



Preparation of lead carbonate from spent lead paste via chemical conversion



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ABSTRACT

Lead paste generated from spent and discarded lead acid battery has been converted to lead carbonate and lead oxides with a view to investigate a method for minimizing environmental pollution associated with spent lead paste recycling. The process includes four steps: namely desulfurization, leaching, carbonation and calcination, presented in the details as the follows. (1) In a spent lead paste, lead sulfate is the major component and is accompanied by lead oxides and metallic lead. On reacting the paste with $(\text{NH}_4)_2\text{CO}_3$, the PbSO_4 is converted to lead carbonate with $(\text{NH}_4)_2\text{SO}_4$, generated as a by-product. (2) The desulfurized paste consisting of lead carbonate and the unreacted lead oxides are then leached with an aqueous solution of nitric acid and H_2O_2 . At a molar ratio of H to Pb > 2.5 and at a slurry density of $100 \text{ g} \cdot \text{L}^{-1}$, the extraction yield of lead from the paste into the aqueous solution is achieved up to 98.0%. (3) In the next step, the Pb (II) in the leaching solution is converted with the addition of Na_2CO_3 (aq) into a lead carbonate precipitate. It was found that under optimal conditions more than 99.9% of Pb can be extracted from the leaching solution into the solid lead carbonate phase. (4) In the final step, the lead carbonate is readily converted by thermal decomposition at a relatively low temperature of 350–450 °C into lead monoxide (PbO) or lead tetroxide powders (Pb_3O_4) that can serve as precursor for making new lead paste and other lead products.

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1. Introduction

Lead is a hazardous element in the environment. Many of its favorable physical and chemical properties such as softness, malleability, ductility, high density, conductivity and corrosion resistance, have resulted in the widespread applications of lead. Lead compounds have also been widely used for a great variety of applications such as in lead battery pastes, matches, pyrotechnics, X-ray absorbing coatings, ceramic glazes and lead glasses. In the past 15 years, the core of the international lead market has shifted to China. China has become the largest producer and the largest consumer of raw and refined lead. Lead-acid battery is still the largest field of demand accounting for over 80% of the total lead consumption in 2010 (Zhu et al., 2010). With increasing production of lead-acid batteries and growth of cars and electric scooters in emerging economies, the issues for dealing with discarded lead-acid batteries have become a focus of serious attention, because of lead's well documented environmental hazardousness (Lyakov et al., 2007).

Spent lead-acid battery comprises four main parts: grids, paste, polymer containers, and waste acid. Among these, treatment of spent lead paste is the most difficult process. Lead paste is a mixture of metallic

lead and its compounds with the following composition range: 50–60 wt.% of lead (II) sulfate, 20–30 wt.% of lead (IV) dioxide, 5–15 wt.% of lead (II) monoxide and 1–2 wt.% metallic lead (Chen and Dutrizac, 1996; Ferracin et al., 2002). Lead paste can be separated from lead grid by physical separation methods. Currently, spent lead-acid battery paste is converted into metallic lead by conventional pyrometallurgical processes. A major drawback with pyrometallurgical methods of lead production from secondary materials is associated with the undesirable emissions of harmful sulfur oxides and lead containing particulates (Bernardes et al., 2004; Kreusch et al., 2007; Lyakov et al., 2007; Rabah and Barakat, 2001).

The management of hazardous waste is seen as a serious challenge in all regions of the world and governed by Basel Convention (Duan et al., 2011). Given the environmental concerns with the pyrometallurgical processes, increasing attentions to hydrometallurgical processes have been devoted in recent years. Several researches, pilot plants and commercial methods have been advanced to overcome the stated problems, especially with respect to the SO_x emissions and lead containing particulates (arising from elevated temperatures > 800 °C) encountered in the smelting route. The hydrometallurgical methods typically convert sulfur in the paste into soluble sulfates by reacting the lead sulfate with reagents such as NaOH and Na_2CO_3 in aqueous solutions (Arai and Toguri, 1984; Gong et al., 1992a, 1992b; Lyakov et al., 2007; Prengaman et al., 2001; Volpe et al., 2009). Lead is converted into insoluble $\text{Pb}(\text{OH})_2$ or PbCO_3 and collected as sludge or filter cake which is

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then dissolved in powerful acids such as H_2SiF_6 or HBF_4 in order to recover lead by electrowinning. Electrowinning is capital intensive and is often suitable only for large scale operations, thus entailing large transportation of hazardous raw materials (Olper, 1993; Prengaman, 1995). Although the purity of the electrodeposited lead is high at 99.99%, only 1/3rd proportion of pure lead is required for grid application and a larger proportion (66%) of lead is re-oxidized (e.g. in Barton mill or hot ball mill) to form PbO powder for preparation of paste materials for making new batteries.

