The role pH plays in the precipitation of lead sulphate from an alkaline waste solution

MSc by Dissertation

by

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Declaration

I declare that this dissertation is my own unaided work. It is being submitted to the Degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

1. ....

(Signature of Candidate)

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Abstract

A local manufacturer of lead chemicals has expressed a definite interest in buying recovered lead sulphate from S.A Precious Metals, a minerals processing company. The recycling of lead provides a means of reducing the strain on resources that is caused by the use of virgin materials such as lead. In addition, recycling prevents any damage caused by improper treatment processes and disposal practices that would otherwise lead to groundwater contamination.

Research into lead precipitation has so far focused mainly on acid waste, perhaps because of the size and influence of the lead acid battery industry. The work described in this dissertation was motivated by the efforts of S.A Precious Metals to process the company's lead-alkaline waste. Initially, the scientists carrying out laboratory-scale tests encountered solids-handling problems. The writer undertook the investigation reported in this document to find a viable means of recovering both lead sulphate and sodium sulphate from solution.

During the batch trials, the researcher recovered lead sulphate via precipitation from the lead-containing solution, while precipitating the sodium plumbate solution (normally considered hazardous waste) with sulphuric acid. This process offers a low-cost answer to the problem that also offers a quick turn-around, saleable by-products and a benign waste stream.

Precipitation to a pH between 6 - 7 using a 20% solution of sulphuric acid added at the point of mixing resulted in a final lead concentration of 2.7 ppm with no ageing period necessary. During solid-liquid filtration, the temperature was maintained above the sodium sulphate temperature of crystallisation of 32 °C, which reduced the amount of sodium sulphate precipitated out into the lead sulphate cake. The final step, which involved crystallising the sodium sulphate out of the lead filtrate solution, yielded high recoveries of sodium sulphate in excess of 61%.

In order to collect the necessary data for large-scale implementation of the process, the writer tested the roles that different parameters such as starting lead and sulphuric acid concentrations, final pH, and filtration and precipitation temperatures played on lead removal from solution. It was found that dropping the pH by several units through acid addition played the governing role in effecting lead sulphate precipitation. Thereafter she compared the final lead concentrations obtained experimentally against the local (Ekurhuleni Metropolitan Municipality) lead discharge environmental requirements limit of 5 ppm and the allowable pH range of 6 – 10 for wastewater effluent.

The optimal technique and process conditions that the researcher developed for precipitation, solids-handling and sodium sulphate crystallisation processes for production on a large scale are not only compliant with environmental regulations but offer maximum recovery and consequently profit.

For maximum value gain and environmental compliance, optimal technique and process conditions were chosen for precipitation, solids handling and sodium sulphate crystallisation processes for production on large scale.

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1. Introduction

One of the many waste streams coming from a process plant recycling waste is in the form of an alkaline leach solution containing high levels of dissolved lead, tin and sodium sulphate amongst other dissolved base metals present in lower amounts. This process stream, categorised on-site as waste, required immediate attention and treatment for the removal of the dissolved lead and for the high alkalinity, in order to comply with storage regulations for hazardous waste, which limit volumes stored, and to avoid paying high costs for hazardous waste disposal.

Globally, tighter controls on waste effluent have placed severe restrictions on residual lead concentration in effluent. Under the United States Environmental Protection Agency, lead has been classified as a priority chemical due to its toxicity (U.S. Environmental Protection Agency, 2012).

In the South African context, for an industrial municipality such as the Ekurhuleni Metropolitan Municipality, the lead discharge limit is 5 ppm (Ekurhuleni Metropolitan Municipality, 2013). However, the Federal American effluent wastewater discharge limit for lead is more stringent and is as low as 0.69 ppm total lead. Besides the lead being a concern, the final pH of the stream should be between 6 and 10 pH units in order to fall within the legal limits for effluent discharge (Ekurhuleni Metropolitan Municipality, 2013). Unsuitable or incomplete treatment of this material before disposal could lead to groundwater and soil contamination.

The concentration limit both in the case of a state in America, which clearly stipulates the discharge limits, and for the local South African municipality together with the stipulated pH range, can be seen in Table 1. For this reason, the outcome of the test work had to be assessed on the final concentration of the filtrate and not on the removal percentage.

Table 1-1: Restrictions placed on lead-containing effluent

Restrictions on waste effluent	Los Angeles (City of Los Angeles , 1999)	South African local municipality Ekurhuleni (Ekurhuleni Metropolitan Municipality, 2013)
Lead concentration limit (mg/l)	5	5
pH lower limit	≥2	6
pH upper limit	≤12.5	10

Earlier tests for removal of lead from such waste solutions had proven unsuccessful, and they resulted in numerous findings including low dissolved lead removal percentages and lead sulphate filtration rates as well as lead sulphate filter cake occluded with sodium sulphate crystals rendering it unsaleable and expensive to treat.

