Conversion of lead chloride into lead carbonate in ammonium bicarbonate solution

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ABSTRACT

This study aimed to characterize the kinetics and mechanism of the phase transformation from lead chloride to lead carbonate in ammonium bicarbonate solution. The dechlorination rate of $PbCl_2$ was consistently high: it increased with increasing concentrations of NH_4HCO_3 and decreased only moderately with the increasing total concentration of Cl^- in the solution. The rate also increased systematically with increasing temperatures, and the apparent activation energy was 14.363 kJ/mol. The reaction obeyed the shrinking-core model, which involved diffusion through the thickening product layer formed on the $PbCl_2$ particles. The pH of the leaching solution strongly influenced the conversion results. A reduction in the pH led to a decrease in the dechlorination rate owing to the conversion of the carbonate ions into slowly reacting bicarbonate species. In contrast, an increase in the pH from 11.0 to 12.0 by the use of ammonium hydroxide led to a significant increase in the conversion rate of $PbCl_2$; the main conversion products were $Pb_3(CO_3)_2(OH)_2$ and $PbCO_3$, with a high conversion rate of around 99%.

1. Introduction

Lead found in the environment has become a global issue of concern owing to its toxicity to organisms and its large anthropogenic input to the environment. Additionally, large amounts of lead-bearing residues are produced annually in the engineering industry (Jha et al., 2012), especially in metallurgical plants (Turan et al., 2004; Şahin and Erdem, 2015). However, a pyrometallurgical process offers the advantages of high efficiency and solidification of dangerous elements, which are important for lead residue disposal. Studies have been conducted on the extraction of lead using a sinter-blast furnace or dross or a short-rotary furnace from lead-bearing residues via oxidation and reduction pyrometallurgical processes (Zheng et al., 2015; Chen et al., 2015).

In industry, chlorine is commonly used as a reactant with most metals, oxides, and sulfides, and it exhibits high activity in certain chemical reactions. However, chlorides have a lower melting point and higher volatility than sulfides and oxides and can be dissolved in aqueous solutions. These properties are advantageous for achieving effective metal separation, extraction, and refinement (Ojeda et al., 2002, 2009). Liu et al. (2010) reported that during the process of chlorine metallurgy, lead chloride was formed from lead concentrate, residue, and dust and easily emitted because of volatilization. However, direct

smelting of lead chloride by pyrometallurgical processes is difficult. Additionally, use of such processes can result in corrosion of the smelting furnace (Barbin et al., 2002). Hence, in practice, conversion of lead chloride should be performed before smelting.

Some previous works investigated the reaction between $PbSO_4$ and aqueous Na_2CO_3; they reported that the reaction could be completed within 30 min at 20 °C or within 15 min at 50 °C (Morachevskii et al., 2001; Arai and Toguri, 1984; Ning et al., 2016; Zhang et al., 2016). Gong et al. (1992a, 1992b) and Lyakov et al. (2007) thoroughly established details of the reaction kinetics and reaction product formation in their works. The latter group noted that the reaction obeyed the shrinking-core model, which involved diffusion through the product layer formed on the particles. The reaction rate increased with increasing concentrations of Na_2CO_3 and decreased with increasing concentrations of the reaction product Na_2SO_4. The rapid nature of the reaction between $PbSO_4$ and aqueous Na_2CO_3 is well known. Additionally, Lu and Chen (1986) examined the reaction between PbS and $(NH_4)_2CO_3$; they found that Pb could precipitate out as $PbCO_3$, yielding high conversion ratios of > 90%. Additionally, > 80% of sulfur was oxidized to elemental sulfur.

However, the disposal process of waste residues containing $PbCl_2$ is not yet well established, because it involves complex treatment

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processes and high costs. Chen et al. (2011) investigated the removal of chloride from electric arc furnace dust. Though sulfation roasting is more efficient in reducing chloride content than are other roasting processes, dechlorination of the remaining water-insoluble substance is difficult. Lin et al. (2013) described a longer process for the conversion of $PbCl_2$ in solution containing NaCl and HCl. In this process, PbOHCl was first precipitated out by adding NaOH, and lead carbonate was obtained by increasing the concentration of NH_4HCO_3. In another study, Tsugita (2003) reported that lead chloride could be converted directly in the presence of CO_3^{2-}. However, in our exploratory experiments, we noted that the conversion rate was low and the conversion products were impure when Na_2CO_3 was used as a conversion reagent, because of the uncontrollable and vigorous reaction between CO_3^{2-} and Pb^{2+}.

As an alternative, NH_4HCO_3—which is typically used as buffering agent—can yield CO_3^{2-} gently in alkaline solution and can thus overcome the above drawbacks. Thus, the aim of the present work is to develop a new and effective method to directly convert $PbCl_2$ into $PbCO_3$ in NH_4HCO_3 solution for the disposal of $PbCl_2$-bearing slag in a smeltery and to promote chlorine metallurgy methods. The kinetics and mechanism of the phase transformation of lead chloride in ammonium bicarbonate solution were examined. The reaction products were systematically determined at different pH values, and correlations between the various products obtained and the reaction conditions employed were established.

2. Materials and methods

All materials used in this study were of analytical grade. The lead chloride sample was screened to obtain a 120–140-mesh fraction (106–125 μm). Distilled water was used for preparation of all solutions.