Development of low cost and eco-friendly technologies should be encouraged in order to further develop the recycling operation, which will not only meet the increasing demand for lead but also conserve raw materials. Methods based on direct leaching of lead paste under hydrothermal conditions have been given considerable attentions. An environmental-friendly method based on leaching of the spent paste with citric acid followed by a low temperature calcinations route for directly converting the paste into PbO has been recently reported (Kumar et al., 2006; Sonmez and Kumar, 2009a, 2009b). Issues concerning separating and recovery of the leaching solution and the availability and costs of the leaching agents of citric acid still need resolving. Schwartz and Etsell (1998) have examined the possibility of recovering metallic lead from ammoniacal ammonium sulfate (AAS) solutions via cementation, using Ni powder as a reductant. Lee (2009) has attempted to prepare pure lead carbonate from lead sulfide dust (PbS) using a hydrometallurgical process.

The objective of this work is to develop a novel process for recovering Pb directly as lead carbonate or lead oxide directly from lead paste via chemical conversion. The flowsheet of the process is shown in Fig. 1. As shown in Fig. 1, the suggested process consists of four main steps. In the first step, lead (II) sulfate part of the lead paste is desulfurized and converted into lead (II) carbonate, which exists with other unreacted components (namely Pb, PbO and PbO_2), is separated from the filtrate. The ammonium sulfate in the solution is recovered as a by-product. In the second step, the desulfurized paste (containing lead carbonate, and unreacted metallic lead, PbO and PbO_2) is leached with aqueous solution of nitric acid and H_2O_2 . The hydrogen peroxide is used to reduce Pb(IV) dioxide to Pb(II) oxide. Lead carbonate and the lead oxides are converted to lead nitrate which is soluble. A small quantity of residue (including metallic lead, lead sulfate, diaphragm paper, et al.) does not leach into this solution and is separated by filtration and can be remelted, refined and alloyed with the grid components. In the third step, sodium carbonate is added into the leach liquor to convert the dissolved lead nitrate into lead carbonate which is then precipitated out. In the final step, the lead carbonate is readily converted into lead monoxide (PbO) or lead tetroxide powders (Pb_3O_4) by thermal decomposition at a relatively low temperature of 350–450 °C.

2. Experimental

2.1. Reactants and raw materials

Lead paste used in the work was provided by Hubei Jinyang Metallurgical Incorporated Co., Ltd, China, a company specializing in the recovery of spent and discarded spent lead-acid battery. In laboratory, the powders were then washed with distilled water to remove any remaining sulfuric acid until the pH value of washed water was above 6.5. The sample was selected from the dried reddish powder by a sieve with the size of less than 120 meshes (corresponding to 125 μm). Then chemical analysis and hydrometallurgy leaching were conducted by using part of the paste whose particle size is less than 125 μm , which accounts for 80% by mass.

An aqueous solution of ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$, 99% purity, Sinopharm Chemical Reagent Co., Ltd, China) was used as the desulfurizing agent to react with PbSO_4 in the paste. Aqueous solutions of nitric acid (HNO_3 , 99% purity, Sinopharm Chemical Reagent Co., Ltd, China) and acetic acid (CH_3COOH , 99% purity, Sinopharm Chemical