These preliminary lead precipitations using sulphuric acid and the alkaline lead leach solution which proved to be unsuccessful prompted this study together with the lack of data on lead sulphate precipitation from highly alkaline sodium hydroxide leach solution.

One of the most common options in treating industrial wastewater is precipitation or direct precipitation (Patterson, Petropoulou, Luo, Cooney, & Gasca, 1991). However, information on the precipitation of lead from a highly alkaline waste stream has not been widely published. Clever and Johnston (1980) gave a thorough review of the solubility values for lead sulphate in water while newer work published by Matlock et al. (2002) and Lenz and Martins (2007) looked at lead solubilities in the acidic region of the pH scale through dealing with lead acid battery waste in the case of the former and lead sulphide precipitation in the latter. A unique opportunity to look at the means of precipitating out this lead was identified when a widely recognised lead supplier expressed the need for recycled lead materials in their attempt to cut down on the use of virgin lead materials as a primary feedstock in their process.

The purpose of this investigation was therefore to create value from the plant waste stream by using precipitation as a means of treatment. This was achieved through the recycling of the maximum amount of lead and sodium sulphate obtained from the high removal rates, as well as rendering any unavoidable liquid waste into a benign form, suitable for disposal to the municipal sewer. This liquid waste could be further processed or re-used as a source of water in the plant. Solving the problem should command a quick turn-around time, involve low costs and produce saleable by-products and low-hazard waste. Samples of the material from actual plant runs were used in doing the test work.

1.1. Problem overview and motivation behind work

A local company involved in the beneficiation of precious metal chemicals and pure products was seeking a solution to a waste management problem. Lead-containing material was often accepted as part of waste materials for recycling by this company.

The material produced in the plant, a highly alkaline stream (almost 200 grams per litre sodium hydroxide) containing dissolved lead and tin, was the source of liquid effluent, which was to be used during the test work in this study. To avoid disposal problems and high costs associated with this process stream, the company had undertaken to conduct research on the conversion of the waste stream into saleable products. The fraction of lead should be minimised so that the material sent to the municipal reticulation system would meet the local government effluent discharge limits. This required that the company embark on a research programme where they would look at putting in place a treatment process for the stream in question, so as to satisfy government restrictions. This was also expected to cut down on disposal costs, allow for the recovery of maximum lead, and gain maximum value from the particular plant stream.

Consequently, as there was also tin in solution, it was expected that this would be removed from the solution simultaneously with the lead. Every effort was made to ensure that this source of lead was kept isolated in the plant through the recommended processing steps; this was introduced as a result of this study because lead is considered to be a major contaminant.

The research focused on using precipitation as its metal recovery technique due to its robustness as a chemical process. The concept of precipitation was first patented in 1762 by de Boissieu as a method for 'purifying dirty water' (Reynolds, 1933), and since then has been a widely-used method for the recovery of heavy metals. Sulphuric acid was chosen as the precipitant with the role of neutralising the solution, in line with the discharge guidelines on pH as seen in Table 1-1. Sulphuric acid was selected as the reagent of choice due to its relatively low cost and ready availability on-site as an established incoming raw material.

The precipitation process had three outputs, namely the filtrate, the lead-tin sulphate cake obtained after solid-liquid separation and sodium sulphate generated via the crystallization process.

The removal of the lead and tin was in such a way that it produced a cake in the form of lead and tin sulphate, leaving behind a filtrate with a low lead concentration.

A further opportunity to be aware of was making another saleable product, sodium sulphate, from this waste stream when the precipitant used is sulphuric acid. The recovery of lead and tin from the solution produced a large amount of sodium sulphate in relation to the lead and tin sulphate produced during the precipitation reaction. Recovering this sodium sulphate added value to the processing of the stream and also avoided wasteful disposal to landfill. Both these products hold commercial value to downstream processors and were integrated as part of the manufacturing processes on-site.

Channels for these materials were identified in the form of downstream manufacturers of lead materials including lead-chemicals and lead alloys as well as detergent manufacturers who can be supplied with crude sodium sulphate as part of the feedstock supply, thereby ensuring that resources are fed back into the supply-chain loop.

1.2. Research objectives

The main objective of this work was to provide the conditions under which lead precipitation from a lead-alkaline waste could take place producing a filtrate low in lead in line with government regulations. All tests were based on precipitation with sulphuric acid.

a. To identify and investigate the conditions that will result in a low lead concentration filtrate and in so doing identify the main variables to be considered as integral in achieving optimal conditions for precipitation.
b. To provide the relevant data required for the process to be scaled up, with the focus being on pH as a key parameter as well as ageing. As this process is intended for use on an industrial scale, it should be taken into account that turnaround is an important factor and should be kept in mind when determining process conditions such as ageing

c. To produce a filtrate in line with the local government stipulated pH range as discussed in Table 1-1.
d. To determine the extent of co-precipitation of the tin together with the lead if any
e. To integrate the results obtained from this study in order to form design data required for a lead recovery circuit incorporating the lead precipitation process, which will be produce, a lead-tin sulphate cake suitable for downstream processing by metal recyclers.

