LEACHING OF SPENT BATTERIES POWDER WITH SODIUM CARBONATE AND CARBON DIOXIDE

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Abstract

The processing of lead from scrap lead-acid batteries by pyrometallurgical route is generally accompanied by emissions of sulphur dioxide and high amount of slags. Therefore, lead is entrapped in the slags as $xNa_2S.yFeS.zPbS$ which makes the slag unsuitable to be disposed off as environmental friendly product. To overcome these difficulties, a sodium carbonate leaching process was investigated. The sample used for this study was a paste powder from spent batteries. The reactions of sized battery paste powder with sodium carbonate media were studied over a broad range of experimental conditions. Carbon dioxide gas was bubbled through sodium carbonate solution at 20°C to form sodium hydrogen carbonate which enhanced the transformation of by-products, hydrocerrusite $(Pb_3(CO_3)_2(OH)_2)$ and sodium lead carbonate $(NaPb_2(CO_3)_2OH)$ into $PbCO_3$ which reduced the emissions of sulphur dioxide and high amount of slags . Results were discussed from kinetic behavior aspect, especially: leaching curves, stoichiometry of the reaction and X-ray diffraction analysis of the reaction products. Under these conditions, lead carbonate recovery of 68 % was obtained in less than about 40 minutes at room temperature.

Key words: Leaching, spent batteries powders, sodium carbonate, carbon dioxide

1.0   Introduction

Nowadays, the importance of recycling is becoming greater of a concern both for the general public and also for the economy. Lead is a bluish white lustrous metal one of the potentially scarce natural resource. Approximately half of the total world leads production results from secondary lead smelting and that 80 – 85% of spent batteries are recycled globally [1]. Lead poses a potential risk to the environment and human health. People and animals are mainly exposed to lead by breathing and ingesting it in food, water, soil or dust. It damages human organs and can also lead to osteoporosis and reproductive disorders, it affects the brain and nerves leading to memory problem and brain damage. Moreover, a long term ingestion of lead might result in heart diseases and high blood pressure. It has been also shown that a relatively low concentration of lead in the environment can slow down vegetation growth (Abbasi *et al.*, (1998); Prengaman *et al.*, (2000).

Lead demand is increasing with the increase of economic growth in developing countries like South Africa. Most automotive and motor industries are using lead-acid battery as source of electricity for the electronic technology of the vehicles. Admittedly, there are several technical challenges which must be overcome in order to develop a viable hydrometallurgical process starting with establishing a cost effective leaching process for desulphurization which will reduce the hazardous waste which poses a potential risk to the environment and human health while saving the scarce natural resources (lead).
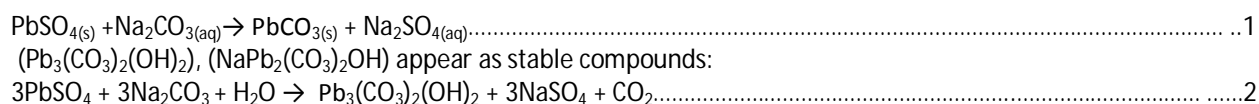
Theoretical studies indicated that desulphurization of the battery paste prior to reduction, greatly enhances the efficiency and economy of the high-temperature (Martini, 2008; Prengaman; Ramus *et al.*, (1993); Prengaman *et al.*, (1989). Various methods for desulphurization lead-acid batteries have been reviewed in literature (Olper *et al.*, (1989); Elmore *et al.*, (19890); Dutrizac). In the plint process, all lead compounds are converted to Pb2+ in an acid/ brine solution Collivgnarelli *et al.*, (1986); Taylor *et al.,* (1984); Yamada *et al.*, (1974). The leachant is then converted to solid lead hydroxide or carbonate that may be loaded into the furnace. Due to unknown nature of the chemistry of the patented Plint process, a detailed experimental investigation is needed to determine the exact nature of the leaching parameters and the behavior of batteries paste and lead dust under leaching conditions. In the process of recovering of lead from the lead-acid batteries, using (Na_2CO_3), the amount of SO_2 is decreased and the production of hydrocerrusite entrapping lead as $xNa_2S.yFeS.zPbS$ in the slag is equally reduced (Gong *et al.*, Elmore *et al.*, 91978); Janvan der lee (2008). The lead trapped in the slag make it unsuitable to be disposed off Arai *et al.*, (1970); Yamada *et al.*, (1974). An alternative investigation using CO_2 process seems to be the most feasible.

South Africa as a developing country where the demand for energy is higher than the supply, it will be very much beneficial for the industries to use this CO_2 process that aims to reduce production costs through energy saving. The high quality products and by- products of high economic value and the small amount of slag which is environmental friendly will be produced with less energy consumption. The aim of this research is to test the feasibility of application of the improved sodium carbonate leaching process for the desulphurization of battery paste with sodium carbonate to completely convert hydrocerussites [$Pb_3 (CO_3)_2(OH)_2$, $NaPb_2 (CO_3)OH$] produced as by-products into lead carbonate.

The process using direct smelting of the battery paste has a drawback. It requires high temperature to decompose the sulphates, the high temperature results in the generation of lead fumes and moderate concentration of sulphur dioxide gas that are costly to be removed from the gas stream(Martine (2008).

It is quite clear that despite the availability of excellent recycling infrastructure for the lead battery (Ramus *et al*, (1993); Olper *et al*, (1998); Collivignarelli *et al.*, (1986)., there is a need for a simpler and a more environmental friendly route in the face of constraining legislations and cost competitiveness. It appears attractive to develop a cost effective process that does not involve smelting or electro-winning.

