–41], and so forth.

In this work, attempts were made to use alum sludge as an Al source for producing $Al(OH)_3$. The process studied involved several steps such as acid treatment, precipitation, dissolution, separation and re-precipitation. Particularly investigated were the effects of two kinds of re-precipitation methods, namely the neutralization with an aqueous sodium bicarbonate ($NaHCO_3$) solution or with CO_2 gas, on the Al $(OH)_3$ products. Then, using the resultant $Al(OH)_3$ to produce LDH was explored.

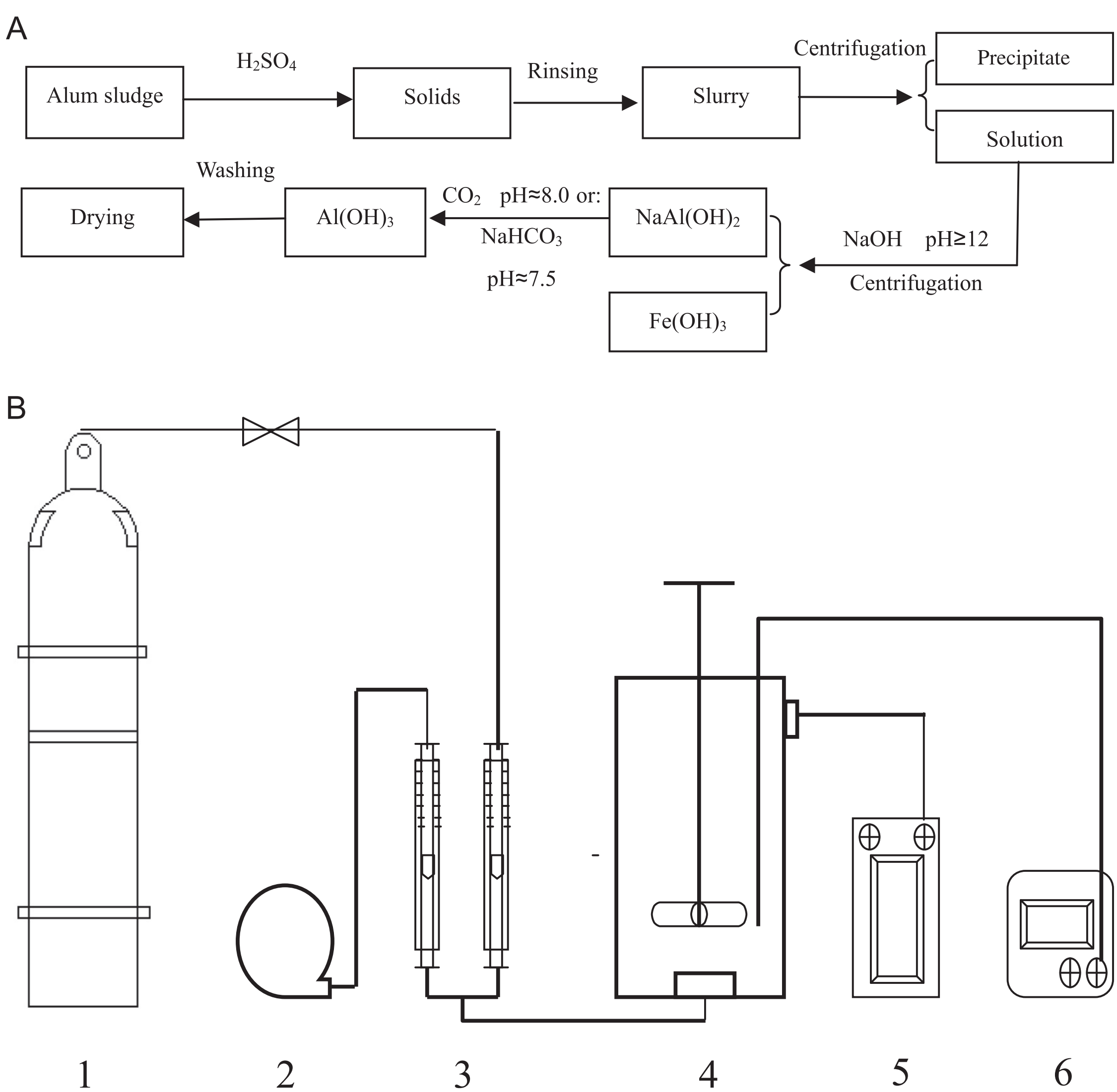

Fig. 1. The schematic drawings showing the utilization of alum sludge to produce aluminium hydroxide. (A) The flow chart. (B) The set-up for the re-precipitation process of aluminum hydroxide by using CO_2. (1-CO_2 cylinder, 2-Air compressor, 3-Rotameter, 4-Reactor, 5-water-bath heater, 6-pH meter.)