Chemical Engineering and Processing 104 (2016) 148–153

Contents lists available at ScienceDirect

Chemical Engineering and Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep

Accelerated desulphurization of waste lead battery paste in a high-gravity rotating packed bed

Peng Ning[a,b], Jun-Qing Pan[c], Xue Li[d], Yue Zhou[b], Jian-Feng Chen[a,b], Jie-Xin Wang[a,b,*]

[a] State Key Laboratory of Organic–Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, PR China
[b] Research Center of the Ministry of Education for High Gravity Engineering and Technology, Beijing University of Chemical Technology, Beijing 100029, PR China
[c] State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China
[d] Department of Chemical Engineering, The City College of New York, New York 10031, USA

ARTICLE INFO

Article history:
Received 25 August 2015
Received in revised form 4 March 2016
Accepted 9 March 2016
Available online 11 March 2016

Keywords:
Rotating packed bed reactor
Fast desulphurization
Intensified mass transfer
Lead paste
Lead sulfate

ABSTRACT

Pb-paste as the major composition in waste lead acid battery has an important role in the process of lead recycling. However, low liquid-solid mass transfer rates in conventional reactors have a significant limitation for the industrial application of Pb-paste desulphurization using hydrometallurgical process. In this paper, a cost-effective mass-transfer intensified approach for Pb-paste desulphurization with Na_2CO_3 solution in a rotating packed bed (RPB) reactor was presented. The effects of various variables on the desulphurization degree of $PbSO_4$ were firstly explored. The results indicated that the increases in rotating speed, Na_2CO_3 concentration and $Na_2CO_3/PbSO_4$ molar ratio were beneficial to the process. Temperature and reactant flow rate had obvious effects on the desulphurization degree only at a low reactant concentration. Further, the desulphurization processes of the simulated Pb-pastes were comparatively investigated. It was found that the RPB reactor markedly intensified the process in a very short contact time (about 1 s), thereby achieving a continuous desulphurization process. Only one cycle liquid-solid contact could make the desulphurization degrees of $PbSO_4$, anode powder and cathode powder reach 99.7%, 98.9% and 97.2%, respectively. Compared to a stirred tank reactor, the desulphurization time was greatly shortened by at least 2 orders of magnitude.

1. Introduction

Lead acid batteries have been widely applied in many fields such as automobile, energy storage, electric vehicles and many other fields [1–5]. Lead acid batteries which are improperly disposed of can corrode and pollute the soil and the ground water. Therefore, it is necessary to promote pathways for recycling them, which is related not only to the sustainable development of the industry of lead acid battery, but also the reduction of the lead pollution to the environment [6–9].

Damped batteries have a complex composition in waste product, which mainly includes $PbSO_4$ (50–60 wt%), PbO_2 (20–30 wt%) and PbO (5–15 wt%) [10–13]. Sulfur content in the paste is about 6%, which causes difficulties in the case of lead recycling processing. This usually requires preliminary desulphurization of the paste. Presently, the pyrometallurgical route has been commonly used for the treatment of waste lead acid battery. However, the problems associated with the use of high temperature beyond 1000 °C for decomposing and reducing $PbSO_4$ are to generate SO_2 emission besides lead fumes. Recently, hydrometallurgical approaches have been thus proposed to eradicate the environment problems. In these processes, sulfur composition in the lead paste can be converted to soluble sulphate by reacting with reagents such as sodium hydroxide, sodium carbonate or ammonium carbonate [13–19]. Sodium carbonate is the most frequently used desulphurization reagent. It involves conversion of lead sulfate to carbonate, hydroxocarbonate, $Pb_3(CO_3)_2(OH)_2$ in accordance with Reactions (1)–(3) [20].

$$PbSO_4(s) + Na_2CO_3(aq) = PbCO_3(s) + Na_2SO_4(aq) \quad (1)$$

$$3PbSO_4(s) + 4Na_2CO_3(aq) + 2H_2O = Pb_3(CO_3)_2(OH)_2(s) + 3Na_2SO_4(aq) + 2NaHCO_3(aq) \quad (2)$$