The dissolution of battery paste ($PbSO_4$) in a Na_2CO_3 media (REF)

$PbSO_{4(s)}$ +$Na_2CO_{3(aq)}$→ $PbCO_{3(s)}$ + $Na_2SO_{4(aq)}$.. ..1
($Pb_3(CO_3)_2(OH)_2$), ($NaPb_2(CO_3)_2OH$) appear as stable compounds:
$3PbSO_4 + 3Na_2CO_3 + H_2O → Pb_3(CO_3)_2(OH)_2 + 3NaSO_4 + CO_2$.. 2

$2Pb_3(CO_3)_2(OH)_2 + 2Na_2CO_3 \rightarrow 3NaPb_2(CO_3)_2OH + NaOH$...3

$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$...4

$Pb_3(CO_3)_2(OH)_2 + 2NaHCO_3 \rightarrow 3PbCO_3 + Na_2CO_3 + 2H_2O$...5

$NaPb_2(CO_3)_2OH + NaHCO_3 \rightarrow 2PbCO_3 + Na_2CO_3 + H_2O$...6

2.0 Method

2.1 Experimental Procedure

A 500ml Erlenmeyer flask fitted with a rubber lid was used as a reactor for the carbonate leaching of battery paste. A magnetic stirrer at a constant speed of 1600 rpm was used to agitate the leaching solution. Five hundred milliliters of 0.28 M of leaching solution (sodium carbonate) were charged into the reactor, and kept at ambient temperature. Battery paste powder samples with particle size in the range of -320 μm + 400 μm mesh lead sulphate -were introduced in the solution and leaching initiated.

The bench experiments were performed for a required time interval, after which the grab samples per time intervals were vacuum filtered and analyzed for the qualitative and quantitative chemical compositions by X-Ray Diffraction (XRD). Tests were run following these conditions as tabulated in Table 1.

Table 1: Species and important parameters

| Species	Concentration (mol/l)	Ratio	Temperature °C	Agitation speed (rpm)	pH
Soda Ash	0.28 M	1:1	25°C	1600	10.89
Lead Sulphate	0.28 M	1:1	25°C	1600	10.89

Carbon dioxide gas was bubbled through sodium carbonate solution at 20°C to form sodium hydrogen carbonate (eq.4) to desulfate the residues of hydrocerrusite ($Pb_3(CO_3)_2(OH)_2$) and sodium lead carbonate ($NaPb_2(CO_3)_2OH$) from first bench experiment to form cerrusites ($PbCO_3$) as part of the second bench experiment at 25°C and stirring rate of 1600 rpm:

3.0 Results

3.1 Effect of Sodium Carbonate on Leaching of Battery Paste Powder

Raw battery paste sample used in these experiments was analyzed using X-Ray Diffraction method. The sample composition was found to be of 96% lead sulphate ,4% lead oxide (PbO_2 and Pb_2O_3) as shown in Figure 4.1, of which is the feed for the leaching process.

Figure 4.2 illustrates typical conversion rate curves of various feed ratio when of -320 μm + 400 μm of battery paste composed of 95% $PbSO_4$ was leached with sodium carbonate solution at 25°C and stirring rate of 1600rpm, In these investigations, the concentration of $PbSO_4$ is fixed while only varying the concentration of leachant (Na_2CO_3). In this Figure, the fractional conversion of lead sulphate to lead carbonate is plotted as a function of time for various molar ratios of $PbSO_4/Na_2CO_3$. It can be observed from Figure 4.2 that the rate of reaction of $PbSO_4$ with Na_2CO_3 in aqueous media is very rapid [14], at the excess amount of sodium carbonate it reaches completion in less than 3 minutes. The reaction rate increases with the increase in the feed ratio at room temperature and atmospheric pressure at a constant stirring rate of 1600rpm.

Counts

90000

40000

10000

0

Lead- acid battery paste

97 % 1 % 2 %

Position [°2Theta] (Cobalt (Co))
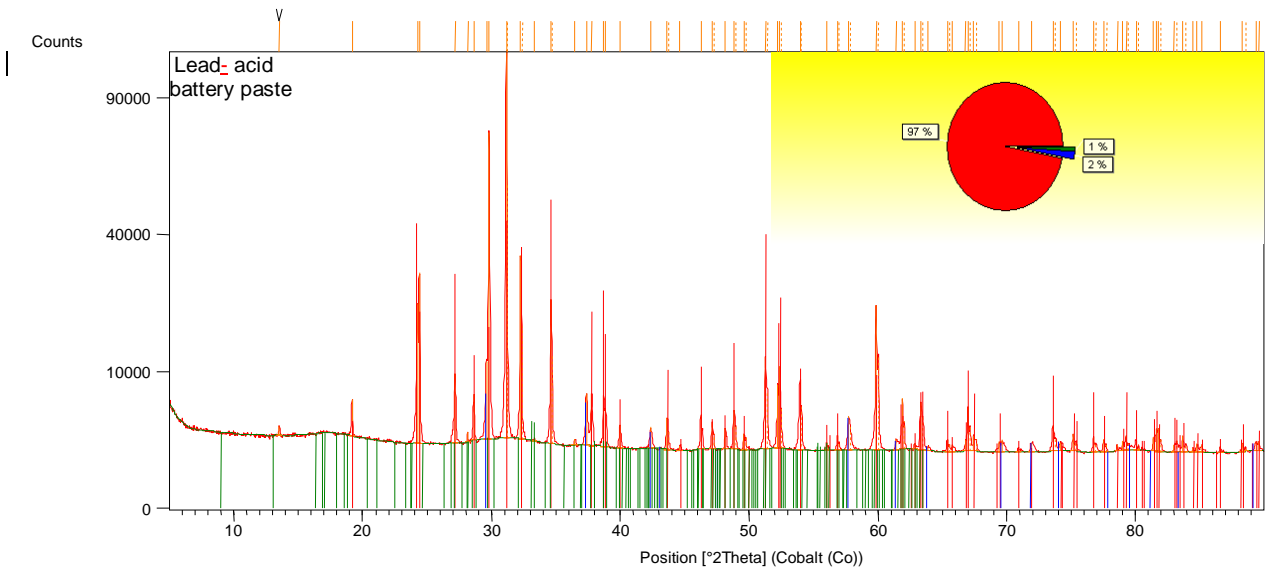
Peak List

01-089-7356; Anglesite; Pb(SO$_4$); Orthorhombic; SQ: 96.00 [%]

01-076-0564; Plattnerite, syn; PbO$_2$; Tetragonal; SQ: 2.00 [%]

01-076-1831; Lead Oxide; Pb$_2$O$_3$.333; Monoclinic; SQ: 1.00 [%]