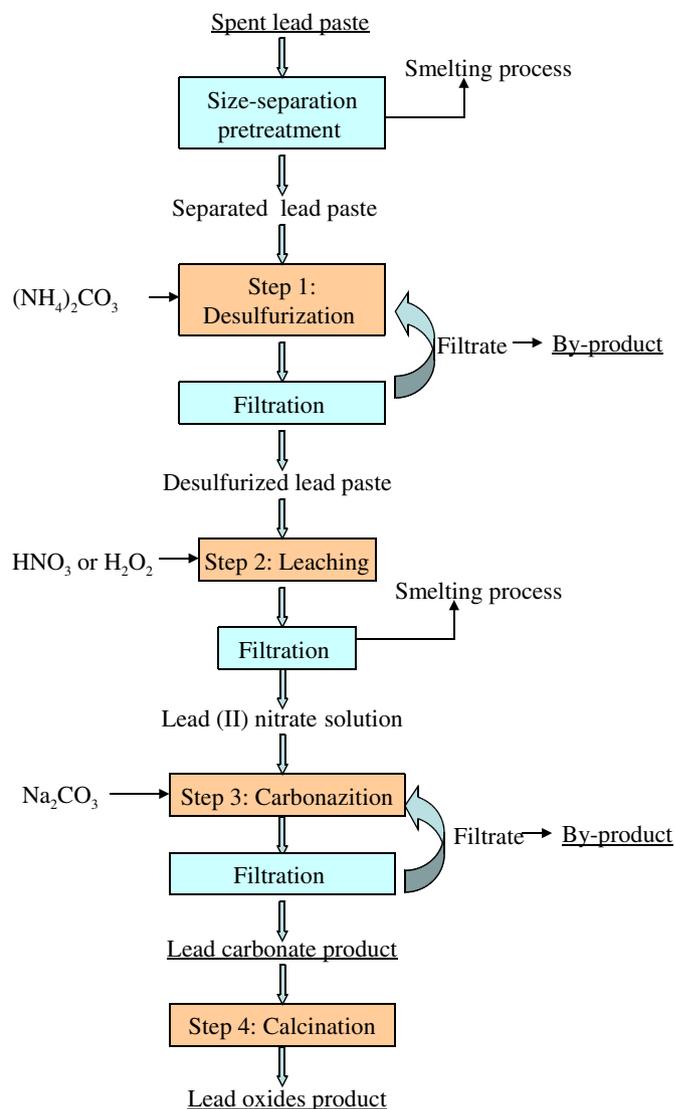


Fig. 1. Schematic flowsheet of the novel process for lead paste.

Reagent Co., Ltd, China) were used as leaching agents for the lead compounds. Hydrogen peroxide (H_2O_2 , 30% w/v, Sinopharm Chemical Reagent Co., Ltd, China) was used along with the acids in order to reduce lead dioxide to lead monoxide. Sodium carbonate (Na_2CO_3 , >99% purity, Tianjin Kerme Chemical Reagent Co., Ltd, China) was used as the carbonation agent for treating the lead nitrate solution.

2.2. Desulfurization of lead paste

100.0 g of the separated fine lead paste was added to ammonium carbonate aqueous solutions of varying concentrations. After completion of the desulfurization reaction, the filtered solids were washed with distilled water, then filtered again and then dried at 60 °C to get a desulfurized filter cake. High-frequency Infrared Carbon & Sulfur Analyzer (HCS-140, Shanghai DeKai Instrument Co., Ltd, China) was used to check for any remaining sulfur in desulfurized paste.

2.3. Leaching of desulfurized paste

Leaching of the desulfurized paste (20.0 g) was carried out at room temperature with 200 mL of nitric or acetic acid (aqueous) solution. Hydrogen peroxide (30% w/v) was added in order to reduce lead (IV) compounds into lead (II) compounds. At the end of the leaching

process, any unreacted or any precipitated product was filtered and the lead content in the filtrate was analyzed by titration with EDTA. Then the solid phase was washed with distilled water and dried at 100 °C.

The extraction yield of lead was calculated according to Eq. (1).

$$\text{Extraction yield of lead} = (V_1 \times C_2) / (W_1 \times C_1) \times 100\% \quad (1)$$

Where W_1 (g) is the mass of the desulfurized paste, V_1 (L) is the volume of leaching solution, C_1 (wt.%) is the percent of lead in the desulfurized paste, C_2 ($\text{g} \cdot \text{L}^{-1}$) is the lead concentration in the leaching solution.

2.4. Carbonation of lead nitrate solution

For the carbonation step, a specific amount of Na_2CO_3 was added into 200 mL leaching solution of lead nitrate (lead concentration of $7.5 \text{ g} \cdot \text{L}^{-1}$) in a 500 mL beaker under constant stirring with a magnetic stirrer. In this step, white lead carbonate was formed as a precipitate. After carbonation, the solid product of lead carbonate was filtrated through ordinary qualitative filter paper, and dried at 100 °C. The lead in the filter after carbonation conversion was analyzed by AAS (WFX-180, Beijing Beifen-Ruili Analytical Instrument (Group) Co. Ltd. China). The carbonation ratio of lead nitrate was calculated according to Eq. (2)

$$\text{Carbonation ratio} = [1 - (V_3 \times C_4) / (V_2 \times C_3)] \times 100\% \quad (2)$$

Where V_2 (L) is the volume of the leaching solution before carbonation; V_3 (L) is the volume of the filter after carbonation conversion; C_3 ($\text{mg} \cdot \text{L}^{-1}$) is the concentration of lead in the leaching solution before carbonation; C_4 ($\text{mg} \cdot \text{L}^{-1}$) is the concentration of lead in the filter after carbonation conversion.

2.5. Calcination of lead carbonate

The resulting lead carbonate powder was heated in air, at a heating rate of $5 \text{ }^\circ\text{C} \text{ min}^{-1}$ and calcined at 350 °C or 450 °C for 1 h. Calcination temperature was determined based on the literature (Karami et al., 2008). The weight loss was measured for each set of the experiment.