* Corresponding author at: State Key Laboratory of Organic–Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, PR China.
E-mail address: wangjx@mail.buct.edu.cn (J.-X. Wang).

http://dx.doi.org/10.1016/j.cep.2016.03.007
0255-2701/

$$2PbSO_4(s) + 3Na_2CO_3(aq) + H_2O = NaPb_2(CO_3)_2OH(s) + 2Na_2SO_4(aq) + NaHCO_3(aq) \quad (3)$$

The transition of sulphate ions into the liquid phase is based on the difference between ion products of lead sulphate and lead carbonate [13]. According to handbook data:

$K_{sp(PbSO4)} = 1.6 \times 10^{-8}; K_{sp(PbCO3)} = 3.3 \times 10^{-14}$

In this system, the desulphurization process is strongly affected by diffusion and mass transfer limitation of $PbSO_4$ and Na_2CO_3 due to high density of lead paste in a traditional reactor [10]. So a relatively high desulphurization degree could be reached only in a long processing time [10,13]. Obviously, it is significant to develop a reactor with high mass transfer efficiency for such a high density liquid-solid system.

Rotating packed bed (RPB) reactor, which can significantly intensify micromixing and mass transfer owing to the generation of a high-gravity environment of tens to hundreds of gravities from the action of centrifugal force, has been widely used in absorption, distillation, polymer devolatilization, nanoparticles preparation, etc. [21–25]. In the RPB, the fluids (even high viscosity systems of polymer and ionic liquid) going through the porous packing tend to be spread or split into very fine droplets, threads and thin films by strong shear force, thereby intensifying micromixing and mass transfer between fluid elements and solid particles [26–30]. Therefore, it is feasible to adopt a RPB reactor for the intensification of the mass transfer process between $PbSO_4$ and Na_2CO_3.In this paper, the intensified desulphurization of lead paste with the RPB reactor in a liquid-solid reaction system was firstly reported. The fast and continuous desulphurization of waste lead paste could be achieved after one cycle liquid-solid contact within a second in the RPB reactor. In addition, the effects of various operating variables were also explored on the desulphurization degree. The stirred tank reactor was used for comparison.

2. Experimental

2.1. Materials and experimental apparatus

Analytical reagent grade sodium carbonate, hydrochloric acid, eriochrome black T, ethylenediamine tetraacetic acid disodium salt (EDTA) and ethanol were purchased from Beijing chemical works of China. Lead sulfate was supplied by Tianjin Fuchen chemical works of China. The simulated anode (positive electrode) powder of damped lead acid battery paste consisted of 40 wt% $PbSO_4$ and 60 wt% PbO_2, while the simulated cathode (negative electrode) powder consisted of 40 wt% $PbSO_4$, 30 wt% PbO and 30 wt% Pb. Deionized water was obtained from a water purification system (RO-DI plus, Hi-tech, PRC).

The experimental setup for the intensified desulphurization of $PbSO_4$ or lead paste was schematically shown in Fig. 1. The RPB reactor mainly consisted of a packed rotator, a fixed casing, an inlet for Na_2CO_3 solution and an inlet for $PbSO_4$ or lead paste suspension. The inner diameter, the outer diameter and the axial length of the rotator were 36 mm, 84 mm and 18 mm, respectively. The distributor consisted of two pipes, each having a slot (3 mm in width and 10 mm in length) which just covers the axial length of the packing section in the rotator. The bed was packed with stainless wire meshes, whose porosity and surface area were 0.90 and 850 m^2/m^3, respectively. The packing consisted of 20 layers. The rotator was installed inside the fixed casing and rotated at a tunable rotating speed. More details about the RPB reactor could be seen in our previous work [24].