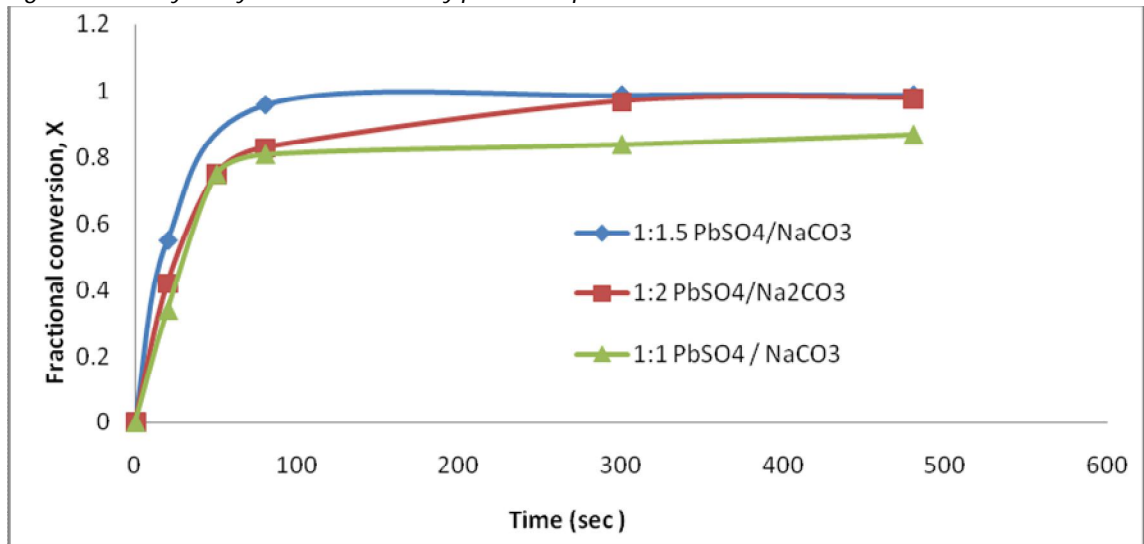Figure 4.1: X-ray analysis of initial battery paste sample

Figure 4.2: Leaching rate curves of lead sulphate in sodium carbonate solutions at 25°C

The rate of conversion is found to increase with increasing concentration of the leachant. At the ratios of 1:1 and 1:1.5 the reaction proceeds at constant rate during the initial stages of leaching, and then the rate decreases as the degree of conversion approaches 1. The rate of decrease in the conversion is dependent on the starting

concentration of the leachant.
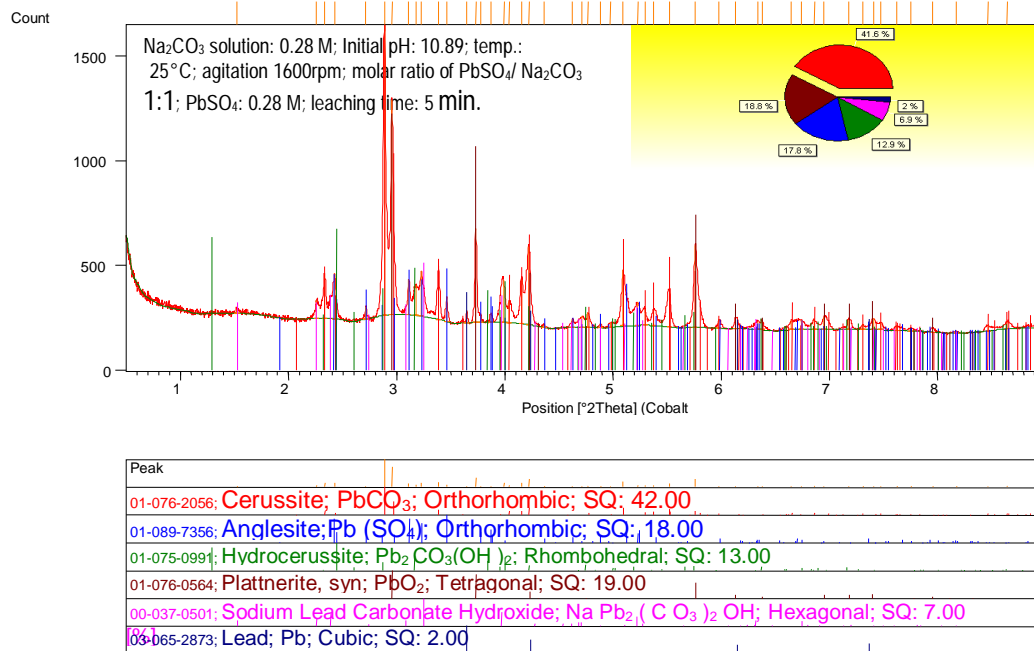
Figure. 4.3: X-ray analysis of the leaching products

To determine the stoichiometric relation of the leaching reaction, X-ray diffraction analyses were performed on the leach products. After 5 minutes of leaching, samples were taken and analyzed for the recovery of lead carbonate, sodium lead carbonate hydroxide and hydrocerrusites. The results of the X-ray diffraction analysis of the leach residue are shown in Figure 4.3. Detectable changes were observed when the leaching conditions were altered.