2.6. Material characterization

X-ray diffraction (XRD) data were collected from desulfurized paste, lead carbonate products and the final calcined products using a X'Pert PRO XRD (Philips, PANalytical B.V., Holland) with $\text{Cu K}\alpha$ radiation and $\lambda = 1.5418 \text{ \AA}$ at scanning rate of 0.28° per second for 2θ from 5° to 75° . Morphologies of the lead carbonate and the final calcined products were investigated by scanning electron microscopy (Sirion 200 SEM, FEI, Holland) operated at 10 kV after coating the samples with gold.

3. Results and discussion

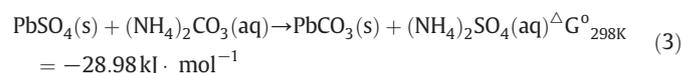
3.1. Desulfurization of lead paste

Desulfurization experiments of lead paste were carried out under the optimized conditions as described in another paper (Zhu et al., 2012). Some optimization parameters were determined with reference to our preliminary experiments and previous literatures (Arai and Toguri, 1984; Gong et al., 1992a, 1992b; Prengaman, 1995).

The desulfurization was performed in a baker immersed in a thermostatic water bath under mechanic agitation to keep solid particle suspension during conversion experiments. 100 g of the separated fine lead paste was added to desulfurization solutions of specified concentration. Accordingly, the desulfurization experiments were carried

out at 35 °C, at a solid/liquid ratio (w/v) of 1:10, and a desulfurization time of 120 min. The results from the desulfurization experiments of the lead paste starting with an initial stoichiometric molar ratio of $\text{CO}_3^{2-}/\text{SO}_4^{2-}$ concentration, showed that desulfurization efficiency increased with increase of molar ratio of $\text{CO}_3^{2-}/\text{SO}_4^{2-}$ achieved by adding further amounts of $(\text{NH}_4)_2\text{CO}_3$. A maximum desulfurization efficiency of around 99.0% was achieved at a molar ratio of $\text{CO}_3^{2-}/\text{SO}_4^{2-}$ of 2. The sulfate ion concentration of the paste was only 0.05% after 60 min desulfurization treatment, which could be satisfactory in the following hydrometallurgical process of desulfurization.

The solubility product constant of PbCO_3 and PbSO_4 is 3.3×10^{-14} and 1.06×10^{-8} , respectively; PbCO_3 is much more insoluble than PbSO_4 . The desulfurization can be summarized as Eq. (3).



The reaction has large driving force and does occur readily as shown by the results in this work.

It was found that PbCO_3 and PbO_2 phases were predominant in the desulfurized lead paste as shown in the XRD pattern (Fig. 2), indicating that most of the PbSO_4 had been converted into PbCO_3 and soluble $(\text{NH}_4)_2\text{SO}_4$. The content of PbO_2 in desulfurized paste was 31.3%, and the total lead content of desulfurized paste was 79.8% (see Table 1).

3.2. Leaching with acid

The desulfurized paste was then leached at ambient temperature ($\sim 25 \text{ }^\circ\text{C}$) with nitric acid and/or acetic acid. A number of factors were found to influence the leaching efficiency. The following parameters were investigated for each of the leaching acid: the molar ratio of acid to total lead (referred to as molar ratio of H/Pb), concentration of the acid, the molar ratio of hydrogen peroxide to lead (IV) dioxide (referred to as molar ratio of $\text{H}_2\text{O}_2/\text{PbO}_2$), solid to liquid phase ratios (w/v), and leaching time.

3.2.1. Effect of type of acid

The results for the leaching experiments are shown in Fig. 3. It was found that HNO_3 is more effective for leaching of desulfurized paste than CH_3COOH . The major components in desulfurized paste, i.e., PbCO_3 , PbO can react with nitric acid. PbO_2 can also react in the

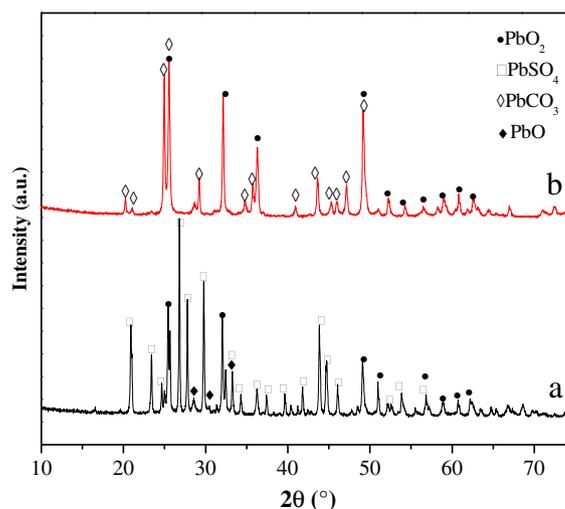
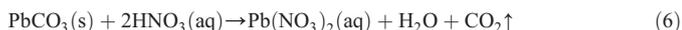
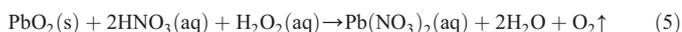
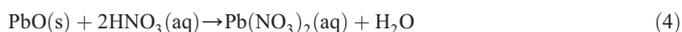


Fig. 2. XRD patterns of (a) the starting lead paste (from industry) and (b) desulfurized paste.

