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The conversion of lead sulphate to lead carbonate in sodium carbonate media

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ABSTRACT

Gong, Y., Dutrizac, J.E. and Chen, T.T., 1992. The conversion of lead sulphate to lead carbonate in sodium carbonate media. *Hydrometallurgy*, 28: 399–421.

The reaction of sized $PbSO_4$ powders with Na_2CO_3 media has been investigated over a broad range of experimental conditions. The reaction obeys the shrinking core model incorporating diffusion through the product layer formed on the particles. The rate increases as the first power of the Na_2CO_3 concentration and decreases with increasing concentrations of the Na_2SO_4 reaction product. The rate is independent of $NaNO_3$ additions, but decreases with increasing concentrations of NaCl or KCl. At a given Na_2CO_3 concentration, the rate decreases as the pH decreases because of the conversion of CO_3^{2-} ions to HCO_3^-. The rate decreases significantly when the pH is raised from 11.5 to 12.0, and this decrease is attributed to changes in the reaction products/product morphologies. At pH values > 12, the $PbSO_4$ dissolves in the solution. The $PbSO_4$ conversion rate increases with increasing temperature, and the apparent activation energy is 15.8 kJ/mol. Hydrocerussite, $Pb_3(CO_3)_2(OH)_2$, is formed under mild reaction conditions, but the formation of $NaPb_2(CO_3)_2(OH)$ is favoured by long retention times, high Na_2CO_3 or NaCl concentrations and elevated temperatures. The experimental results support a mechanism based on rate control by the diffusion of carbonate ions through the solution trapped in the pores of the constantly thickening product layer formed on the agglomerated $PbSO_4$ particles.

INTRODUCTION

Over 60% of the world's total output of lead is used for the manufacture of lead–acid storage batteries, and this single use continues to grow at the expense of all other applications [1]. Because spent storage batteries are readily collected and recycled, they constitute the bulk of the feed to the large secondary lead industry, which produces approximately half of the world's annual lead output of around 5 million tonnes [2]. Although the treatment of the lead metal grids from the spent batteries is relatively straightforward, the pro-

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cessing of the battery paste, which consists of an intimate mixture of lead sulphate, lead oxide, lead metal and sulphuric acid electrolyte, creates a number of environmental problems [3]. Direct smelting of the battery paste in the presence of carbon requires high temperatures to decompose the sulphates; the high temperatures result in the generation of lead fumes and moderate concentrations of SO_2 gas that are costly to remove from the gas stream.

One solution to the environmental problems associated with the recycling of lead–acid storage batteries is to react the battery paste with sodium carbonate to convert the lead to easily smelted lead carbonate and to reject the sulphate as Na_2SO_4. Although the reaction of $PbSO_4$ with Na_2CO_3 can be effected directly in the smelting process [4,5], the reaction is more conveniently carried out in an aqueous medium under near-ambient conditions. In fact, a number of commercial processes incorporate a sodium carbonate leach [6,7] or a sodium carbonate/sodium hydroxide leach [8] as the initial step in the treatment of spent lead–acid storage batteries.

The reaction of $PbSO_4$ with Na_2CO_3 is also of relevance to other metallurgical operations. Lead is a major constituent of the zinc oxide product made by the fuming of zinc-rich lead blast furnace slags. Such zinc oxide fumes are commonly leached with Na_2CO_3 solution to remove the associated fluorides and chlorides, and the use of sodium carbonate solutions also converts the lead present in the fume into an insoluble carbonate, such that the discarded solution contains <1 mg/l Pb [9]. Copper refinery anode slimes can be advantageously de-leaded by reacting the $PbSO_4$ present in the anode slimes with Na_2CO_3 solution and then leaching the resultant lead carbonate with acetic acid [10]. This approach significantly reduces the "lead burden" during the subsequent processing of the anode slimes and offers the possibility of a marketable lead acetate by-product.

The rate of reaction of $PbSO_4$ with Na_2CO_3 in aqueous media is known to be rapid. Bulakhova and Ben'yash [11,12] noted that the reaction was essentially complete within 30 min at 20°C and within 15 min at 50°C. The rate depended slightly on the stoichiometric ratio of $PbSO_4/Na_2CO_3$, and over 99% lead sulphate conversion was achievable at the higher temperature in the presence of excess Na_2CO_3. Arai and Toguri [13] also reported rapid conversion rates which increased with increasing stirring speeds for the $-100+150$ mesh ($-147+104$ μm) $PbSO_4$ particles used. The temperature dependence of the reaction suggested an apparent activation energy of 4.7 kJ/mol. Furthermore, the reaction was independent of the sulphate concentration of the solution, but increased directly with the Na_2CO_3 concentration. It was concluded that the rate was controlled by the diffusion of carbonate ions through the liquid boundary surrounding the $PbSO_4$ particles.

Although it is commonly assumed that the reaction of $PbSO_4$ with Na_2CO_3 solutions produces only $PbCO_3$ [13], this assumption is an oversimplification. The *E*h–pH diagram for the Pb–S–CO_3–H_2O system shows the exis-

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tence of both cerussite ($PbCO_3$) and hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), and the transition of cerussite to hydrocerussite occurs at around pH 10 [14]. Hence, the reaction of $PbSO_4$ with excess Na_2CO_3 generates $Pb_3(CO_3)_2(OH)_2$ rather than $PbCO_3$. At pH values > 12, plumbonacrite ($Pb_{10}O(CO_3)_6(OH)_6$) becomes a dominant reaction product [15], and it has been demonstrated that the relative amounts of hydrocerussite, plumbonacrite and PbO formed on electro-oxidized lead vary systematically with time [16]. The implication is that one lead carbonate species can be easily converted into another. In addition, the compound $NaPb_2(CO_3)_2OH$ is known to precipitate over a broad range of conditions in the presence of sodium ion [17,18].

Although the rapid nature of the reaction between $PbSO_4$ and aqueous Na_2CO_3 is well known, the details of the reaction kinetics, as well as the diversity of the reaction products, are not thoroughly established. Due to the importance of such information to the metallurgical industry, the kinetics of reaction of Na_2CO_3 solutions with sized $PbSO_4$ powders were studied. The reaction products were systematically determined, and efforts were made to correlate the various products with the reaction conditions.

EXPERIMENTAL

Materials

All materials were reagent grade. The reagent $PbSO_4$ was wet screened to yield a −65 +100 mesh fraction (−208 +147 μm) for study. Scanning electron microscope-energy dispersive X-ray (SEM–EDX) analysis of the −208 +147 μm fraction, Fig. 1, showed spheroidal aggregates which were composed of intergrown $PbSO_4$ crystals 1–6 μm in size, Fig. 2. The $PbSO_4$ crystals are dispersed uniformly throughout the spheroids, and there is no indication of any zoning or morphological variations. Although the wet screening operation affects the sizing of the spheroidal agglomerates, it does not have any significant influence on the size of the individual $PbSO_4$ crystals. Presumably similar material was used by Arai and Toguri [13], and it is believed that battery paste also consists of tiny intergrown particles.

Procedures

For the particulate leaching tests, 1 g of −208 +147 μm $PbSO_4$ was added to 1 l of Na_2CO_3 solution contained in a glass reaction vessel heated in an oil bath controlled to ±0.5°C. An excess of Na_2CO_3 was always present such that the Na_2CO_3 concentration did not change significantly during the experiments. At timed intervals 3 ml aliquots were withdrawn from the vessel using a syringe fitted with a 0.45 μm filter. The volume of the aliquots taken was

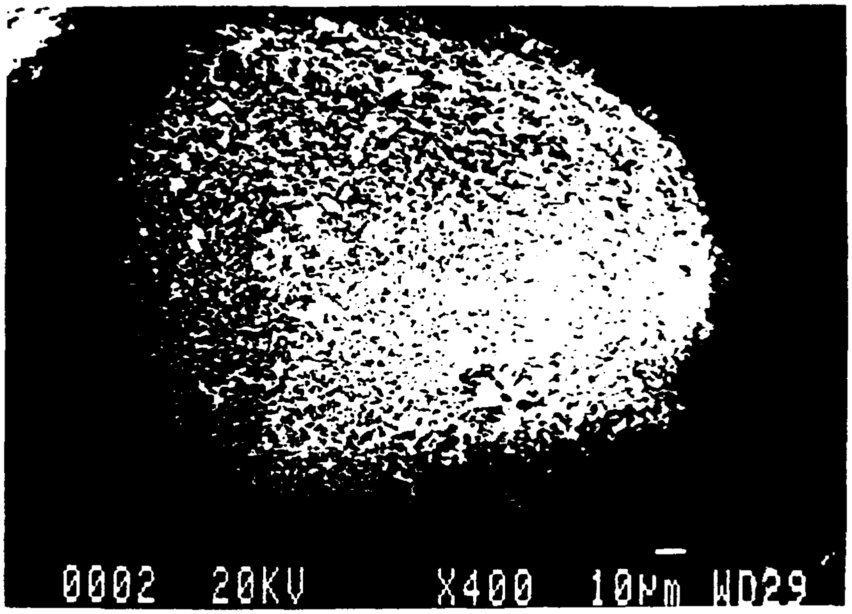

Fig. 1. Secondary electron micrograph showing the agglomerated −65 +100 mesh (−208 +147 µm) $PbSO_4$ particles used for the conversion experiments (loose powder mount).