3.2 Kinetic Behavior

In order to have a better understanding of the mechanism of the leaching reaction, kinetic studies were carried out. As shown in Figure 4.2, the conversion rate of lead sulphate is very rapid. However, by considering only the initial stage of the reaction, apparent rate constants, k's, can be calculated from
the slope of the straight line section of the leaching curves. These calculated values of k' can then be used to discuss the effect of various factors on the leaching rate.
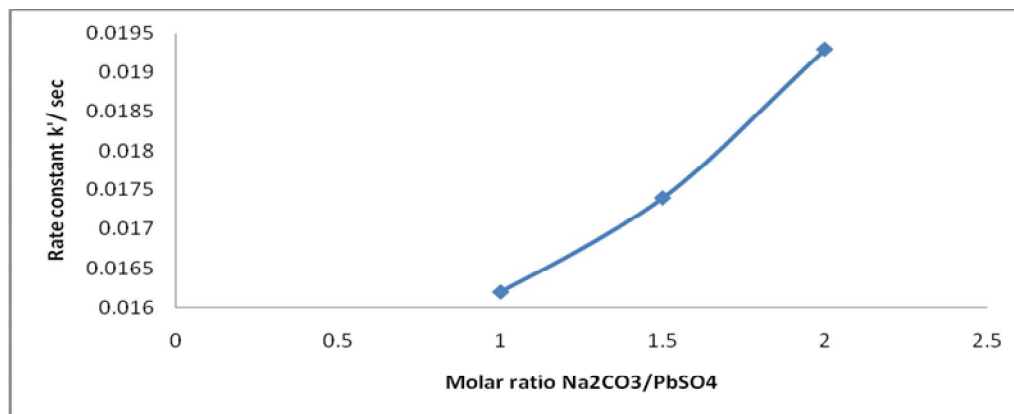
Figure 4.4: Effect of the concentration of leachant on the apparent rate constant k'

The rate constants were determined from the individual curves presented in Figure 4.2. Rate constant, k', is plotted against the initial concentration of the leachant. The k' values increase with increasing initial concentration of the leachant, indicating the existence of a first order relationship.
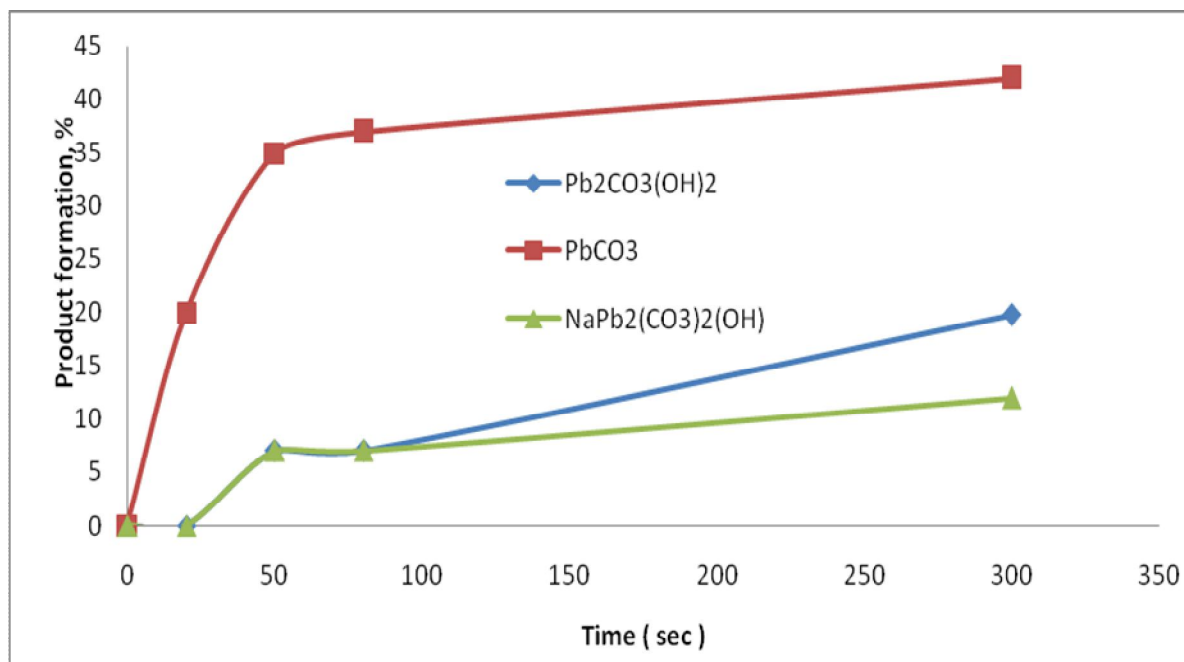
4.3 The Effects of Feed Ratio $PbSO_4/Na_2CO_3$

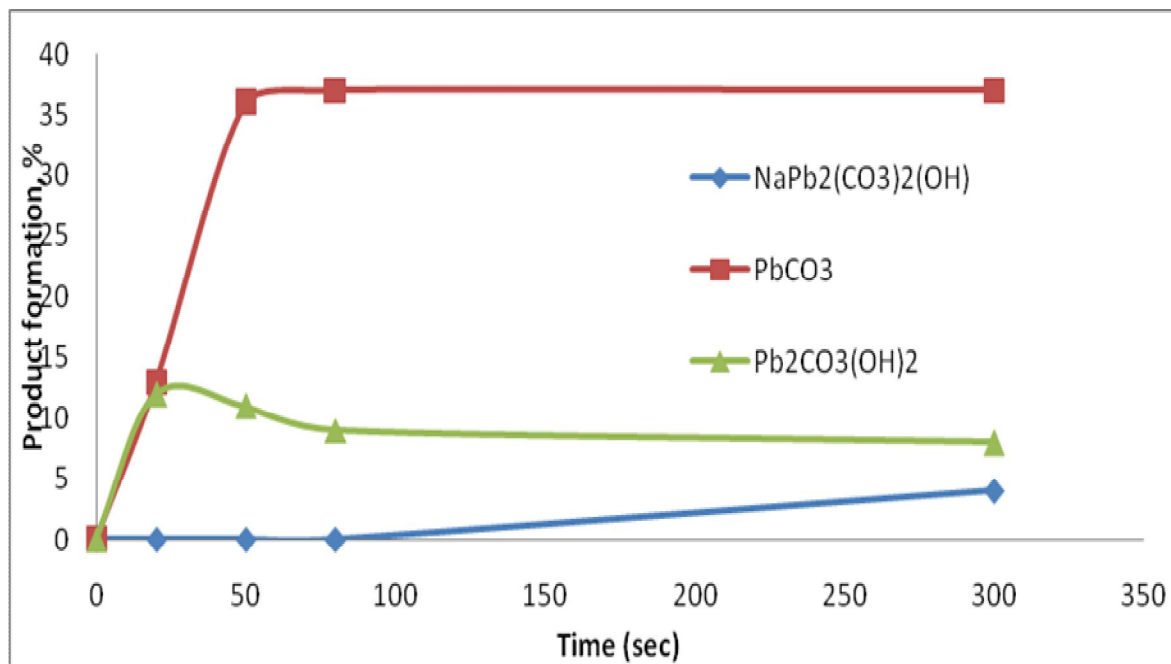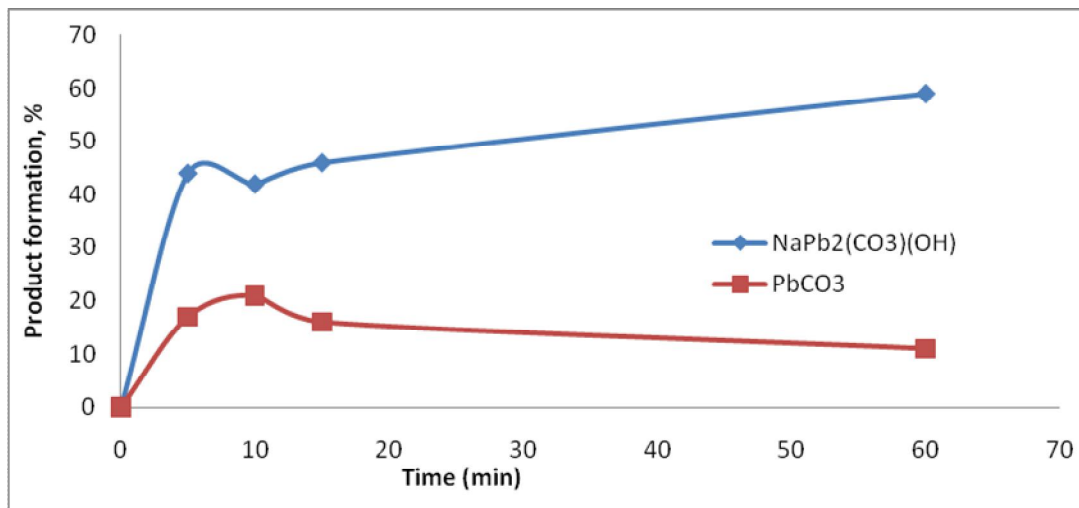*Figure 4.5: Effect of feed ratio 1:1, $PbSO_4/Na_2CO_3$ on the formation of product*