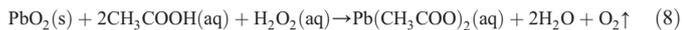
Table 1
Chemical compositions of the lead paste specimen (wt.%).

Compound	As-received battery paste	Desulfurized paste
PbO ₂	29.5	31.3
PbSO ₄	60.5	1.0
Total lead	75.6	79.8

presence of H₂O₂. The leaching reactions for each of the component in the desulfurized paste are suggested as shown Eqs. (4)–(6).



The reactions of lead paste with acetic acid may be probably given as Eqs. (7)–(9).



For a molar ratio of H/Pb = 2.5, and a leaching time of 60 min, extraction yield of lead with HNO₃ and CH₃COOH was 97.8% and 92.0%, respectively (shown in Fig. 3). The reason is that HNO₃ is stronger and more acidic than an equal concentration of CH₃COOH. Therefore, HNO₃ is considered a suitable leaching agent for leaching the desulfurized paste into an aqueous solution and more preferable than acetic acid.

3.2.2. Effect of molar ratio of H/Pb

Fig. 4 presents the variation of leaching efficiency of Pb with molar ratio of acid to total lead at a solid density of 100 g · L⁻¹. As shown in Fig. 4, when the molar ratio of H/Pb increased from 1.5 to 2.5, extraction yield of lead increased considerably. However, extraction yields remained nearly constant at H/Pb molar ratios greater than 2.5. Lead extraction increased with the increasing acid concentration. At an acid concentration of 0.95 mol · L⁻¹ HNO₃ solution are higher (while

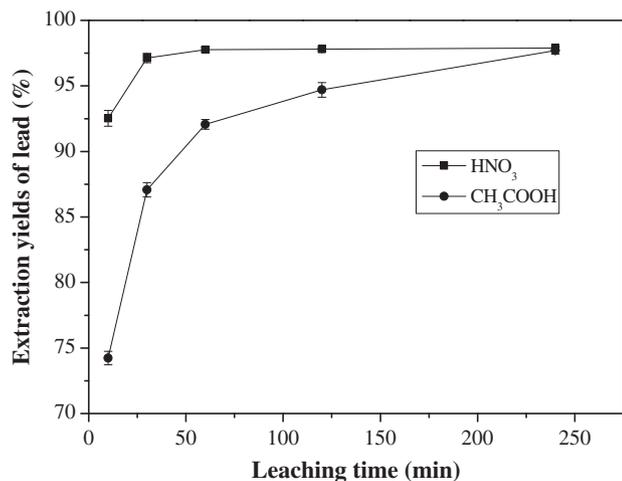


Fig. 3. Comparison of extraction yield of lead between nitric acid and acetic acid for dissolving of Pb from desulfurized paste (temperature 25 °C, solid/liquid phase ratios (w/v) 1/10, molar ratio of H/Pb 2.5).

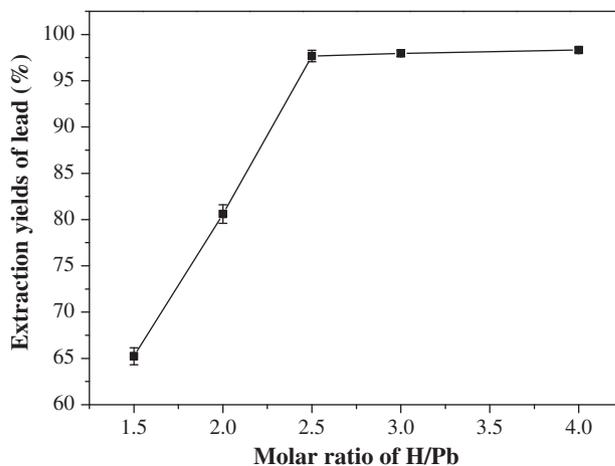


Fig. 4. Effect of molar ratio of H/Pb (nitric acid) on extraction yield of lead from desulfurized paste (temperature 25 °C, phase ratios (w/v) 1/10, leaching time 30 min).

keeping the molar ratio of H/Pb at a constant value of 2.5), 98.5% of lead was leached as shown in Fig. 4. In further application, a HNO₃ solution of 0.95 mol · L⁻¹ may be suggested as the optimum concentration. Thus the optimum amount of nitric acid as given by the H/Pb ratio of 2.5 is greater than the stoichiometric ratio of 2 for the suggested reactions.