2. Literature review

2.1. Introduction

The removal of heavy metals from industrial waste solutions has become a subject of increasing interest to companies involved in minerals processing. The reasons are a rising demand both for relatively inexpensive feedstock and resources, and for recycled secondary materials to use in downstream processes. For example, a local manufacturer of lead chemicals has expressed a definite interest in buying recovered lead sulphate from S.A. Precious Metals. The sulphate can be used to produce pure lead as well as lead that can be mixed with other metals to produce alloys for the cable industry.

However, for minerals processing companies the recycling of lead offers more than financial advantage. It also provides a means of reducing the strain on environmental resources that is caused by the use of virgin materials such as lead. When lead waste is disposed of improperly, it leads to groundwater contamination. This avoidance of harm to the environment is the most important consideration for mineral processing operations. There is an additional advantage that is shared by both the producer and the buyer: recovery can be used to obtain sustainably sourced materials that can then become feed for downstream processes.

Even if the industrial demand for lead fluctuates or drops, there is a growing consensus that every effort should be made to continue research into managing waste associated with lead extraction. The reasons are twofold: an improvement in the technology will cut back disposal costs by reducing hazardous waste by-products; and it will generate revenue by fulfilling the need for a secondary source of lead in the market.

2.1.1. Technologies used in waste management

In order to cope with the increasing supply of complex and unfamiliar waste materials, researchers are constantly seeking methods and technologies capable of treating waste that is chemically different from other compositions. At times these adaptations involve the use of modifications to existing technology, while at others the engineers apply recently formulated methods.

Perry's Chemical Engineers' Handbook (1999) listed precipitation as one of the ‘most widely used technologies for hazardous waste management’. De Boissieu patented the concept that first introduced what we call precipitation in 1762, as a method of ‘purifying dirty water’ (Reynolds, 1933). Since then the process has been further developed for a range of liquids and solutions, and is now a highly regarded and widely used technology for heavy metal removal.

Musapatika (2010) reported on the other conventional methods used in the industrial treatment of wastewater, commenting on the main advantages and disadvantages of each while providing his reason for choosing to work on wastewater treatment by adsorption.

These methods include:

- electro-deposition
- precipitation and cementation (as a second and final step)
- ion exchange
- complexation
- solvent extraction
- foam flotation
- electrolysis
- oxidation
- membrane technology
- coagulation.

Adapted from Musapatika (2010)

Another point Musapatika (2010) made was that when the design engineer chooses which of the methods listed above is most suited to a particular use, it is common practice to assess their merits in terms of kinetics and metal selectivity.

Although, as already mentioned, engineers have considered precipitation the preferred solution to heavy metal recovery for many years (Patterson, Petropoulou, Luo, Cooney, & Gasca, 1991), research and development in the field of lead precipitation have been lagging behind. For example, while a certain amount of attention has been devoted to lead waste solutions of an acidic nature, very little has been paid to the treatment of alkaline lead waste. Barakat (1998) presents his work on the leaching of lead-containing scrap where an acidic leach is done before precipitation with sodium hydroxide. Similarly, work done by Scott et al. (1997) also involved recovery of lead amongst other heavy metals, from an acidic leach medium using electrolysis together with precipitation of lead as lead sulphate. On the other hand Lenz and Martins (2007) extracted the lead from waste using alkaline leach solutions before precipitating the lead out as a sulphide.

Although the gap in this area of research could be attributed to the drop in global demand for lead, the importance of lead recovery has not diminished in any way. Indeed, the need for further research has become more urgent because of the increasingly strict controls governments are imposing on the disposal of lead-containing waste. These now prohibit the release of any liquid effluent from an industrial process that contains more than 5 parts per million (ppm) of lead in solution (Ekurhuleni Metropolitan Municipality, 2013).

The list below identifies some of the industrial sources that generate lead-bearing waste:

- acid car batteries
- mining ores
- electric arc furnace dust
- redundant petroleum compounds
- solder waste from manufacturing or de-soldering.

Once these by-products have been leached, they undergo lead removal via precipitation.

The focal point of analysts working in this field of research is often the precipitation of lead sulphate, which occurs in acid batteries, making it necessary to recharge them. Scientists working on this topic have contributed a great deal of information on the behaviour of lead sulphate, specifically in solutions of sulphuric acid. Included amongst them were:

- Crockford and Addlestone (1936);
- Craig and Vinal (1939);
- Danel and Plichon (1982);
- Purdum and Rutherford (1933);
- Kolthoff et al. (1942); and

Paige, Kornicker, Hileman & Snodgrass (1992).

The last of these made it possible for researchers to determine the volume of lead sulphate solubilised by the sulphuric acid, otherwise referred to as ‘the solubility’. In this instance the solubility is the concentration of the solute that remains dissolved in the solution. Many of the manufacturing industries generating the lead-bearing waste discussed above have benefited from applications of these research findings, which have enabled them to process waste cost-effectively while complying with government regulations on effluent content.