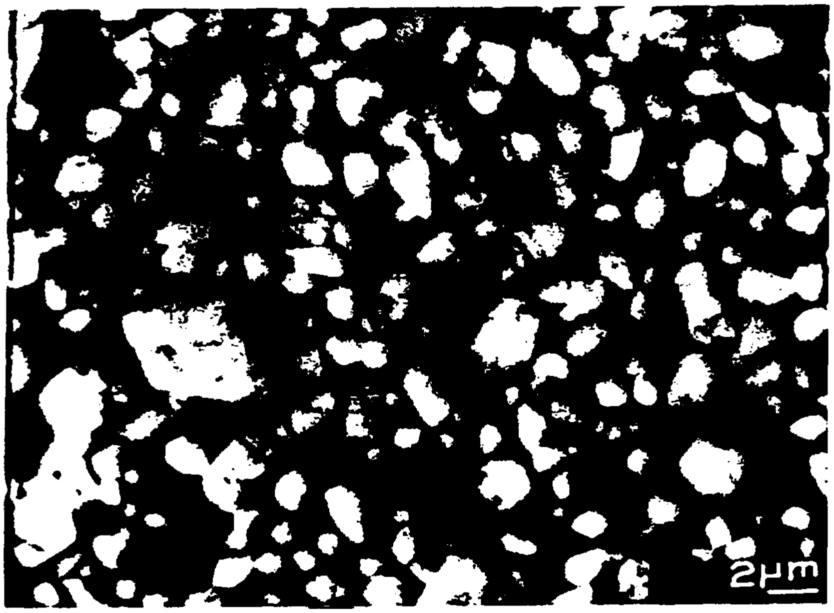

Fig. 2. Backscattered electron micrograph of the individual $PbSO_4$ crystals which form the agglomerated particles shown in Fig. 1 (polished section).

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small relative to the 1 l total volume of the solution. A high stirring speed was always employed to ensure the complete suspension of the $PbSO_4$ particles.

Analytical procedures

The reaction of $PbSO_4$ with Na_2CO_3 solution yields soluble sodium sulphate:

$$PbSO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + PbCO_3 \qquad (1)$$

Due to the fact that $PbSO_4$ is essentially insoluble, the reaction kinetics can be monitored by following the amount of dissolved sulphate ion. In these experiments, the SO_4 concentration was determined using a Dionex ion chromatograph with an HPIC AS4 column, a 2.4 m*M* Na_2CO_3–3.0 m*M* $NaHCO_3$ eluent, and conductivity detection. It was observed that, at Na_2CO_3 concentrations greater than 0.02 *M*, in a sample injected into the ion chromatograph, the conductivity peak of the sulphate ion was reduced. This effect was overcome by dilution of the sample to reduce its carbonate concentration, by using matrix-matched standard solutions, or by prior removal of the carbonate ions by ion exchange with an Onguard-H column.

The various solid reaction products were examined both in loose powder mounts and in polished sections. The reaction products were studied using optical microscopy and the high resolution capabilities of the scanning electron microscope (SEM) with an energy dispersive X-ray analysis system (EDX). The various reaction products were also examined by X-ray diffraction analysis using an automated diffractometer or a Debye-Scherrer camera. Details of the various mineralogical techniques have already been published [19].

RESULTS AND DISCUSSION

Effect of Na_2CO_3 concentration

Figure 3 illustrates some of the reaction curves realized when 1.0 g of −208 +147 μm $PbSO_4$ was reacted at 30°C with various concentrations of Na_2CO_3. As has been observed by previous workers [11–13], the reaction rates are consistently fast. Even for solutions containing only 0.02 *M* Na_2CO_3, complete conversion of the $PbSO_4$ is achieved within 60 min. The reaction is complete within 10 min when the solution is more concentrated than 0.1 *M* Na_2CO_3. The rates are so fast in concentrated sodium carbonate media that only two or three solution samples could be obtained before the reaction was essentially complete.

Figure 4 shows the cross section of three −208 +147 μm $PbSO_4$ particles, which were leached for 1 min at 30°C in a 0.2 *M* Na_2CO_3 solution. The po-

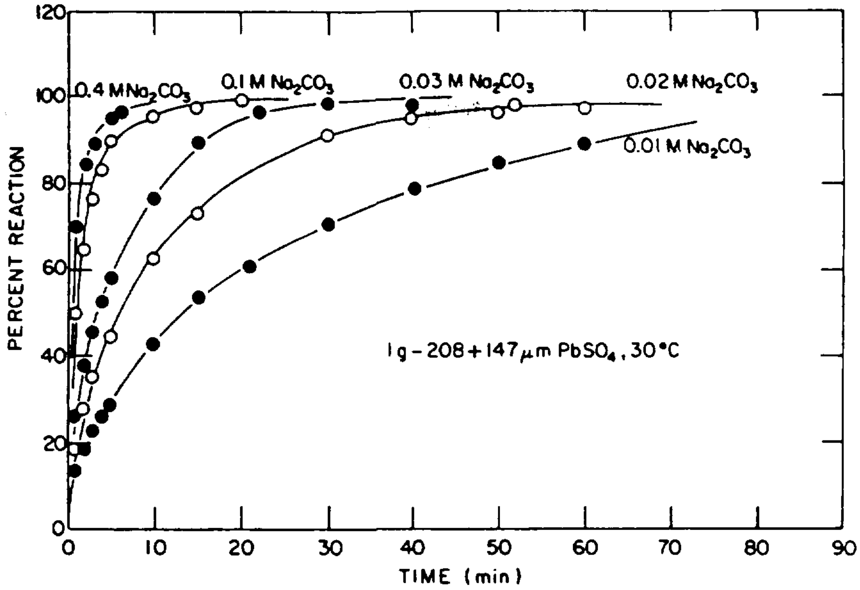


Fig. 3. Reaction curves illustrating the effect of Na_2CO_3 concentration on the conversion of sized $PbSO_4$ powders.

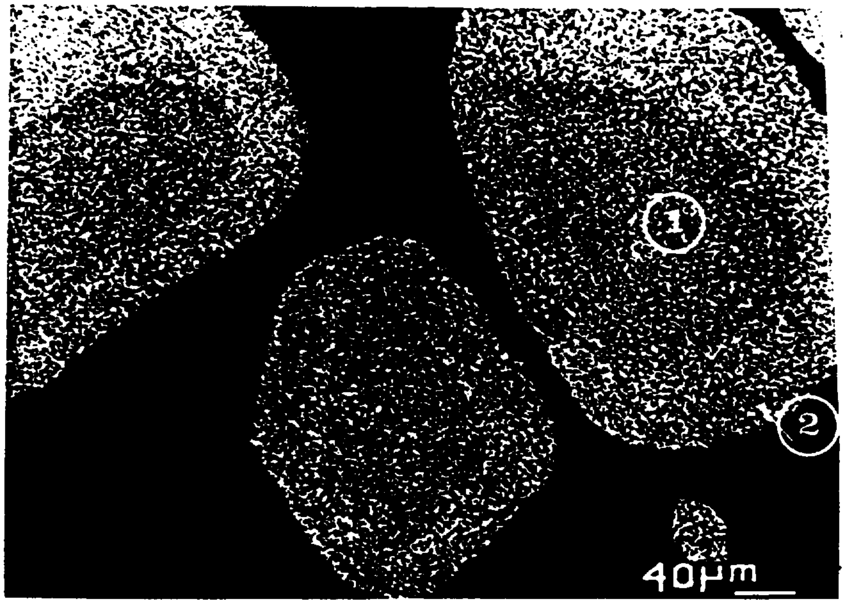
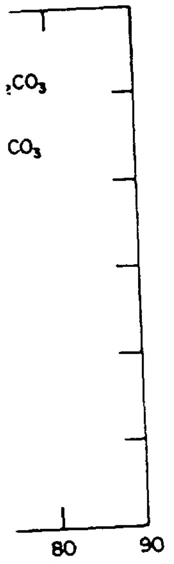


Fig. 4. Backscattered electron micrograph of partly reacted $PbSO_4$ particles that illustrates the topochemical nature of the $PbSO_4$ conversion reaction (polished section). *1* $=PbSO_4$; *2* $=Pb_3(CO_3)_2(OH)_2$.