3.2.3. Effect of H₂O₂ dosage

Hydrogen peroxide acts as the reductant for PbO₂ thus facilitating leaching of Pb(IV) (Sonmez and Kumar, 2009a). Fig. 5 demonstrates the lead extraction by leaching with various dosages of hydrogen peroxide. It can be seen from Fig. 5 that extraction yields of lead increased with the increase of hydrogen peroxide dosage until the molar ratio of hydrogen peroxide/PbO₂ reached a value of 2, twice the value as required by stoichiometry. Oxygen gas is generated from the reduction reaction of hydrogen peroxide with PbO₂ and can be visibly observed as rising bubbles from the aqueous phase. The in-situ stirring effect can further help increase the reaction efficiency with the increase in its concentration. The extraction yield of lead did not increase any further beyond molar ratio of hydrogen peroxide/PbO₂ at 2.

3.3. Carbonation of lead nitrate solution

The lead nitrate solution has been obtained by leaching of desulfurized paste as discussed previously. There are many ways to recover lead from the lead nitrate solution. The crystalline salt of lead

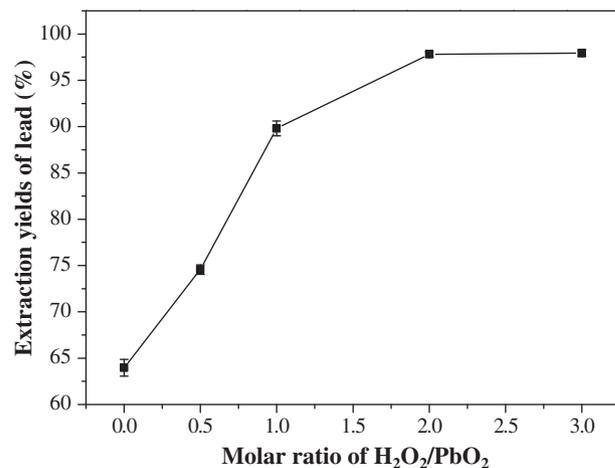


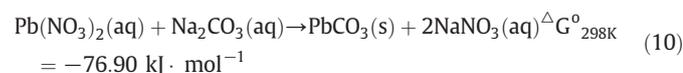
Fig. 5. Effect of the concentration of H₂O₂/PbO₂ molar ratios on extraction yield of lead from desulfurised solids (temperature 25 °C, phase ratios (w/v) 1/10, leaching time 60 min, molar ratio of H/Pb 2.5).

nitrate can be obtained by an evaporation method and further purified by the recrystallization technique. Karami et al. (2008) discussed the synthesis of nano-structured lead oxide through reaction of lead nitrate solution and sodium carbonate solution by the sonochemical method. Nano-structured lead oxide can be produced at the temperature of 320 °C from lead carbonate.

In this process, carbonation of lead nitrate solution was carried out by a precipitation reaction where the slurry was made by dispersing carbonate particles into the solution. As shown in Fig. 6, carbonation ratio reached more than 99.9% at the mole ratio of $\text{CO}_3^{2-}/\text{Pb}^{2+}$ of 1.5.

Fig. 7 shows the effect of carbonation time on the carbonation ratio of lead nitrate. As shown in Fig. 7, a conversion ratio of 97% for carbonation was obtained for a molar ratio of 1.5 for $\text{CO}_3^{2-}/\text{Pb}^{2+}$ with a duration time of 10 min. The carbonation ratio increased with the increase of carbonation time and 99.8% of lead can be carbonated at 30 min.

The solubility constant of PbCO_3 is only 3.3×10^{-14} , while $\text{Pb}(\text{NO}_3)_2$ is highly soluble in aqueous solutions. The carbonation can be summarized as Eq. (10).



According to the thermodynamics analysis result, the reaction is thermodynamically feasible in the carbonation process. The carbonation conversion reaction has large driving force and does occur readily as shown by the results in this work.

For the carbonation of lead nitrate in the solution, the required minimum pH was 8.0. Carbonized precipitation product was filtered and dried at 100 °C. The XRD pattern of the product is shown in Fig. 8, which is a pure lead carbonate pattern according to the standard card (JCPDS File No. 70–2052) (Criado et al., 1982). The SEM image of the product of lead carbonate is shown in Fig. 9. As shown in Fig. 9, the distribution of particle size is within the range of 0.1–1 μm .