Figure 4.6: Effect of feed ratio 1:1.5, $PbSO_4/Na_2CO_3$ on the formation of product

Figure 4.7: Effect of feed ratio 1:2, PbSO$_4$/Na$_2$CO$_3$on the formation of product

The lead carbonate species is converted into another species (NaPb$_2$(CO$_3$)$_2$OH), In addition NaPb$_2$(CO$_3$)$_2$OH precipitate over a broad range of conditions in the presence of sodium ion [22, 23]. It can be observed that more of NaPb$_2$ (CO$_3$)$_2$OH is formed at a ratio of 1:2 and long residence time while the concentration of PbCO$_3$ gradually decreases.
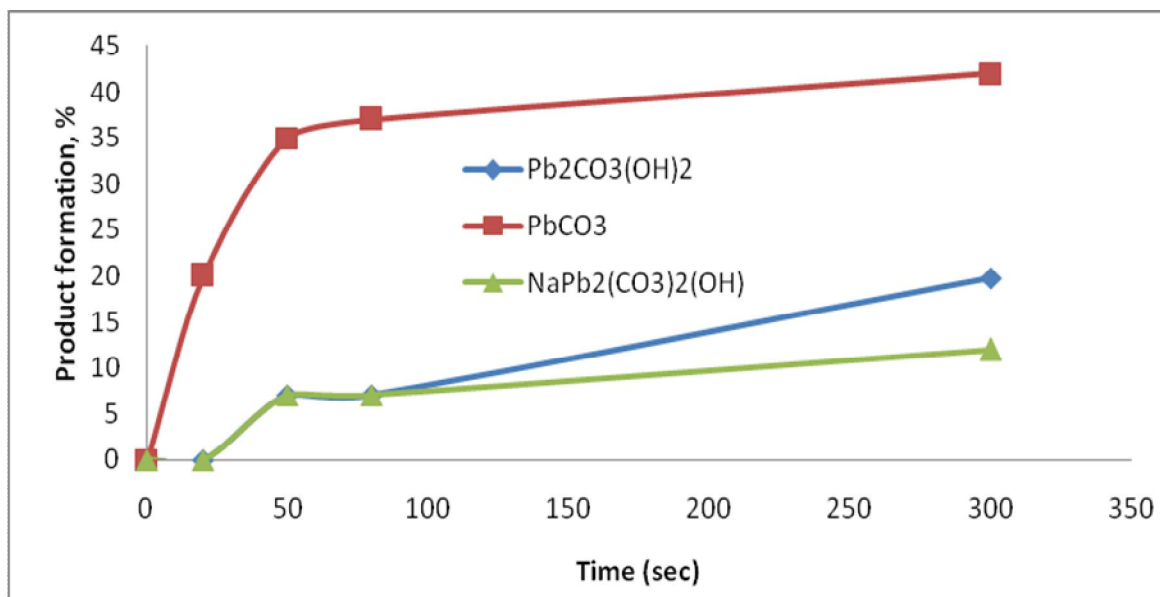
3.4   Effects of Leaching Temperature

Figure 4.8: Temperature effects on the formation of the products at 25°C at ratio