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rous texture of the particles is evident, and, as was shown in Fig. 2, such particles are composed of individual 1–6 μm $PbSO_4$ crystals, which are agglomerated into the −208 +147 μm spheroidal particles used in the conversion experiments. Despite the short retention time and relatively mild reaction conditions employed, approximately 42% $PbSO_4$ conversion occurred. The reaction is clearly topochemical, and there is a sharp reaction interface between the $PbSO_4$ core and the reaction products. This interface is illustrated in more detail in Fig. 5. The individual, 1–6 μm $PbSO_4$ crystals in the core, as well as the sharp reaction interface between the unreacted $PbSO_4$ crystals and the fine grained reaction products, are apparent.

The topochemical nature of the reaction suggests that the conversion data can be described by a shrinking core model. When the conversion data were fitted to the conventional shrinking core equation, however:

$$1-(1-\alpha)^{1/3}=k_1 t \qquad (2)$$

pronounced negative deviations from linearity were observed.

When the data were fitted to the shrinking core model involving rate control by diffusion through the constantly thickening product layer formed on the particles:

$$1-3(1-\alpha)^{2/3}+2(1-\alpha)=k_p t \qquad (3)$$

good fits were obtained for degrees of $PbSO_4$ conversion up to 90% (i.e., for

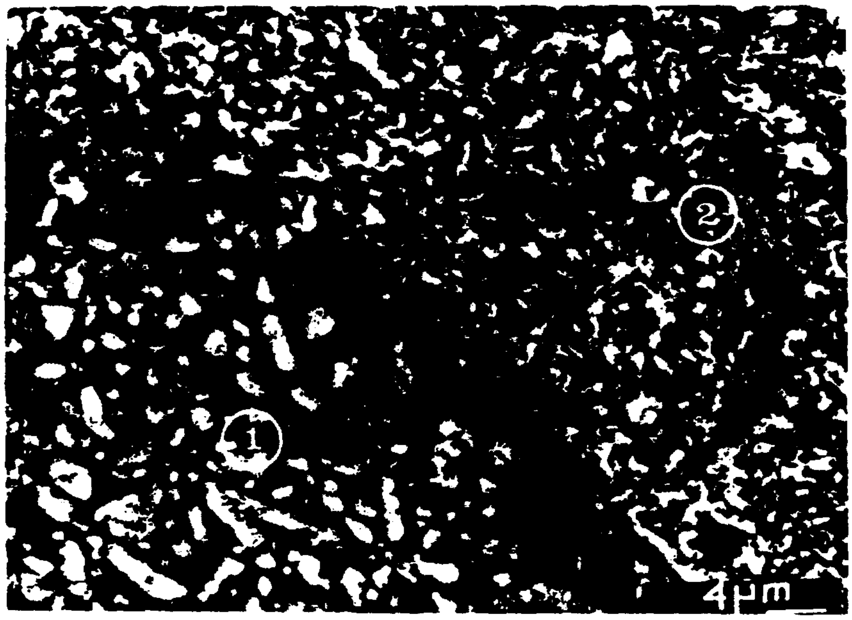


Fig. 5. Backscattered electron micrograph showing the interface between the unreacted $PbSO_4$ crystals and the reaction products in one of the particles illustrated in Fig. 4 (polished section). 1 = $PbSO_4$ core; 2 = $Pb_3(CO_3)_2(OH)_2$ rim.

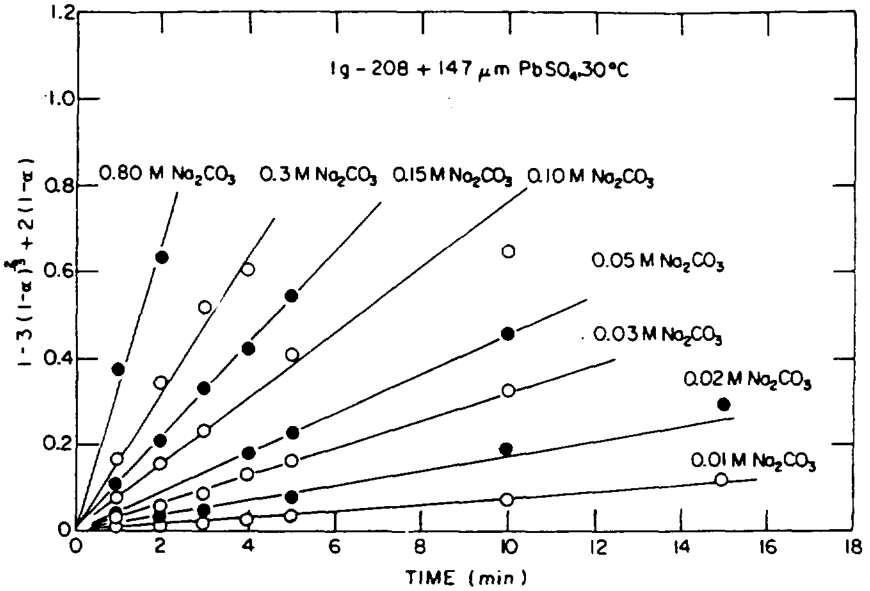


Fig. 6. Graphs of $1-3(1-\alpha)^{2/3}+2(1-\alpha)$ versus time for the reaction of $PbSO_4$ with various concentrations of Na_2CO_3.

$1-3(1-\alpha)^{2/3}+2(1-\alpha)\approx 0.6$), Fig. 6. Accordingly, the data for the individual conversion curves were fitted to eq. (3), and the derived rate constants, k_p, were used as an index of the reaction rate.

Rate constants were calculated from the experiments carried out at the various Na_2CO_3 concentrations, and these are presented as a function of the Na_2CO_3 concentration in Fig. 7. It is evident that the rate increases systematically with increasing Na_2CO_3 concentrations in the 0.01–1.0 *M* Na_2CO_3 range. The rate constants were found to vary according to the following relationship:

$$\log k_p = -0.27 + 0.88 \log [Na_2CO_3] \tag{4}$$

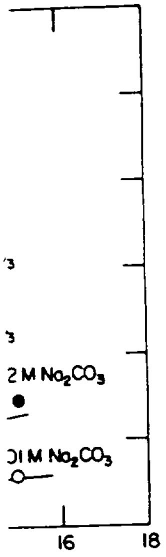
$$k_p \propto [Na_2Co_3]^{0.88} \tag{5}$$

When the rate constants were replotted as a function of the calculated carbonate ion concentration, it was found that the rate varied as the 0.81 power of the CO_3^{2-} concentration.

$$\log k_p = -0.35 + 0.81 \log [CO_3^{2-}] \tag{6}$$

$$k_p \propto [CO_3^{2-}]^{0.81} \tag{7}$$

Varying the Na_2CO_3 concentration of the solution also results in a significant change in the solution pH. In order to examine the influence of the



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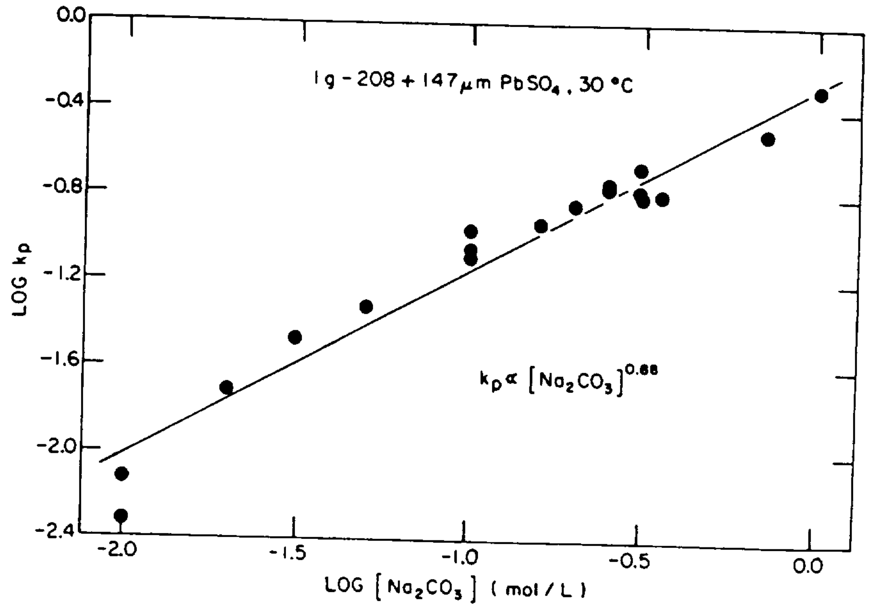


Fig. 7. Effect of the Na$_2$CO$_3$ concentration on the rate of conversion of PbSO$_4$.