The XRD patterns of the calcined products from lead carbonate are shown in Fig. 10. The results showed that the lead carbonate decomposed completely at the temperatures of 350 °C when held for 1 h. As shown in Fig. 10(a), the lead carbonate has been converted to a crystalline phase of orthorhombic α -PbO (JCPDS File No.87-0604) (Yang et al., 2012; Živković, 1979). When the calcination temperature was 450 °C, lead tetroxide (Pb_3O_4 , JCPDS File No.08-0019) (Munson and Riman, 1991), was formed, as shown in Fig. 10(b).

The SEM images of the calcined products from lead carbonate are shown in Fig. 11. The SEM images showed the changes of morphologies of the calcined products at different temperatures. As shown in

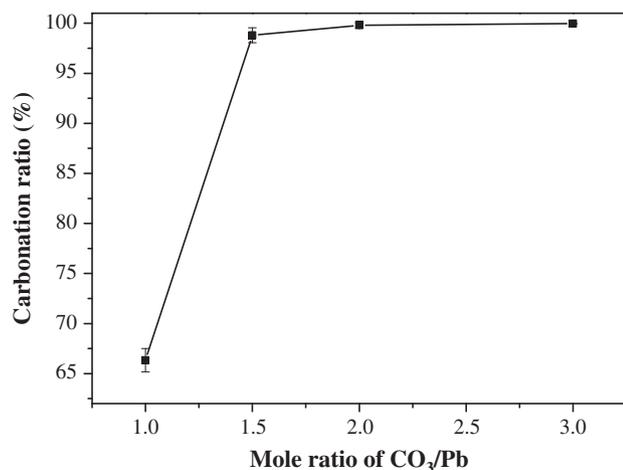


Fig. 6. Effect of the molar ratio of CO_3/Pb on carbonation ratio (carbonation time 30 min, temperature 25 °C).

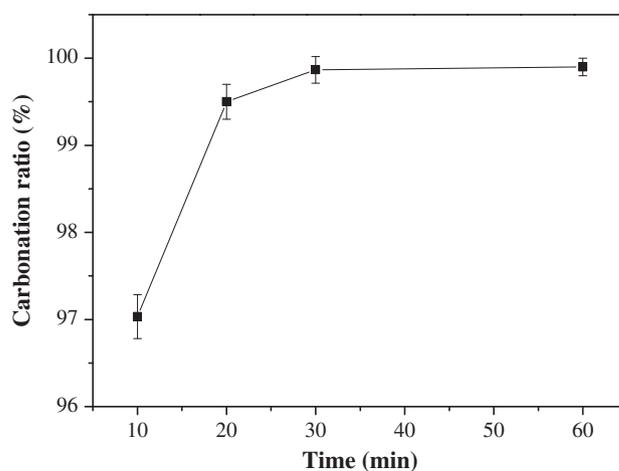


Fig. 7. Carbonation ratio with different reaction time (mole ratio of CO_3/Pb 1.5, temperature 25 °C).

Fig. 11(a), the morphology of the calcined products at 350 °C showed crystals in the size of 200–500 nm. When the calcination temperature was 450 °C, the particles became smaller with the size of 200–300 nm, as shown in Fig. 11(b).

The spent lead paste can be used to produce lead oxides powders after simple chemical conversion steps. The lead oxides powders calcined at a relatively low temperature is of high-purity at over 99.9%. This simple recycling method for waste lead acid battery paste has a positive effect on the recovery of lead oxide from the starting materials of spent lead paste. Lead oxides could be directly used as the active substances for new lead-acid batteries.

4. Conclusions

A research investigation for the preparation of lead carbonate product and lead oxide product from lead paste spent lead acid battery has been performed using a novel process. Lead paste was desulfurized with ammonium carbonate solution, and then lead sulfate in the paste was converted into lead carbonate and ammonium sulfate. The lead carbonate is separated as insoluble solid along with the unreacted lead oxides and metallic lead. The desulfurized solid lead paste was then leached with nitric acid, optimally at a H/Pb molar ratio of 2.5. Hydrogen peroxide was also used as a reductant in the leaching step in order to facilitate the dissolution of PbO_2 by a reduction reaction of Pb(IV) to Pb(II). In the 3rd step, the lead nitrate in the solution was carbonated

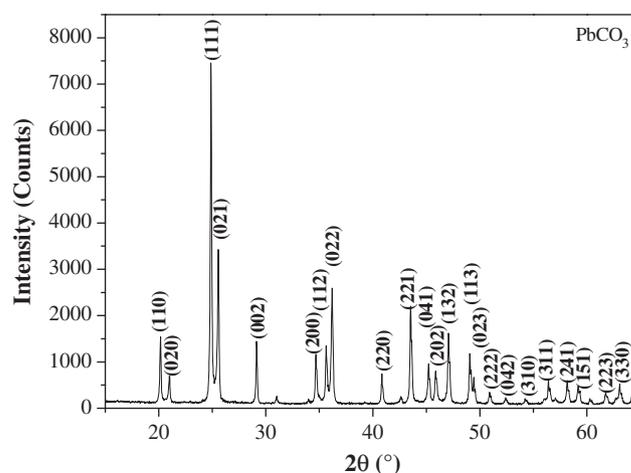


Fig. 8. XRD pattern of the lead carbonate product.