Another topic to which a great deal of attention has been paid is the morphology of the lead sulphate crystals produced during precipitation. Little & Nancollas (1970) discuss the morphology of lead sulphate crystals in relation to the kinetics of the precipitation reaction, although they tend to offer little on the actual conditions pertaining to lead removal via precipitation. Kolthoff's report on his research provided more detail, in that it investigated the effect of feed concentration on particle size and rate of growth (Kolthoff & Van't Riet, 1959). Packter (1980) also noted the relation between crystal size and solubility, stating that the largest crystals generally came from solutions with highly soluble metal salts. As the concentration of these salts increased, so too did the crystal lengths before being precipitated out of solution.

While the published work mentioned above may not address directly the conditions for the effective precipitation of lead sulphate from a caustic medium, it is helpful in providing information on the particle sizes and shapes produced by this reaction, because they ultimately affect the filtration rates. These in turn may influence the turnaround time required for the process. Especially in the case of a large-scale operation, it is important that batches should be processed within a sufficiently short time space.

2.2. Feed solutions

2.2.1. Lead leach solutions

While lead sulphate is commonly produced throughout the world, most of the experimental work carried out in respect of recovery has focused on recovering lead from waste solutions of an acidic rather than an alkaline nature. Marani (1995) has published research on the precipitation of lead as a sulphate from an alkaline solution. Among the few cases in which scientists report findings for lead precipitation from an alkaline leach solution is the work published by Youcai and Stanforth (2001) and Min (2000) on the precipitation of lead from a leach solution of electric arc furnace dust. They found that when they used sodium sulphide, almost 100% of the lead in solution was precipitated as lead sulphide.

Experimental investigations into the precipitation or removal of lead have tended to be based on feed solutions of lead nitrate mixed together with sulphuric acid or sodium sulphate as the precipitant, in order to mimic lead waste solutions. While the results reported by Marani (1995) showed figures within a wide pH range of 4–11, in general none of the published findings have contained much information on the actual conditions used to effect precipitation for the experiments. Marani focused on reporting the reaction times as well as the trends in solubility during ageing, but did not provide information on the initial (before precipitation) pH of the various solutions or on the concentrations of sulphate required to effect precipitation. It follows that any attempt to compare the results of the experiments carried out by these scientists is made difficult because owing to the lack of information one cannot substantiate any differences or similarities that may have been observed. Furthermore, when Marani (1995) looked at the effect of carbonate on lead sulphate reactions, the results he presented, which showed a high pH solution being used in the absence of carbonate, failed to consider what the results of the same experiment using an acidic solution would have been.

The research done by the writer on lead recovery from a sodium plumbate solution has an extra level of complexity.

Unlike precipitations from acidic lead solutions such as lead nitrate, which falls under the lead (II) complex, those from caustic lead solutions, such as sodium plumbate, belong to the lead (IV) complex. The precipitation reaction reduces the caustic lead solution to a lead (II) type after which it has to undergo sulfation.

Little has been published on the complete residence time required when the feed solution is in the form of lead (IV). However, if the researcher finds that the reduction reaction required extends the overall residence time, this would make a significant difference to the experimental results. The reason is that this may be the factor in determining a) the feasibility of the process and b) the operating and process conditions under which the lead will precipitate.

The equations display the reduction of lead, the crystallisation of lead sulphate and the overall reaction required in this study if the resultant alkaline lead solution is to be used as feed material. Any excess sodium hydroxide still in the lead plumbate solution presented to the precipitation is assumed to undergo a simple neutralisation reaction with sulphuric acid.

Equation 2-1: Reduction of lead (IV) to lead (II)

$$Pb^{4+} + 2e^{-} \rightarrow Pb^{2+}$$

Equation 2-2: Reaction mechanism for precipitation of lead sulphate from a lead (II) solution

$$Pb^{2+}\,(aq) + SO_4^{2-}\,(aq) \leftrightarrow PbSO_4\,(s)$$

Equation 2-3: Overall reaction for precipitation of lead using sulphuric acid from a sodium plumbate solution

$$2Na_2PbO_3(aq) + 4H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2Na_2SO_4(aq) + O_2(g) + 4H_2O(l)$$

2.2.2. Lead input concentration

The experiments carried out during this study precipitated lead-tin sulphate from alkaline lead and tin leach solutions ranging from 170 ppm to 4000 ppm in lead, and 1400 ppm to 2700 ppm of tin. While the reader is reminded that the focus of these tests was the removal of lead, it is important to highlight that this combination of lead and tin in the final product makes the material valuable to solder manufacturers (Scott, Chen, Atkinson, Todd, & Armstrong, 1997). Several authors including Youcai and Stanforth (2001) and Min (2000) have reported on the precipitation of lead and zinc to form a sulphide from a caustic leach solution. While there were relatively higher values of contained lead in the solutions used during their test work (up to 10 grams of lead per litre), the experiments included little or no tin content.