Na$_2$CO$_3$ concentration at constant pH, a series of experiments was carried out at 30°C. The Na$_2$CO$_3$ concentration was varied from 0.02 to 0.10 M, but the pH and Na concentration of the solution were kept constant at 11.3 and 0.10 M, respectively, by the addition of NaOH and HCl. Reaction curves similar to those presented in Fig. 6 were obtained, and rate constants (k_p) were calculated from each curve. A linear relationship was realized when log k_p was plotted versus log [Na$_2$CO$_3$] (compare Fig. 7), and the rate varied as the 1.20 power of the Na$_2$CO$_3$ concentration. Overall, the experiments carried out at the various Na$_2$CO$_3$ concentrations suggest that the rate of conversion of PbSO$_4$ varies as the first power of the sodium carbonate concentration:

$$k_p \propto [Na_2CO_3] \tag{8}$$

Arai and Toguri [13] observed that the initial PbSO$_4$ conversion rate varied as the 1.0 power of the ratio of Na$_2$CO$_3$/PbSO$_4$ for solutions containing 0.016–0.048 M Na$_2$CO$_3$, and their observation is consistent with the current work.

Effect of temperature

Figure 8 illustrates several conversion curves obtained when 1 g of −208 +147 μm PbSO$_4$ was reacted in 0.1 M Na$_2$CO$_3$ media at various tempera-

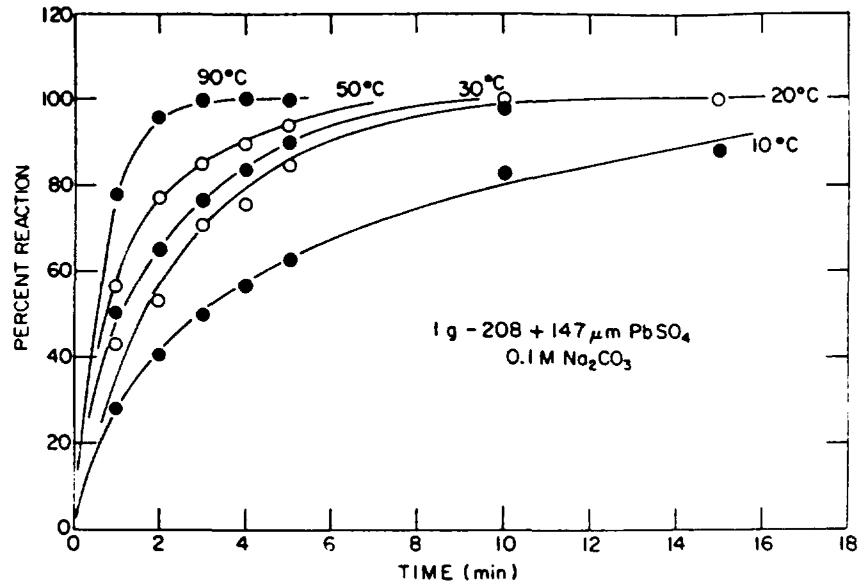


Fig. 8. Reaction curves realized at various temperatures in 0.1 M Na_2CO_3 media.

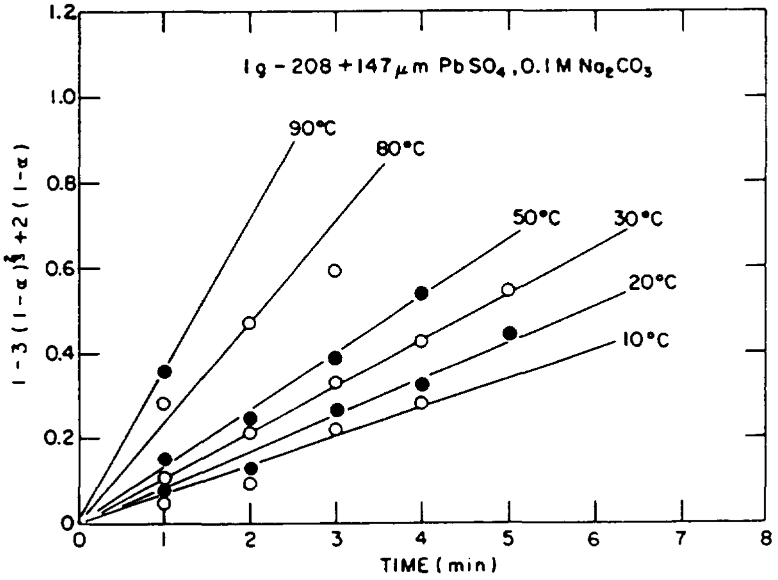
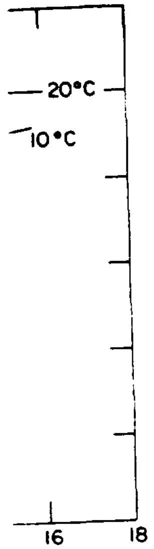


Fig. 9. Graphs of $1-3(1-\alpha)^{2/3}+2(1-\alpha)$ versus time for the reaction of $PbSO_4$ at various temperatures in 0.1 M Na_2CO_3 media.



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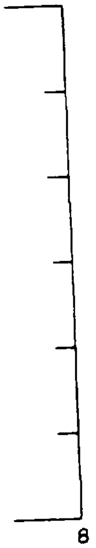

tion of PbSO$_4$ at various

tures. Figure 9 presents the same data plotted according to eq. (3). Clearly, the rates are rapid at all temperatures, and similar observations were made in previous studies on this system [11,13]. Even at 10°C, 90% reaction is achieved within 15 min; at 50°C, essentially complete conversion of the PbSO$_4$ is noted within 5 min of the start of the reaction.

Rate constants were determined from the individual curves presented in Fig. 9, and these rate constants are shown on the Arrhenius plot illustrated in Fig. 10. It is apparent that a consistent set of data is obtained and the implication is that a single rate-controlling process applies over the 10–90°C temperature range studied:

$$\log k_p = 1.697 - 825/T \qquad (9)$$

The activation energy calculated from the data is 15.8 kJ/mol. Although this value is somewhat higher than the 5 kJ/mol activation energy deduced by Arai and Toguri [13] over the 20–45°C temperature range, both values are low and both probably reflect rate control by the diffusion of some aqueous species.

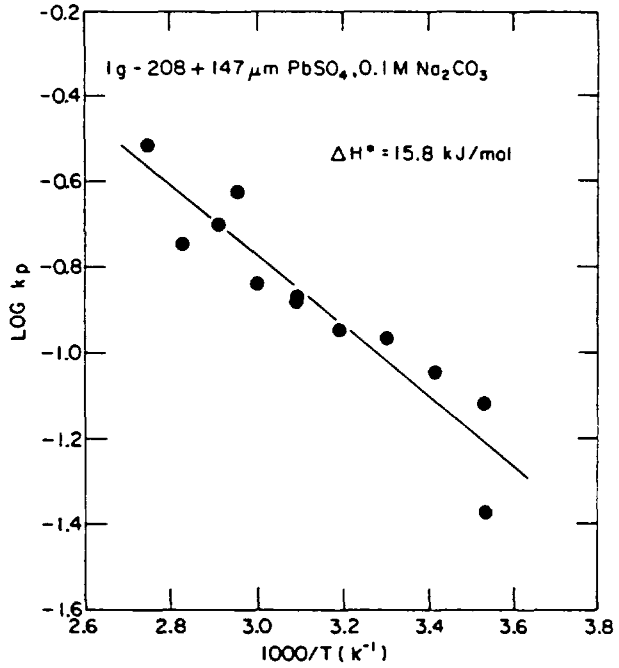

Fig. 10. Arrhenius curve for the conversion of PbSO$_4$ in 0.1 *M* Na$_2$CO$_3$ media over the 10–90°C temperature range.