It is observed from Figure 4.8 that the rate of formation of cerrusite at a temperature of 25°C is very fast and 42% of it is formed within 5 minutes of reaction. Small traces of NaPb$_2$(CO$_3$)$_2$OH are lowly formed [15].The formation of NaPb$_2$(CO$_3$)$_2$OH increases with reaction time and from first 3 minutes of reaction increase with the decreases of PbCO$_3$ as illustrated from Fig 4.9. The long residence time at 45°C favors the formation of the compound NaPb$_2$(CO$_3$)$_2$OH at a constant stirring rate of 1600 rpm.
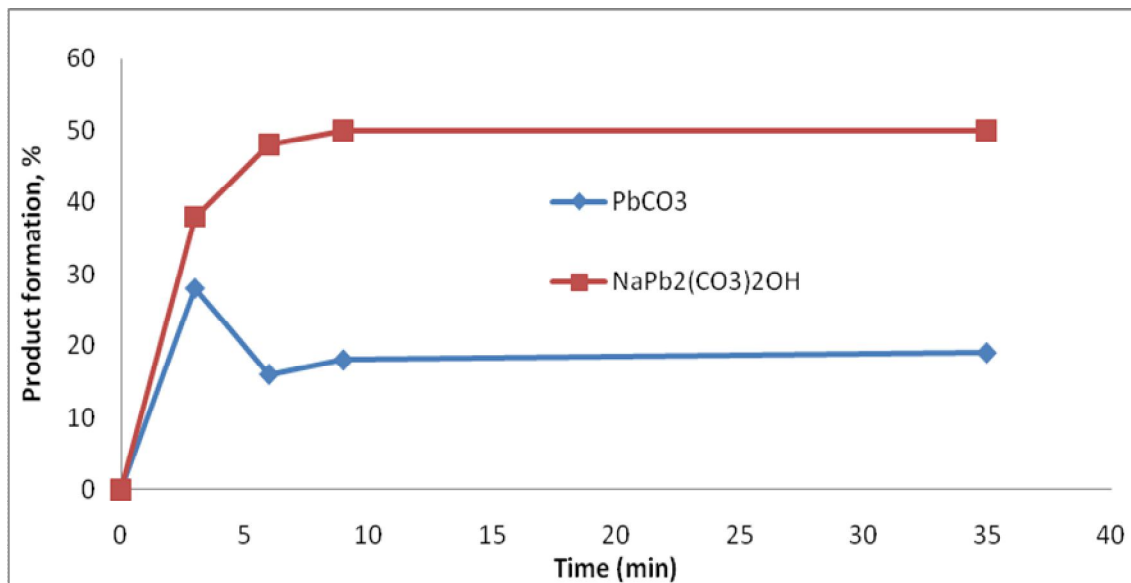
Figure 4.9: Temperature effects on the formation of the products at 45°C

The percentage composition of the $NaPb_2(CO_3)_2OH$ remain stable from above 10 minutes of reaction for the temperature of 45°C while there is a slight increase in cerrusite concentration.
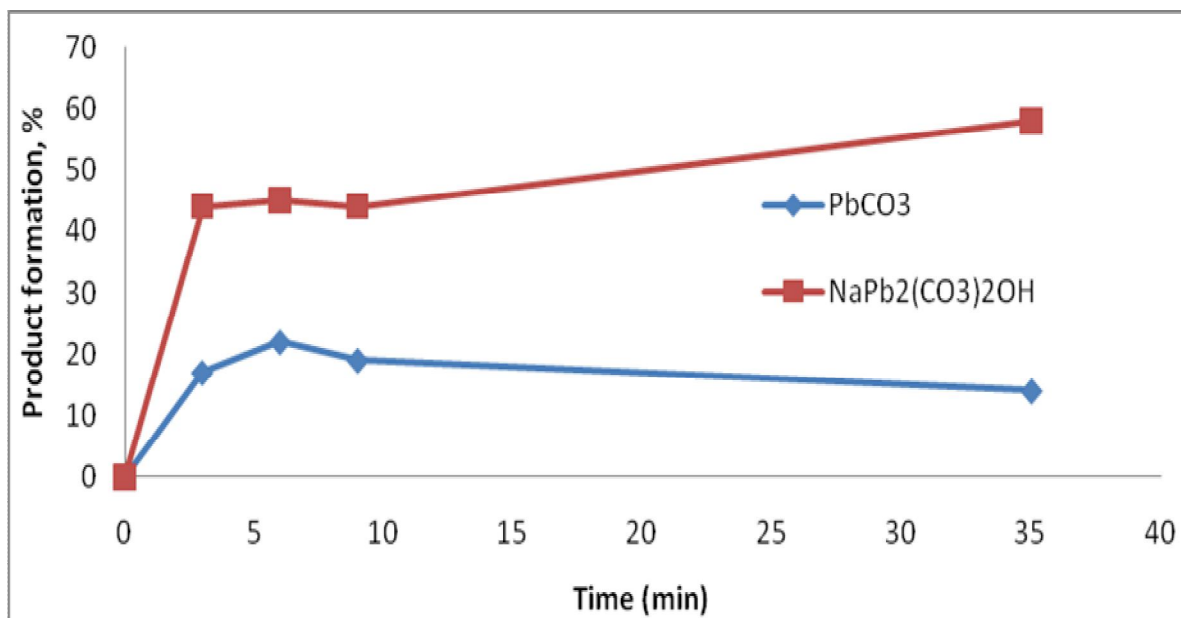

Figure 4.10: Temperature effects on the formation of the products at 60°C at ratio 1:1 and 1600rpm