2.2.3. The precipitant

The scope of the test work in this study covers the use of sulphuric acid to precipitate out lead sulphate from an alkaline process solution. While this study uses two different strengths of sulphuric acid for precipitations, other authors have published data on a variety of sulphuric acid feed concentrations as shown below.

Table 2-1: Working sulphuric acid concentration used by various authors

Author	Working sulphuric acid range
Craig and Vinal, 1939	0-50 %
Crockford and Brawley, 1934	0-80 %
Purdum and Rutherford, 1933	0-0.245 %
Crockford and Addlestone, 1935	80-103 %
Kolthoff et al., 1942	0-4.8 %
Danel and Plichon, 1982	0-70 %
Marani, 1995	Sodium sulphate
Packter and Alleem, 1980	Sodium sulphate
Novosel and Ijubicic, 1978	Sodium sulphate
Little and Nancollas, 1970	0.976 %

It is relevant to make reference to pH curves, which look at the change in pH given a known volume of acid added. In this case we will be looking at generating curves for a diprotic acid and a strong base comprising plumbate an anionic complex ion. With the diprotic acid two equivalence points are expected. This normally indicates the endpoint during an acid-base titration, which is often also the point of neutralisation when the acid balances out the base. pH curves will be plotted given the data generated during the test work.

While this dissertation focuses on the performance of sulphuric acid in precipitating out lead sulphate from a sodium plumbate solution, it is important to recognise that other precipitants can be used for lead. For example, sodium sulphide is commonly used for the removal of lead, as is made evident by the number of papers published on its use following a typical precipitation mechanism, with the same kinetics and complexities.

Youcai and Stanforth (2001) examined a case where lead was selectively precipitated using sodium sulphide from a highly alkaline sodium hydroxide solution that also contained zinc. In this case, the researchers used the same amount of sodium hydroxide in the feed solutions as the author in her experiments. They reported that, while all the lead can be removed when using sodium sulphide to precipitate out the lead, almost no removal of lead was achieved when using sodium sulphate instead. Lenz and Martins (2007) also claimed an almost 100% removal of lead using sodium sulphide, also from a strongly alkaline solution with a high zinc and lead content. Lewis (2010), who also used sodium sulphide to precipitate out lead, started with a lead nitrate solution as feed, obtaining a concentration 0.2 mg/l of residual lead in the filtrate.

The US Environmental Protection Agency listed the solubility of lead sulphate as 0.4 g per litre of water. Purdum and Rutherford (1933) and Clever (1980) reported values in slight excess of 0.04 g per litre showing a major discrepancy between these two different types of literature. The writer surmises that the value recorded by Clever, based on an average of values reported by various authors including Kolthoff, Perlich and Weiblen (1942), Crockford and Brawley (1934) and Little and Nancollas (1970), shows integrity and repeatability.

Table 2-2: Solubility of lead compounds (Clever & Johnston, 1980)

Solubility of lead compounds in water at 25 ^{O}C (mol/litre H_20)	
Lead nitrate	1.80
Lead chloride	$3.907X10^{-2}$
Lead bromide	$2.659X10^{-2}$
Lead fluoride	$2.73X10^{-3}$
Lead iodide	$1.648X10^{-3}$
Lead sulphate	$1.461X10^{-4}$
Lead carbonate	$6.55x10^{-5}$

While other key issues around the precipitation of lead sulphate have been reported, including work done on secondary lead compounds formed during precipitation and their role on the stability of the precipitate and the effect various additives have on the crystallisation process , these should be considered as being outside the scope of this report.

The test work established some of the major impacts that using sulphuric acid over other precipitants has on the process. These were considered on an industrial scale in light of the following:

- process control

- commercial feasibility
- plant equipment
- environmental impact

2.3. Products of precipitation

2.3.1. Filtrate

Solubility of lead sulphate

More relevant to this particular study is the focus given to the reported values of the lead sulphate solubility in sulphuric acid or water at different temperatures and feed sulphuric acid concentrations.

The following authors discussed in

Table 2-3 have published work while using the following temperatures and concentrations of sulphuric acid, with a majority of the work being done at ambient temperature, with the exception of Crockford and Brawley (1934) and Crockford and Addlestone (1936), who were the only authors to publish experimental data at higher temperatures for the solubility of lead sulphate in sulphuric acid. This study will focus on operating in a lower temperature range so as to avoid costly materials of construction.