Effect of solution pH

The effect of the solution pH on the conversion of 1 g of −208 +147 μm $PbSO_4$ in 0.1 *M* Na_2CO_3 media at 30°C was examined, and conversion curves similar to those shown in Figs. 3 and 8 were obtained. Although the data obtained over the pH range 7.0–11.3 could be adequately described by eq. (3), the results realized at pH values above 11.3 could not be fitted to the shrinking core equation. Significant negative deviations were observed. Thus, in order to compare the data obtained over the entire pH range on a common basis, recourse was made to an empirically derived initial rate constant. This was calculated by fitting the data obtained for less than 95% reaction to a parabolic equation:

$$\% \text{ Reaction} = a + bt + ct^2 \qquad (10)$$

and calculating the rate (d(% Reaction)/dt) at $t=0$. Although without theoretical significance, the initial rate constants (k_{initial}) thereby obtained allow the data realized over the entire pH range to be compared on a common basis.

Initial rate constants were deduced from each of the conversion curves, and these initial rate constants are displayed as a function of pH in Fig. 11. The pH of a 0.1 *M* Na_2CO_3 solution at 30°C in 11.3, and a near-maximum rate is obtained in such a solution. Reducing the solution pH with HCl causes a systematic decrease in the rate of conversion of $PbSO_4$ that seems to be related to the protonation of the carbonate ion to the significantly less reactive bicarbonate ion:

$$CO_3^{2-} + H^+ \rightarrow HCO_3^- \qquad (11)$$

Very low rates are observed at pH = 7 where the calculated carbonate ion concentration is 4×10^{-4} *M*. Further reductions in pH result in the decomposition of the bicarbonate ion with the evolution of CO_2. A single conversion test was carried out using a 0.1 *M* $NaHCO_3$ solution (pH = 8.5), and the results of that test are also shown in Fig. 11. The results obtained with the bicarbonate solution agree with those from the pH-adjusted carbonate solutions, and the implication is that the carbonate ion concentration, determined by the carbonate/bicarbonate equilibrium (eq. (11)), controls the $PbSO_4$ conversion rate in solutions having pH values in the 7.0 to 11.3 range. Increasing the pH above the natural pH value of 11.3 by the addition of NaOH results in a sharp decrease in the $PbSO_4$ conversion rate that continues to pH 12.0. As will be shown later, the reaction products change significantly in the pH range 11.3–12.0 and, presumably, the changes in the solid phases and their morphologies have an impact on the overall $PbSO_4$ conversion process and on the form of the conversion curves. When the pH is increased above 12.0 by the addition of higher concentrations of NaOH, the apparent conversion rate increases sharply. Such a rate increase is somewhat misleading, however,

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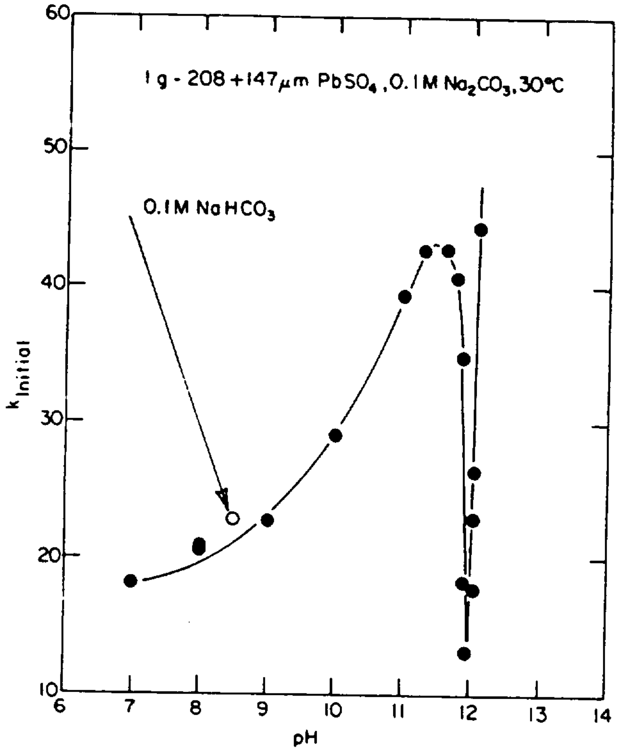

Fig. 11. Effect of the pH of a 0.1 *M* Na_2CO_3 solution on the rate of conversion of $PbSO_4$ at 30°C.

as it appears that the reaction of excess NaOH with $PbSO_4$ forms various soluble lead and sulphate species. When the NaOH concentration exceeds 0.2 *M*, the 1 g $PbSO_4$ sample completely dissolved within 5 min. The results summarized in Fig. 11 suggest that the addition of NaOH to a commercial reaction system [8] is not desirable. The presence of excess NaOH will either suppress the $PbSO_4$ conversion rate or will result in some degree of lead dissolution.

Effect of Na_2SO_4 concentration

Arai and Toguri [13] reported that the $PbSO_4$ conversion reaction was independent of the concentration of the Na_2SO_4 reaction product for Na_2SO_4 concentrations in the 0.0–0.03 *M* range. The narrow concentration used in their experiments was dictated by the difficulty in measuring small amounts of dissolved sulphate against a high initial sulphate background. In the current work, the influence of the Na_2SO_4 reaction product was evaluated for sulphate concentrations in the 0.0–1.5 *M* Na_2SO_4 range. The experiments were done by adding 0.5 g of −208 +147 μm $PbSO_4$ to 1 l of 0.1 *M* Na_2CO_3 solution at 30°C. At various times, the leach slurry was rapidly filtered on a wide-diameter Buchner filter, and the solids were water-washed to stop the reaction. The solids were then analyzed for residual sulphate, and the reaction curves were calculated from the residual sulphate analyses. Of course, each point on a reaction curve represents a separate experiment with a fresh 0.5 g $PbSO_4$ sample. The data were plotted according to eq. (3), and some of the curves obtained are given in Fig. 12.

Rate constants were derived from each of the curves and the resulting values are shown as a function of the Na_2SO_4 concentration in Fig. 13. The magnitude of the rate constants is slightly lower than that noted in the previous figures (e.g., Fig. 7), and presumably the difference is due to the smaller quantity of $PbSO_4$ reacted and the different methods used to determine the extent of $PbSO_4$ conversion. Nevertheless, it is apparent that the $PbSO_4$ conversion rate decreases as the Na_2SO_4 concentration of the solution increases:

$$k_p = 0.0704 - 0.0300[Na_2SO_4] \tag{12}$$

As will be seen later, the presence of moderate concentrations of sulphate ion in the 0.1 *M* Na_2CO_3 solution results in a change in the reaction products initially formed on the $PbSO_4$ particles. Presumably, these changes affect the porosity of the product and, thereby, the diffusion of the sodium carbonate. The presence of high concentrations of Na_2SO_4 will also modify the solution

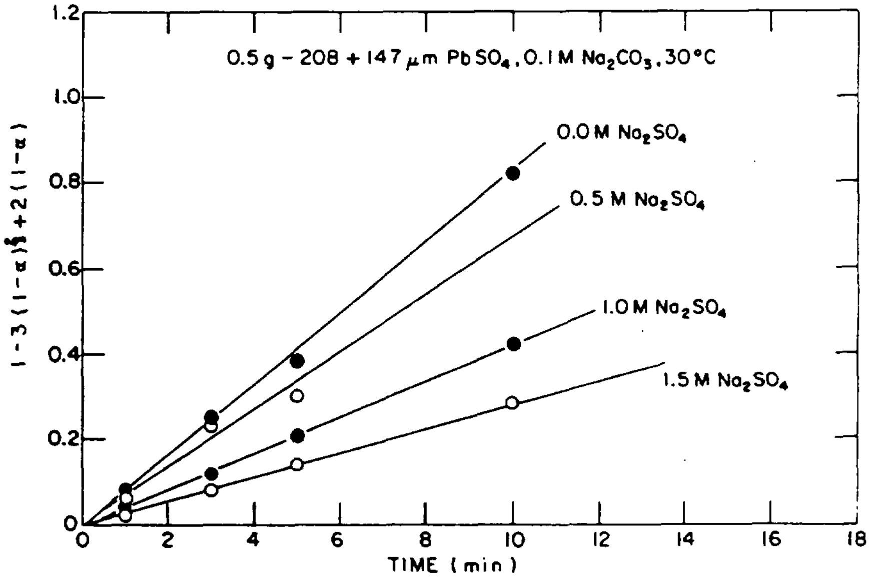

Fig. 12. Graphs of $1-3(1-\alpha)^{2/3}+2(1-\alpha)$ versus time for the reaction of $PbSO_4$ in 0.1 *M* Na_2CO_3 media containing various concentrations of Na_2SO_4.