Conversion experiments were performed in a 1500 mL flat-bottomed flask, with five necked tops for sample extraction and process control(Fig. 1). A mechanical stirrer and a mercury thermometer were placed in the solution. The temperature in the flask was adjusted using a thermostatically controlled water bath to within ± 0.5 °C. All tests were conducted at temperatures between 30 °C and 80 °C. Agitation was carried out by the mechanical stirrer, and the stirring speed was fixed at 150 rpm. For each test, 1000 mL solution containing desired concentrations of NH_4HCO_3 was added to the conversion reactor. When the temperature reached a desired value, 50 g $PbCl_2$ samples were added to solution, and 5 mL of slurry was extracted using a sample collector at appropriate time intervals for Cl^- analysis after its separation into liquor and residue. Ammonium hydroxide and ammonium
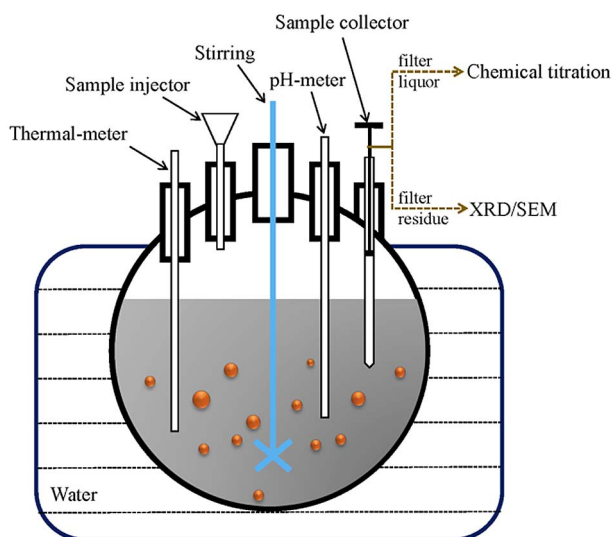
chloride were employed to regulate the pH and $[Cl^-]_T$, respectively, of the reaction solution.

Direct calculation of the percentage of converted lead is difficult because $PbCl_2$ and $PbCO_3$ are insoluble in NH_4HCO_3 solution. Therefore, the dechlorination rate of lead chloride was used to characterize the conversion rate of $PbCO_3$. This calculated dechlorination rate could also be used to calculate the reaction rate. The Cl^- concentration in the filter liquor was analyzed by argentometry (Fu, 2004). The phase and morphology of the filter residue were detected by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD studies were performed using the Rigaku D/MAX 24000 diffractometer with Cu/Kα radiation. The morphologies of antimony were determined by SEM (JEOL JSM-6360LV) coupled with energy dispersive X-ray microanalysis (EDX).

The dechlorination rate of $PbCl_2$ was calculated using the following equation:

$$Dechlorination\ rate = \frac{5x_{Cl^-}}{0.06385} \times 100\% \qquad (1)$$

where x_{Cl^-} is the concentration of Cl^- in filter liquor, g/mL.

3. Results and discussions

3.1. Effects of operation parameters on conversion of lead chloride

Parameters that may influence the conversion rate of $PbCl_2$, such as the NH_4HCO_3 concentration, reaction temperature, and $[Cl^-]_T$ (i.e., the total content of Cl^- in solution), were examined.

3.1.1. Effect of NH_4HCO_3 concentration

Fig. 2(a) shows the dechlorination results of $PbCl_2$ particles obtained at different NH_4HCO_3 concentrations at the reaction temperature of 50 °C, solution pH of 10.0, and mechanical stirring speed of 150 rpm. As observed, the reaction rate in the early stages of the reaction (< 30 min) was high, even at a low NH_4HCO_3 concentration (i.e., 0.2 mol/L), and reaction equilibrium was achieved within 40 min. The dechlorination rate increased significantly when the concentration of NH_4HCO_3 increased from 0.2 to 1.0 mol/L. The dechlorination rate reached 99.96% at the NH_4HCO_3 concentration of 0.6 mol/L within 90 min.

3.1.2. Effect of temperature

To determine the effect of temperature on the transformation of $PbCl_2$, conversion experiments were conducted at varying temperatures ranging from 30 °C to 80 °C at 0.6 mol/L NH_4HCO_3; the results are shown in Fig. 2(b). Similar to the results for the effects of the NH_4HCO_3 concentration, high reaction rates were obtained even at a low reaction temperature of 30 °C, and dechlorination rates of 52.81% and 90.29% were achieved within 10 and 40 min, respectively. However, it was noted that the conversion rate increased with an increase in the reaction temperature.

3.1.3. Effect of $[Cl^-]_T$

In the present work, the influence of the reaction product, NH_4Cl, as a measure of $[Cl^-]_T$ was evaluated in the concentration range of 0.36–0.45 mol/L. The experiments were conducted in 0.6 mol/L NH_4HCO_3 solution at 50 °C, and the results are presented in Fig. 2(c). As shown in the figure, the dechlorination rate decreased slightly with increasing $[Cl^-]_T$ concentration. For instance, the dechlorination rate decreased from 99.96 to 94.88% as $[Cl^-]_T$ increased from 0.36 to 0.45 mol/L. Hence, $[Cl^-]_T$ is expected to have a minor influence only on the diffusion of the carbonate ions to $PbCl_2$.

3.2. Kinetics analysis of conversion of lead chloride

Fig. 3 shows the phase composition of the products generated at

Fig. 1. Schematic plot of the reaction set-up.