Table 2-3: Authors and the conditions under which their work on lead solubility was done

Author	Working temperature range	Working sulphuric acid range
Craig and Vinal, 1939	0 and 25 ^{o}C	0-50 %
Crockford and Brawley, 1934	0, 25, 35 and 50 ^{o}C	0-80 %
Purdum and Rutherford, 1933	20 ^{o}C	0-0.245 %
Crockford and Addlestone, 1935	25, 35 and 50 ^{o}C	80-103 %
Kolthoff et al., 1942	25 ^{o}C	0-4.8 %
Danel and Plichon, 1982	20 ^{o}C	0-70 %
Marani, 1995	Room temperature	Sodium sulphate
Packter and Alleem, 1980	25 ^{o}C	Sodium sulphate

Novosel and Ijubicic, 1978	20 °C	Sodium sulphate
Little and Nancollas, 1970	25 °C	0.976 %

Effect of temperature on lead sulphate solubility

The solubility of lead sulphate has been reported over the range of 0 to 60 °C with a majority of the work being done at 25 °C. Table 2-4 displays the results of the experimental work completed by Crockford and Brawley (1934) on the solubility of lead sulphate at various sulphuric acid concentrations and temperatures. Besides being able to show the role that sulphuric acid concentration has on lead solubility, this set of data serves to emphasise the role that temperature has on the solubility, where it was demonstrated that at higher temperatures, the solubility increases.

Special attention should be paid to the solubility data provided at 20% sulphuric acid due to its wide use by the researcher during this study. From the table, it can be seen that increasing the temperature by 25 °C sees the solubility more than doubling. With a further 10 degree increase to 35 °C, the solubility again experiences a 2.4 fold increase to 2.8 ppm. At 50 °C, compared with a value of 1.2 at 25 °C, there is a higher than 6-fold increase to a concentration of 8 ppm. With this value being over the limit in terms of the municipal by-laws, this data set presents an emphasis on the importance of temperature on lead sulphate solubility.

Both these data and the data from Craig and Vinal (1939) shown in Figure 2-1 below demonstrate that solubility of lead sulphate increases with an increase in temperature.

Table 2-4: Solubility of lead sulphate at different sulphuric acid concentrations at four different temperatures (Crockford & Brawley, 1934)

Lead sulphate (ppm)	**Temperature (°C)**			
Acid concentration (wt. %)	0	25	35	50
0	33	44.5	49.7	57.7
0.005	8	10	11	24
0.01	7	8	10	21
0.02	6.4	7	8	18
0.05	5.2	6	6.6	15
0.1	4.6	5.2	5.6	13
0.2	3.4	3.8	4.5	12
0.5	2	2.5	4.3	11.5
1	1.8	2.2	4.2	11.3
5	1.6	2	4	10.3
10	1.2	1.6	3.8	9.6
20	0.5	1.2	2.8	8
30	0.4	1.2	2	4.6
40	0.4	1.2	1.8	2.8
50	0.4	1.2	1.8	2.8
60	0.4	1.2	2	2.8
70	1.2	1.8	2.4	3
75	2.8	3	3.8	6.6
80	6.5	11.5	24	42

Kolthoff et al. (1942) and Purdum and Rutherford (1933) both completed work at lower sulphuric acid concentrations while other authors such as Crockford and Brawley (1934) published data over a wide range of concentrations.

Effect of sulphuric acid concentration on lead sulphate solubility

Table 2-4 is also useful in showing how lead sulphate solubility is affected by changes in sulphuric acid concentration, where the lead sulphate solubilities decrease at points where higher acid concentrations are used until such a point where a 75 % acid concentration is reached, as the table shows that at 80 % acid, the solubility trend goes in the opposite direction and increases.

The error in this data set was reported to be as high as 2 % for the lead sulphate figures at the very low and the very high sulphuric acid concentrations and as low as 0.2 ppm for the intermediate levels of sulphuric acid (Crockford & Brawley, 1934) based on a method of analysis used from work completed by Kolthoff and Rosenblum (1933).

Figure 2-1 serves to confirm this effect with the results published by Craig and Vinal (1939) from test work carried out to determine lead solubilities over a wide range of sulphuric acid concentrations at 0 °C and 25 °C, obtaining lead solubilities between 0 and 5 ppm. The higher temperature curve produces higher solubilities but at the same time mimics the trend found occurring at 0 °C, with the solubility reaching a maximum at 10% sulphuric acid before dropping below 1 ppm at about 70% sulphuric acid. While Crockford and Brawley (1934) show a drop in solubility below 70% sulphuric acid before increasing back to the same concentration, the reverse is true for the results shown by Craig and Vinal (1939) in Figure 2-1. Here the solubility increases before reaching a concentration of 10% sulphuric acid after which time it decreases to a minimum concentration.