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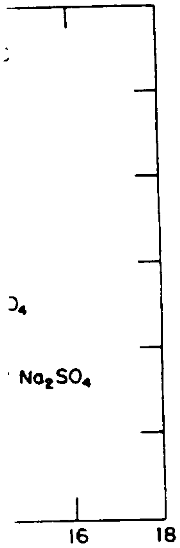

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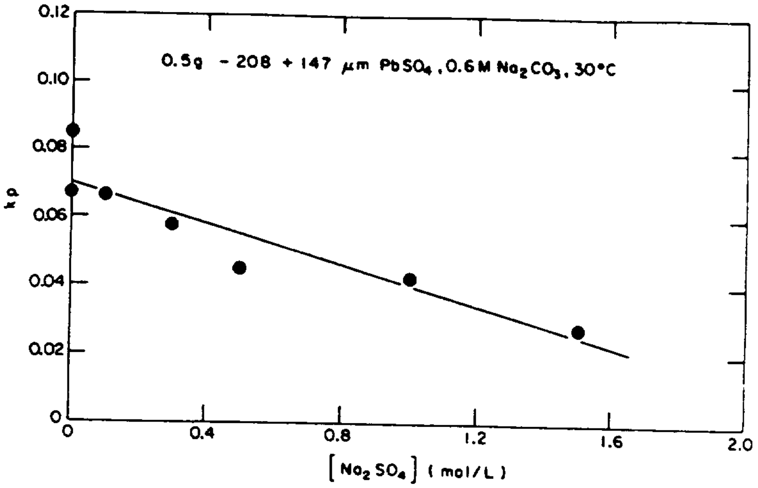


Fig. 13. Effect of the Na_2SO_4 concentration on the rate of $PbSO_4$ conversion in 0.1 M Na_2CO_3 media.

properties, but such changes are expected to have only a minor influence on the diffusion of the carbonate ion to the $PbSO_4$. The addition of 1 M Na_2SO_4 to the 0.1 M Na_2CO_3 medium reduces the rate by about 40%. Such a dependence would not have been apparent over the 0.03 M Na_2SO_4 concentration range employed by Arai and Toguri [13].

Effect of the concentrations of $NaNO_3$, NaCl and KCl

Figure 11 shows that the $PbSO_4$ conversion rate changes dramatically when NaOH is added to the 0.1 M Na_2CO_3 solution (i.e., for pH values greater than 11.3). Although the observed changes are probably attributable to the OH^- concentration, some of the observed effect could be due to the Na concentration or to the elevated ionic strength of the solution. To investigate this possibility, a series of experiments was carried out at 30°C using 0.1 M Na_2CO_3 solutions to which were added various concentrations of $NaNO_3$. Conversion curves similar to those presented in Fig. 6 were obtained, and rate constants were derived from each conversion curve using eq. (3). These rate constants are plotted as a function of the $NaNO_3$ concentration in Fig. 14. It is evident that $NaNO_3$ concentrations up to 1.0 M have no significant effect on the conversion reaction. The implication is that neither sodium ion nor ionic strength significantly impact on the $PbSO_4$ conversion reaction.

Similar tests were carried out with various concentrations of NaCl or KCl being added to the 0.1 M Na_2CO_3 solution at 30°C. Conversion curves, similar to those illustrated in Fig. 6, were obtained and rate constants were calculated from each curve using eq. (3). These rate constants are also plotted

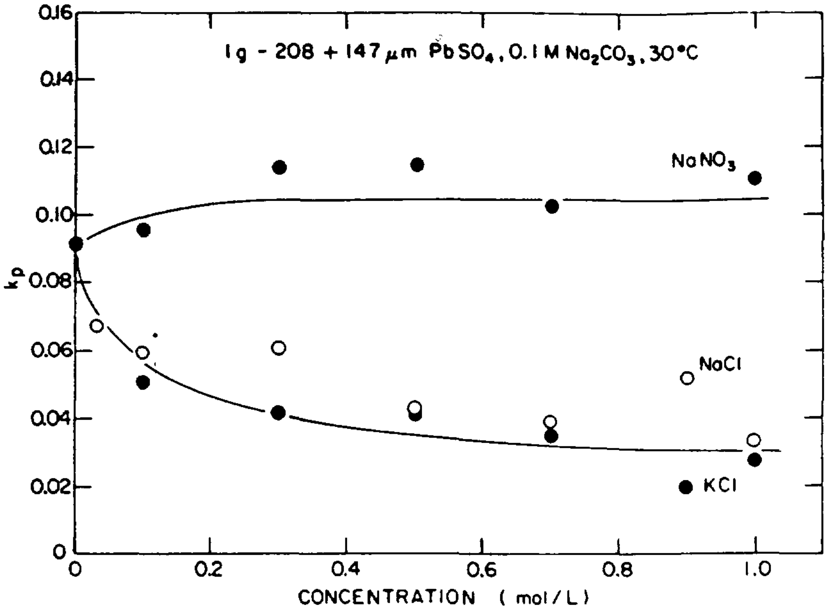
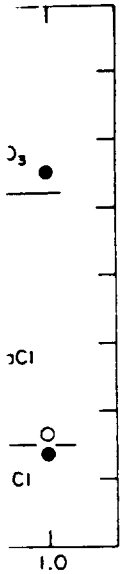


Fig. 14. Effect of the concentrations of $NaNO_3$, NaCl and KCl on the rate of $PbSO_4$ conversion in 0.1 M $NaCO_3$ media.

as a function of the NaCl or KCl concentration in Fig. 14. Increasing the concentration of either NaCl or KCl over the concentration range 0.0–1.0 M results in a significant reduction in the $PbSO_4$ conversion rate, and both chlorides reduce the rate by about the same amount. This effect cannot be attributed to the dissolution of the $PbSO_4$ in the chloride solutions, as such a dissolution reaction would result in higher apparent rates. The effect of the added chlorides on the conversion rate is also not caused by the depression of the pH of the 0.1 M Na_2CO_3 solution. The addition of 1.0 M KCl to the 0.1 M Na_2CO_3 solution increased the pH from 11.3 to 11.4 and, as noted in Fig. 11, such a pH increase will have little effect on the $PbSO_4$ conversion rate. The added chlorides may affect the activity of the carbonate ion and hence the concentration gradient for carbonate ion diffusion, but further work would be required to evaluate this possibility.

Reaction mechanism and reaction products

The results of Fig. 6, coupled with the product morphologies shown in Figs. 4 and 5, suggest that the reaction is controlled by the diffusion of some species through the solution trapped in the pores of the constantly thickening product layer formed on the agglomerated $PbSO_4$ particles (shown in Figs. 1 and 2). As the reaction proceeds, the reaction path increases because the product layer



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on the agglomerated particles becomes thicker and this thickening results in the observed "parabolic" kinetics. That the reaction is controlled by diffusion in the solution trapped in the pores of the product layer, is supported by the rapidity of the reaction, as well as by the relatively low (15.8 kJ/mol) apparent activation energy. That the reaction increases as the first power of the Na_2CO_3 concentration, but decreases with increasing concentrations of the Na_2SO_4 reaction product, suggests that the diffusion of carbonate ion through the thickening product layer controls the reaction. Such a mechanism is also consistent with the lack of any significant rate change when $NaNO_3$ is added to the solution.

When the pH of the carbonate solution is lowered, the carbonate ion is converted to bicarbonate. The lower carbonate ion concentration present in the less basic solutions results in reduced $PbSO_4$ conversion rates. The abrupt reduction in the rate, caused by the addition of excess NaOH to the Na_2CO_3 solution, seems to be related to a change in the reaction product/product morphology that restricts the aqueous diffusion process and results in significant deviations from the shrinking core model.

The reaction products formed when −208 +147 μm $PbSO_4$ aggregated particles were leached at 30°C in 0.1, 1.0 and 2.0 *M* Na_2CO_3 solutions were determined as a function of time. In the 0.1 *M* Na_2CO_3 medium, hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) was the major reaction product formed for retention times as long as 4 h; traces (<1%) of $NaPb_2(CO_3)_2(OH)$ and $PbCO_3$ were sometimes also detected. After 8 h of reaction, both $Pb_3(CO_3)_2(OH)_2$ and $NaPb_2(CO_3)_2(OH)$ were present in major quantities; for retention times longer than 23 h, only $NaPb_2(CO_3)_2(OH)$ was present. In the solutions containing 1.0 or 2.0 *M* Na_2CO_3, $NaPb_2(CO_3)_2(OH)$ was the major product, even after 1 min of reaction, although minor amounts of $Pb_3(CO_3)_2(OH)_2$ and traces of $PbCO_3$ were sometimes detected. The above products suggest the following conversion reaction:

$$3PbSO_4 + 2Na_2CO_3 + 2H_2O \rightarrow Pb_3(CO_3)_2(OH)_2 + 2Na_2SO_4 + H_2SO_4 \quad (13)$$

The initial formation of $Pb_3(CO_3)_2(OH)_2$ is consistent with the reported *E*h–pH diagram for the Pb–S–CO_3–H_2O system [14], and any $PbCO_3$ which forms locally is rapidly converted to hydrocerussite:

$$PbSO_4 + Na_2CO_3 \rightarrow PbCO_3 + Na_2SO_4 \quad (14)$$

$$3PbCO_3 + 2OH^- \rightarrow Pb_3(CO_3)_2(OH)_2 + CO_3^{2-} \quad (15)$$

Although Arai and Toguri [13] reported that $PbCO_3$ was the only product formed when $PbSO_4$ powder was reacted with Na_2CO_3 media, their published X-ray powder diffraction pattern does not entirely match that of $PbCO_3$. Many "extra" lines are present in their pattern and the relative line intensities do not agree with those of $PbCO_3$.