From the first 10 minutes of reaction the amount of $NaPb_2(CO_3)_2OH$ increases with time while $PbCO_3$ decreases as illustrated in Figure 4.10.The long residence time at 60°C favours the formation $NaPb_2(CO_3)_2OH$ while $PbCO_3$ is getting consumed with time. It can be seen from the Figure 3.8 to Figure 4.9 that high temperature with long residence time compliments the formation of $NaPb_2(CO_3)_2OH$ [4]. Clearly the rates are rapid at all temperatures, and similar observations were made in previous studies on this reaction [14, 15]. Even at 45°C and 60°C, optimum formation of cerrusite is achieved within first 5 minutes of reaction.
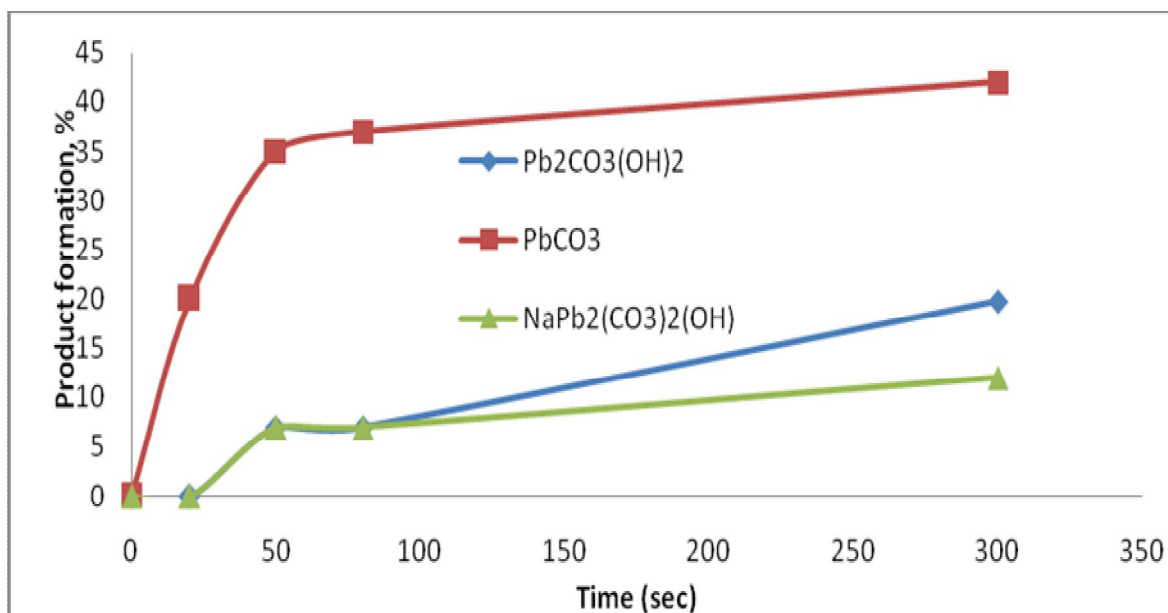
237

3.5   Effects of Stirring Rate on the Solution

Figure 4.11: Leaching behavior at 1600 rpm, ratio, 1:1 $PbSO_4/Na_2CO_3$ and 25°C

The effects of agitation on the apparent reaction rate are shown in Figure 4.11 .The rate of formation of the $PbCO_3$ gradually increase with time which also favors the formation of the undesired products. As it is observed from the curves in Figure 4.11, that 42% of $PbCO_3$ is formed within first 4 minutes of reaction at a stirring rate of 1600 rpm.
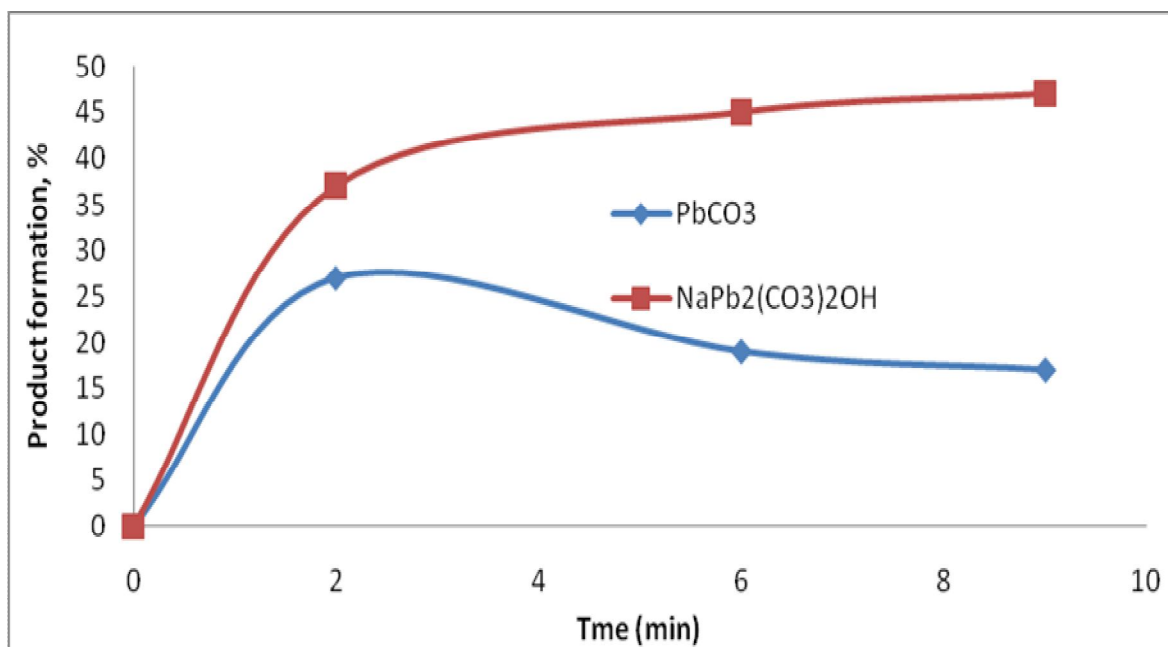

Figure 4.12: Leaching behavior at 700 rpm, ratio, 1:1 $PbSO_4/Na_2CO_3$ and 25°C

From Figure 4.12 is observed that the formation of $NaPb_2(CO_3)_2OH$ is increasing with reaction time and $PbCO_3$ at 700rpm stirring rate, at a constant temperature of 25°C.The stirring rate of 700rpm compliments the formation of

more of $NaPb_2(CO_3)_2OH$ from the beginning of the reaction. By judging from these two Figures (Figure 4.12 and Figure 4.13) it can be concluded that the rate of formation of $PbCO_3$ is inversely proportional to the rate of formation of $NaPb_2(CO_3)_2OH$ [4].