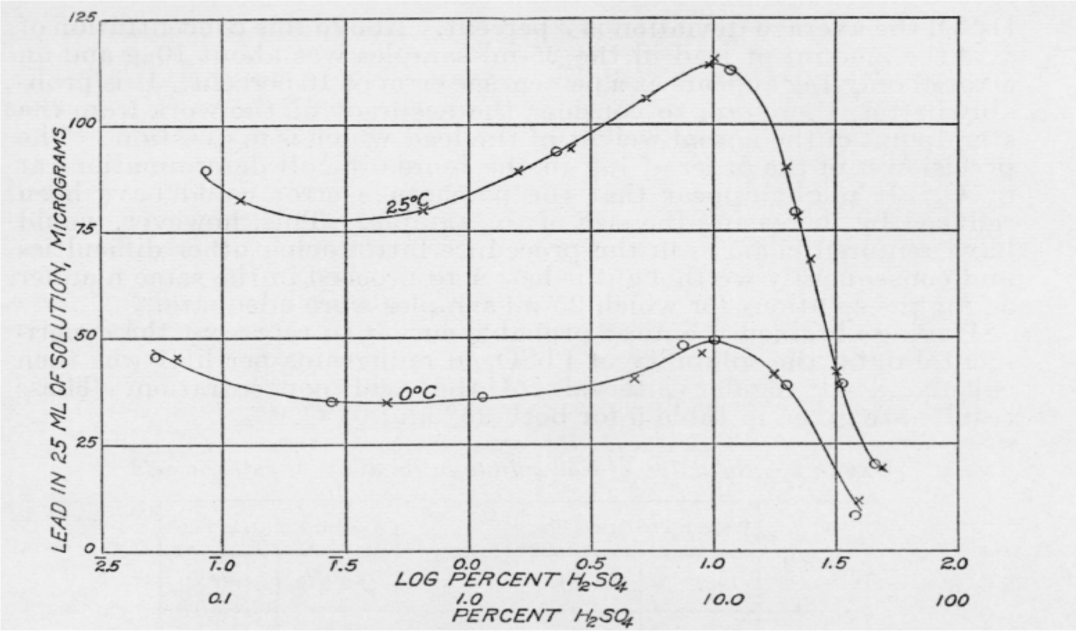


Figure 2-1: Solubility of lead sulphate in different concentrations of sulphuric acid (Craig & Vinal, 1939)

Effect of sodium sulphate concentration through co-precipitation on lead sulphate solubility

In order to establish the role which sulphate concentration plays in the precipitation of the lead sulphate, it is necessary to analyse in isolation those figures obtained for the solubilities of lead sulphate with varying sulphate concentration. In this case, figures have been published for those solubilities with varying sodium sulphate concentration.

Paige, Kornicker, Hileman JR. and Snodgrass (1992) looked at these solubilities of lead sulphate while varying the sodium sulphate concentration at 60 °C, based on the leaching of uranium ore in sulphuric acid, while Kolthoff et al. (1942) , Novosel and Ljubicic (1978) and Huybrechts and Delangeron (1930) published their solubility data at temperatures at or below 30 °C .

If the data from Novosel and Ljubicic (1978) and Paige et al. (1992) are plotted on the same set of axes, assuming that the density of the solution is close to 1 requiring no conversion between weight and volume of solution, the results show that Novosel and Ljubicic (1978) obtained higher lead solubilities at the lower temperature with the solubility data being farther apart from one another the lower the sodium sulphate concentration and vice versa.