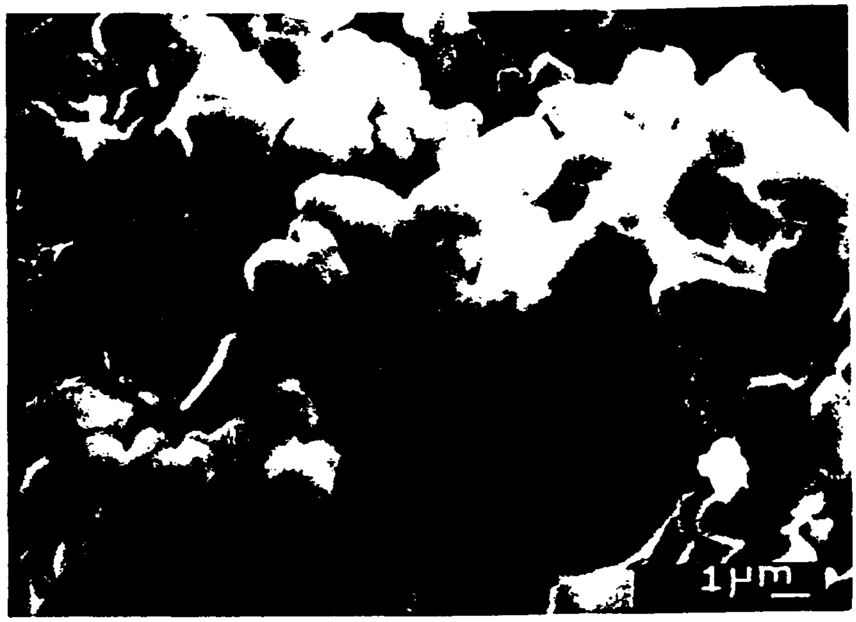

Fig. 15. Secondary electron micrograph of the surface of an unreacted −208 +147 μm $PbSO_4$ particle (loose powder mount).

Figure 15 is an SEM micrograph of an unreacted $PbSO_4$ agglomerated particle, and Fig. 16 shows the same surface after it was converted to $Pb_3(CO_3)_2(OH)_2$ in 0.1 *M* Na_2CO_3 solution at 50°C. Figure 5 shows the hydrocerussite in polished cross section. The unreacted $PbSO_4$ consists of numerous 1–6 μm $PbSO_4$ crystals intergrown into larger −208 +147 μm particles. Significant porosity exists between the intergrown $PbSO_4$ crystals. On contact with the Na_2CO_3 medium, the blocky $PbSO_4$ crystals are converted into a fine grained mat of intergrown hydrocerussite particles. Although some porosity is still evident, the hydrocerussite layer is clearly less porous than the unreacted $PbSO_4$, and the more dense hydrocerussite forms a diffusion barrier for the carbonate ions.

The hydrocerussite formed according to eqs. (13) and (15) is slowly converted to $NaPb_2(CO_3)_2(OH)$ in 0.1 *M* Na_2CO_3 media and very rapidly in 1.0 or 2.0 *M* Na_2CO_3 solutions:

$$2Pb_3(CO_3)_2(OH)_2 + 2Na_2CO_3 \rightarrow 3NaPb_2(CO_3)_2(OH) + NaOH \qquad (16)$$

The compound $NaPb_2(CO_3)_2(OH)$ was also present in major amounts after 1 h of reaction in 0.5 or 0.7 *M* Na_2CO_3 media, but was not detected in the products made in solutions containing less than 0.1 *M* Na_2CO_3. Although the initial conversion of $PbSO_4$ to hydrocerussite is rapid, the subsequent reaction of $Pb_3(CO_3)_2(OH)_2$ to $NaPb_2(CO_3)_2(OH)$ (eq. (16)) is kinetically

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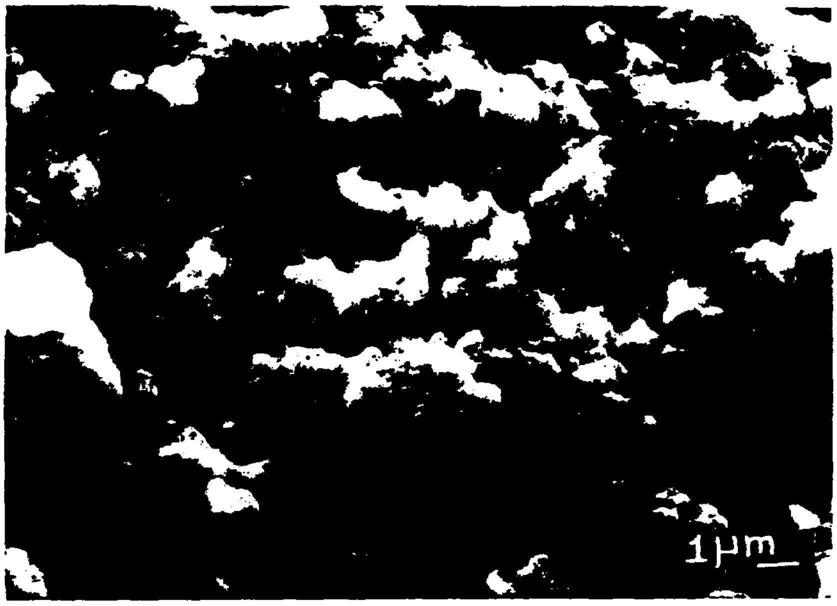

Fig. 16. Secondary electron micrograph of the hydrocerussite layer formed on the surface of a −208 +147 μm PbSO$_4$ particle (loose powder mount).

slower. Hydrocerussite was the major reaction product formed after 60 min of reaction in 0.1 *M* Na_2CO_3 media for temperatures ranging from 10 to 60°C. Both $NaPb_2(CO_3)_2(OH)$ and $Pb_3(CO_3)_2(OH)_2$ were present in major amounts at 65°C and 75°C, but $NaPb_2(CO_3)_2(OH)$ was the major species at temperatures above 80°C. When NaCl was added to the 0.1 *M* Na_2CO_3 solution, only $Pb_3(CO_3)_2(OH)_2$ was detected in the 60-minute reaction products when the NaCl concentration was less than 0.5 *M*. When the NaCl concentration was 0.5 *M* or higher, $NaPb_2(CO_3)_2(OH)$ was the dominant reaction product and hydrocerussite was present only in minor amounts. The formation of $NaPb_2(CO_3)_2(OH)$ is favoured by long retention times, high Na_2CO_3 or NaCl concentrations and elevated temperatures.