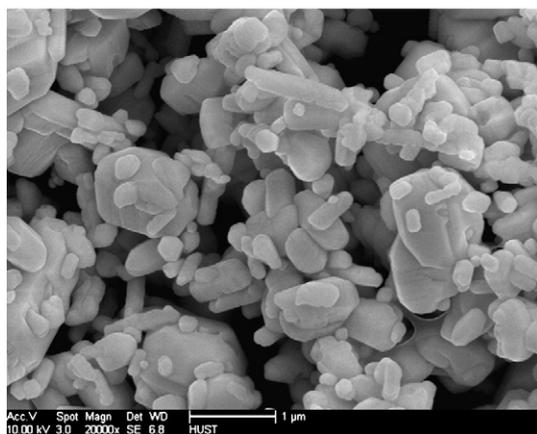


Fig. 9. SEM image of the lead carbonate product.

into a solid insoluble phase of lead carbonate, PbCO_3 . Over 99.9% of lead could be extracted from the lead nitrate solution. The lead carbonate was shown to convert into PbO (containing some Pb or Pb(IV)) as a precursor for making new pastes. A new cleaner flowsheet for recovering lead from lead paste is also proposed. This process may complement other hydrometallurgical-calcinations processes being currently developed (Li et al., 2012; Yang et al., 2011, 2012) depending upon the local and/or global availability and relative costs of competing reagents.

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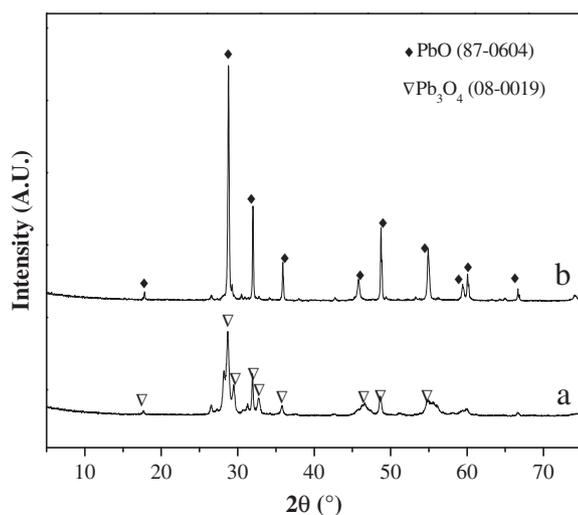


Fig. 10. XRD patterns of calcined products from the lead carbonate at different temperatures in air: (a) 350 °C, (b) 450 °C.

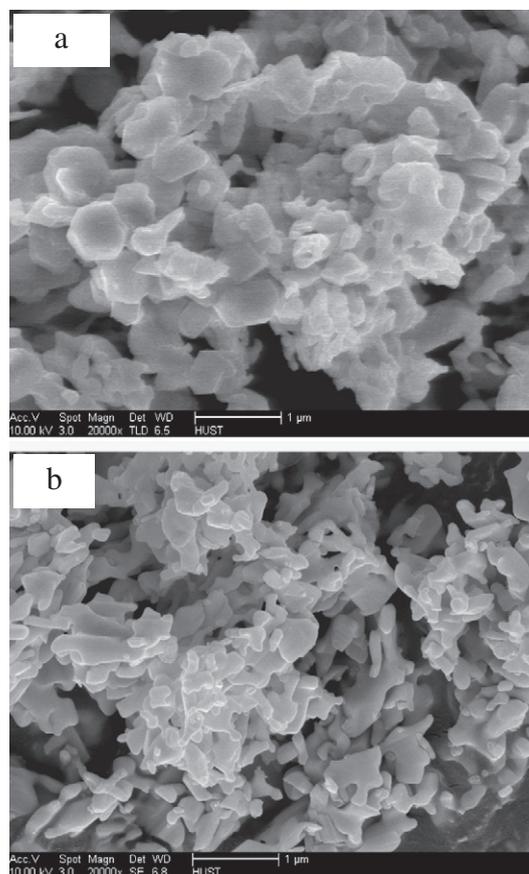


Fig. 11. SEM images of calcined products from the lead carbonate at different temperatures in air: (a) 350 °C, (b) 450 °C.

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