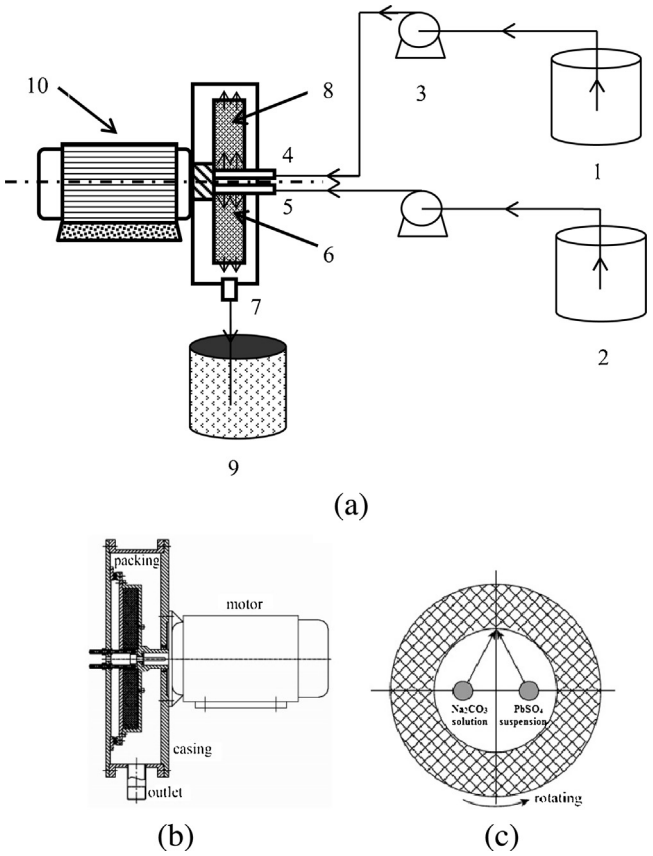

Fig. 1. (a) Scheme of experimental setup (1, A storage for Na_2CO_3 solution; 2, A storage for $PbSO_4$ or lead paste suspension; 3, Pump; 4, Solution inlet; 5, Suspension inlet; 6, Liquid distributor; 7, Product outlet; 8, Mesh packing; 9, Product storage; 10, Electromotor). (b) Structure of RPB. (c) Illustration of the fluid pattern of the desulphurization process within RPB.

2.2. The intensified desulphurization process

The intensified desulphurization process of $PbSO_4$ or lead paste was performed in the RPB reactor as follows. Firstly, a certain amount of $PbSO_4$ (lead paste) and Na_2CO_3 with $n(Na_2CO_3)/n(PbSO_4)$ of 1.2 were respectively added in deionized water to form $PbSO_4$ (lead paste) suspension and Na_2CO_3 solution with a concentration of 0.825 mol/L. $PbSO_4$ (lead paste) suspension was pre-stirred for 1 min by a homogenizer with a speed of 9000 rpm because of its high density to be conveniently feed. Subsequently, 500 mL of Na_2CO_3 solution and 500 mL of $PbSO_4$ (lead paste) suspension with the same flow rate of 1100 mL/min from their reservoirs were simultaneously pumped into the RPB reactor with a high rotating speed of 1500 rpm. Liquid and solid streams were sprayed onto the inside edge of the rotator through a slotted pipe distributor, and had a vigorous contact, mixing and reacted in the packing. Finally, the as-obtained suspension was collected from the outlet of the RPB. 20 mL of the sample was taken, followed by the centrifugation at 4000 rpm for 10 min. 10 mL of the supernatant liquid was obtained for the analysis of the desulphurization degree. The product was separated from the mother liquor by filtration, washed with deionized water and ethanol, and then dried in a vacuum drying oven at 90 °C for 10 h for XRD analysis.

For a comparison, the similar desulphurization process was performed in a stirred tank reactor (STR). Firstly, $PbSO_4$ (lead paste) suspension was also pre-stirred for 1 min by a homogenizer with a speed of 9000 rpm. 500 mL of Na_2CO_3 solution with the same concentration of 0.825 mol/L was then rapidly added into 500 mL of the above suspension with the same $n(Na_2CO_3)/n(PbSO_4)$ of