Figure 17 shows a number of particles which have been converted entirely to $NaPb_2(CO_3)_2(OH)$ by the reaction of $PbSO_4$ in 2.0 *M* Na_2CO_3 solution at 30°C. The particles consist of a porous core and a less porous rim. Both X-ray diffraction analysis and SEM–EDX studies showed the rims and cores to be nearly identical in composition, although the cores sometimes contained traces of $Pb_3(CO_3)_2(OH)_2$. Clearly, however, there is a significant difference in the morphology of the rims and cores. Presumably, the compact rim is a consequence of recrystallization or volume change phenomena, which occur at the periphery and progress towards the core. Although this type of rimming

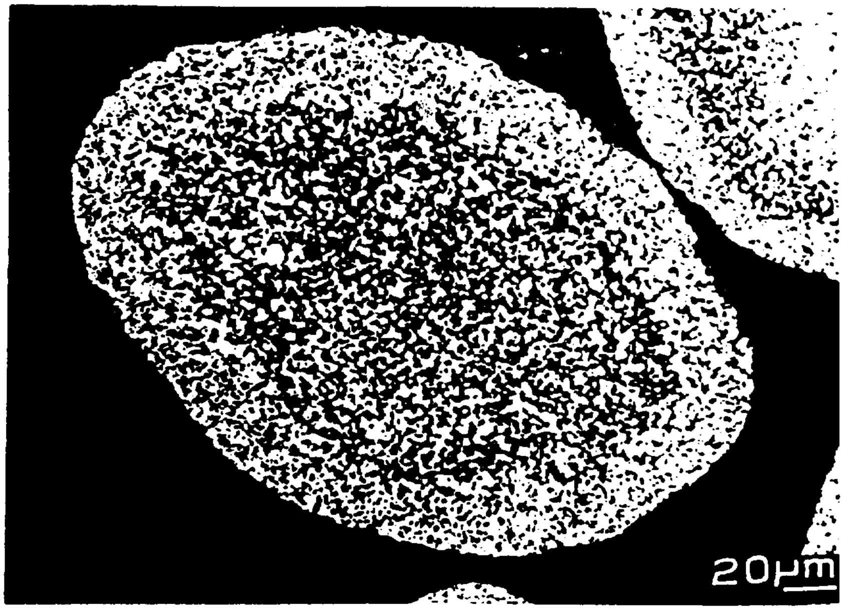

Fig. 17. Backscattered electron micrograph of a number of particles of $NaPb_2(CO_3)_2(OH)$ that illustrates the compact $NaPb_2(CO_3)_2(OH)$ rim on a more porous $NaPb_2(CO_3)_2(OH)$ core (polished section).

effect is most common on particles of $NaPb_2(CO_3)_2(OH)$, it has also been observed on some particles of hydrocerussite.

Figure 11 shows that the $PbSO_4$ conversion rate in 0.1 *M* Na_2CO_3 media decreases sharply in the pH range 11.5–12.0. This decrease is believed to be caused by variations in the product composition and morphology. As the pH increases, progressively greater amounts of $Pb_{10}O(CO_3)_6(OH)_6$ and $Pb_4O_3(SO_4)(H_2O)$ are detected in the $Pb_3(CO_3)_2(OH)_2$ reaction product:

$$10PbSO_4 + 6Na_2CO_3 + 8OH^- \rightarrow Pb_{10}O(CO_3)_6(OH)_6 + 12Na^+ + 10SO_4^{2-} + H_2O \quad (17)$$

$$4PbSO_4 + 6OH^- \rightarrow Pb_4O_3(SO_4)(H_2O) + 3SO_4^{2-} + 2H_2O \quad (18)$$

Small amounts of PbO are also formed:

$$PbSO_4 + 2OH^- \rightarrow PbO + SO_4^{2-} + H_2O \quad (19)$$

At pH 12.0, where the rate is the slowest, all the phases are present in major amounts, as is evident in Fig. 18. The particle shown in Fig. 18 consists of an outer indistinct band of $Pb_4O_3(SO_4)(H_2O)$ which surrounds a fine intergrowth of $Pb_4O_3(SO_4)(H_2O)$ and $Pb_{10}O(CO_3)_6(OH)_6$. Hydrocerussite, $Pb_3(CO_3)_2(OH)_2$, is present near the core of the particle, as are several bright

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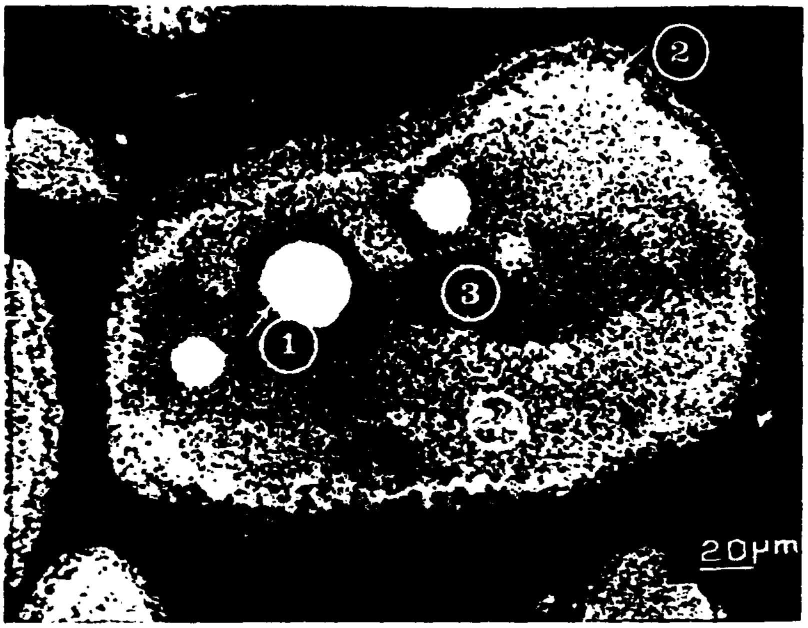

Fig. 18. Backscattered electron micrograph of a PbSO$_4$ particle reacted in 0.1 *M* Na$_2$CO$_3$ solution, the pH of which was raised to 12.0 by NaOH (polished section). *1* = PbO; *2* = Pb$_4$O$_3$(SO$_4$)(H$_2$O); *3* = Pb$_3$(CO$_3$)$_2$(OH)$_2$; *4* = Pb$_{10}$O(CO$_3$)$_6$(OH)$_6$.

masses of PbO. Although the association of hydrocerussite with PbO is consistent, the order of the Pb$_4$O$_3$(SO$_4$)(H$_2$O)-Pb$_{10}$O(CO$_3$)$_6$(OH)$_6$ banding shows considerable variation from particle to particle. The slow reaction of these particles could be due to the poorly permeable nature of the bands, or to the refractory nature of the PbO and Pb$_4$O$_3$(SO$_4$)(H$_2$O) phases.

The presence of high concentrations of Na$_2$SO$_4$ in the 0.1 *M* Na$_2$CO$_3$ solution results in a decline in the PbSO$_4$ conversion rate (Fig. 13). The slower rates may be due to the presence of Pb$_4$(SO$_4$)(CO$_3$)$_2$(OH)$_2$ which was detected as an initial reaction product in solutions containing more than 0.3 *M* Na$_2$SO$_4$. The amount of Pb$_4$(SO$_4$)(CO$_3$)$_2$(OH)$_2$ decreases with prolonged exposure to the solution, and the Pb$_4$(SO$_4$)(CO$_3$)$_2$(OH)$_2$ phase was generally present only in trace amounts in the products examined after 10 min of reaction:

$$4PbSO_4 + 2Na_2CO_3 + 2OH^- \rightarrow Pb_4(SO_4)(CO_3)_2(OH)_2 + 4Na^+ + 3SO_4^{2-} \quad (20)$$

$$3Pb_4(SO_4)(CO_3)_2(OH)_2 + 2Na_2CO_3 + 2OH^- \rightarrow 4Pb_3(CO_3)_2(OH)_2 + 3SO_4^{2-} \quad (21)$$

CONCLUSIONS

The reaction of -65 $+100$ mesh (-208 $+147$ μm) particles of $PbSO_4$ with Na_2CO_3 media has been investigated over a wide range of conditions. The -208 $+147$ μm particles consisted of intergrown aggregates of 1–6 μm $PbSO_4$ crystals. The reaction of the agglomerated $PbSO_4$ particles was topochemical in nature and obeyed the shrinking core model, incorporating diffusion through the constantly thickening product layer formed on the particles. The $PbSO_4$ conversion rates were consistently rapid; they increased as the first power of the Na_2CO_3 concentration, but decreased moderately with increasing concentrations of the Na_2SO_4 reaction product.

The rate increased systematically with increasing temperature, and the apparent activation energy was 15.8 kJ/mol. The presence of up to 1.0 *M* $NaNO_3$ in the carbonate solution had no significant effect on the $PbSO_4$ conversion rate, but similar concentrations of NaCl or KCl resulted in a pronounced rate decrease. The pH of the sodium carbonate solution has a significant influence on the $PbSO_4$ conversion rate. Reducing the pH causes the rate to decrease because of the conversion of the carbonate ion to the slowly reactive bicarbonate species. Increasing the pH from 11.5 to 12.0 with NaOH causes a dramatic reduction in the reaction rate that seems to be related to changes in the reaction products and product morphologies. When the pH is above 12, the $PbSO_4$ dissolves in the solution. The results suggest that the reaction of $PbSO_4$ with Na_2CO_3 solutions is controlled by the diffusion of the Na_2CO_3 reactant through the constantly thickening product layer formed on the agglomerated $PbSO_4$ particles.

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