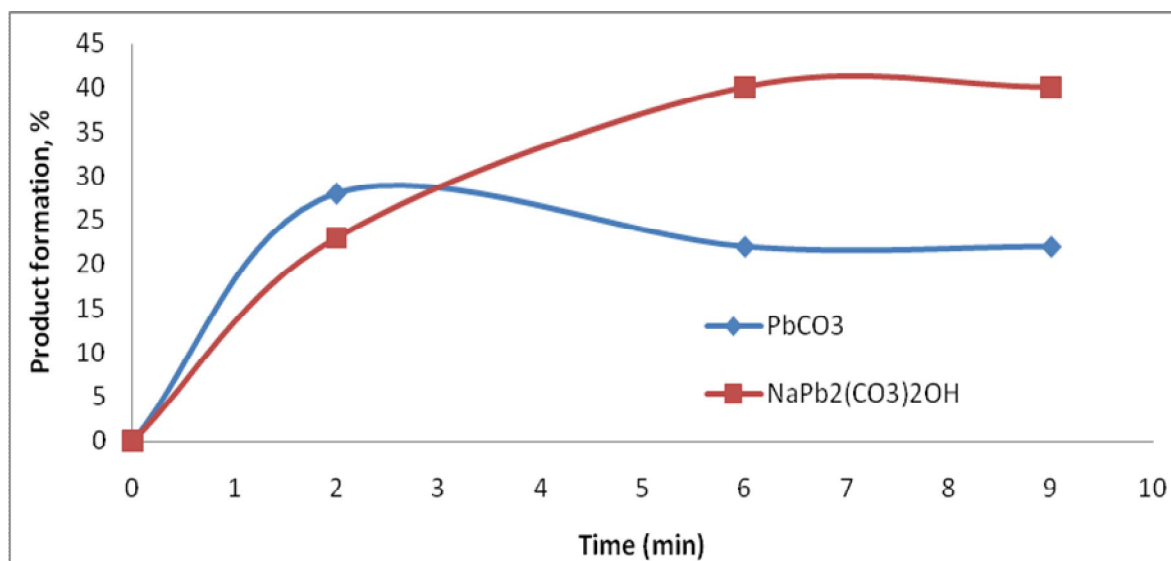*Figure 4.13: Leaching behavior at 100 rpm, ratio, 1:1.5 $PbSO_4/Na_2CO_3$ and 25°C*

Between 3 minutes of reaction the percentage formation of $NaPb_2(CO_3)_2OH$ increases with time while $PbCO_3$ decreases with time and from 6 minutes and above the concentrations remain constant. Low stirring rates compliments the formation of $NaPb_2(CO_3)_2OH$ while the high stirring rates favors the formation of $PbCO_3$ with the increase in reaction time as observed from the above figures.

Figure 4.11 to Figure 4.13 show the comparison between test done at 1600 rpm, 700 rpm, 1600 rpm at 25°C and feed ratio1:1 $PbSO_4/Na_2CO_3$.

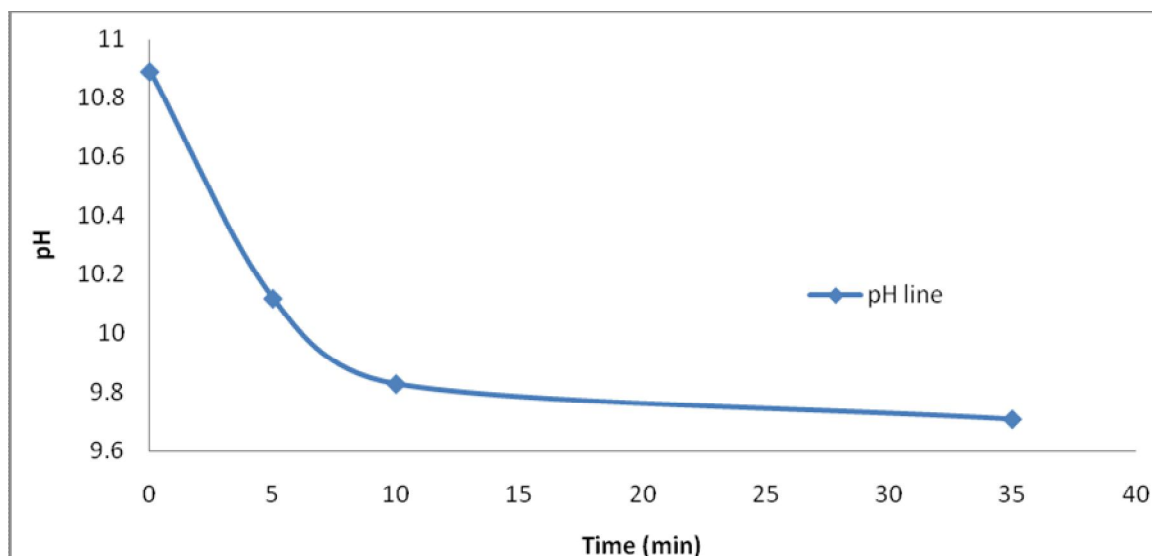### 3.6   Effects of Reaction on the pH of the Solution

Figure 4.14: Effect of reaction time on pH of the solution

239

The pH decrease as the reaction proceeds as it can be observed from Fig. 4.14, the starting pH was 10.89 and it has decreased with time until it reaches the values of 9.71 at 35 minutes. The reaction rate is inversely proportional to the pH, as it can be observed that when the reaction rate is very rapid in less than five minutes of reaction the pH decrease is also rapid. Reading from Fig.4.11, it can be concluded that the decrease in pH values favors the formation of sodium lead carbonate hydroxide $NaPb_2(CO_3)_2OH$.

4.0   Conclusions

The feasibility of the desulphurization of lead sulphate in sodium carbonate solution has been evaluated from kinetic aspect based on the experimental results obtained on the leaching rates, stoichiomentry of reaction and X-ray analysis of the reaction products. The conversion rate of lead sulphate proceeds rapidly at initial stage of leaching, and the rate is directly proportional to the concentration of lead carbonate.

Hydrocerrusite ($Pb_3(CO_3)_2(OH)_2$) is formed under mild operating conditions and appear as an intermediate product of the reaction, but the formation of $NaPb_2(CO_3)_2OH$ is favoured by long retention time and high Na_2CO_3 and elevated temperatures. The reaction of $NaHCO_3$ with $NaPb2(CO_3)_2OH$ and ($Pb_3(CO_3)_2(OH)_2$) is slower than the one of $PbSO_4$ and Na_2CO_3 from first bench experiment because of the slowly reactive HCO_3^- species. The pH of the solution decreases with increasing retention time as a result slows the reaction rate.

Under investigated leaching conditions, lead carbonate recovery of 68 % can be obtained in less than about 40 minutes at ambient room temperature.

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