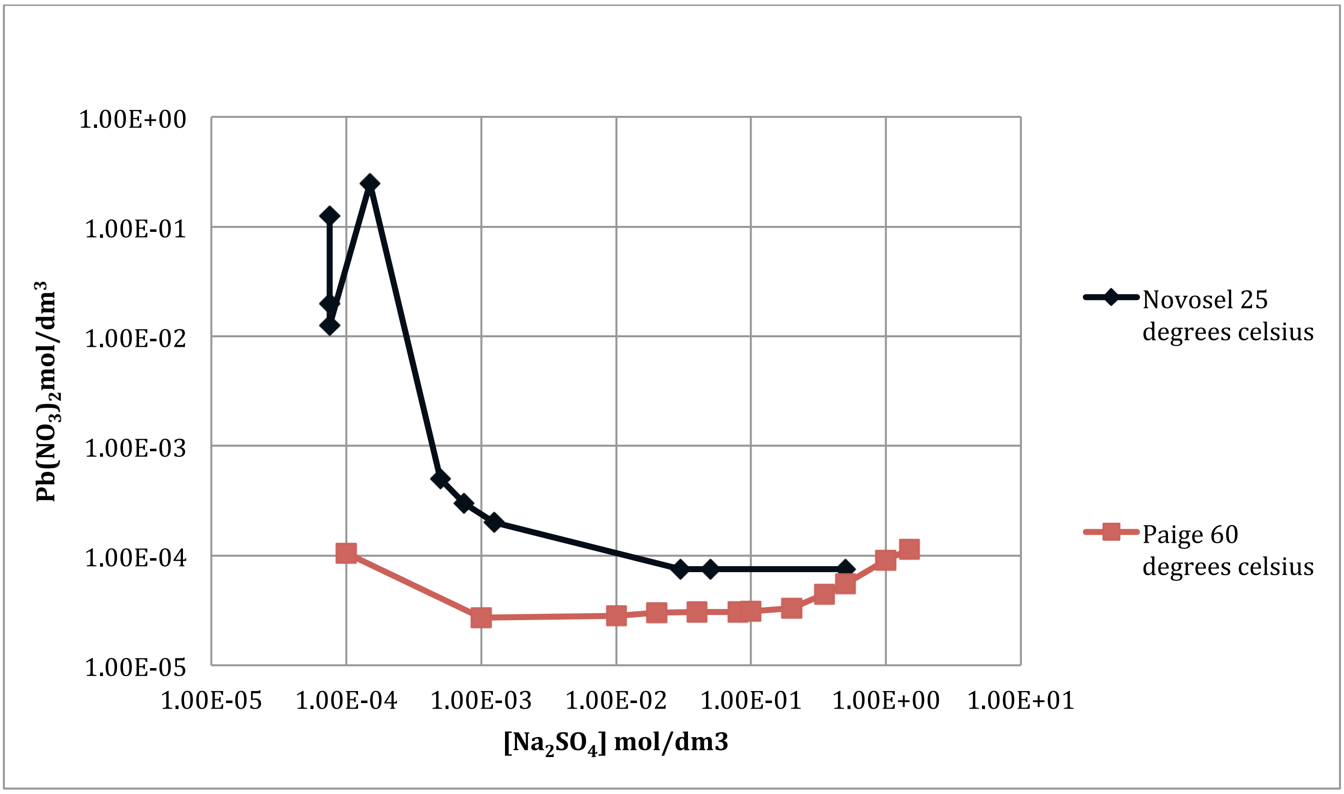


Figure 2-2: Solubility of lead sulphate in sodium sulphate solutions. Adapted from Novosel and Ljubicic (1978) and Paige et al. (1992)

Table 2-5 shows results from a study done by Kolthoff et al. (1942) on the solubility of lead sulphate in sodium sulphate. The solubility of lead sulphate remains low (in the range of 2.7-4.8 milligrams of lead per litre) when increasing the concentration of sodium sulphate from a molarity of 0.001 to 0.5. A maximum solubility of 4.8 was recorded at minimum (0.001) and maximum sodium sulphate concentrations (0.35 and 0.5) and the solubility of lead sulphate with no sodium sulphate in solution was reported as 31.5 milligrams of lead per litre, showing the effect low concentrations of sodium sulphate have on decreasing solubility. Even by having a sodium sulphate molarity of 0.001, an 85% decrease in the lead sulphate solubility is realised. However, at the same time, further increasing the molarity of the sodium sulphate has little effect on the solubility and only serves to further decrease the solubility by a maximum of 6%.

The solution being highly alkaline, almost 200 grams per litre sodium hydroxide, the amount of sodium hydroxide crystallising would ensure a high concentration of sodium sulphate in solution, which would help keep the lead solubility low, according to the trend noted in Table 2-5.

Table 2-5: Solubility of lead sulphate in sodium sulphate solutions at 25 ^{0} C. ± 2^0 C (Kolthoff, Perlich, & Weiblen, 1942)

Molarity of Na_2SO_4	**Solubility of lead sulphate**	
	Milligrams of Pb per litre	Moles of $PbSO_4$ per litre X 10^4
0	31.5	15.2
0.001	4.8	2.4
0.01	3.3	1.6
0.02	2.9	1.4
0.04	2.7	1.3
0.08	2.7	1.3
0.1	3.4	1.6
0.2	3.9	1.9
0.35	4.8	2.3
0.5	4.8	2.3

This same trend can be observed while looking at work by Paige et al. at 60 °C where the solubility of lead is seen dropping at very low concentrations of sodium sulphate and thereafter increasing with increasing concentrations of sodium sulphate, with the increase in the amount of lead present happening at a sodium sulphate molarity of 0.1 in Table 2-5, whereas the data from Kolthoff et al. (1942) showed the lead solubility increasing from a molarity of 0.01.

This would suggest that increasing the sulphate concentration through the addition of sodium sulphate helps to decrease the solubility of lead. This could happen as a result of more lead sulphate precipitating out and forming a solid with the increase in sulphate.

Impact of pH on solubility

One of the key questions to be answered during this study was what the major determining factor is in the lead removal – the sulphate concentration or the pH effect, as no literature source had answered this in terms of the precipitation of lead sulphate when the starting solution is a highly alkaline leach solution.

Karra, Haas, Tare and Allen (1985) stated during their study on the heavy metal precipitation from mixed metal wastewater that ‘the optimum pH values for minimum solubility differ for different metals.' In order to find the optimal conditions for the precipitation of lead sulphate, an investigation was made into the role pH plays alongside that of sulphate concentration on the solubility of the lead sulphate, where it was found that literature sources failed to provide this information for the higher pH scale and focus on solubilities at pH levels lower than 5. While Marani (1995) looked at the effect of pH on solubility, there was no mention of the starting conditions of the solution before precipitation.

Ramette and Stewart (1961) clearly showed the effect that pH adjustment alone has on lead solubility by using increasing amounts of perchloric acid, while keeping the concentration of perchlorate constant.

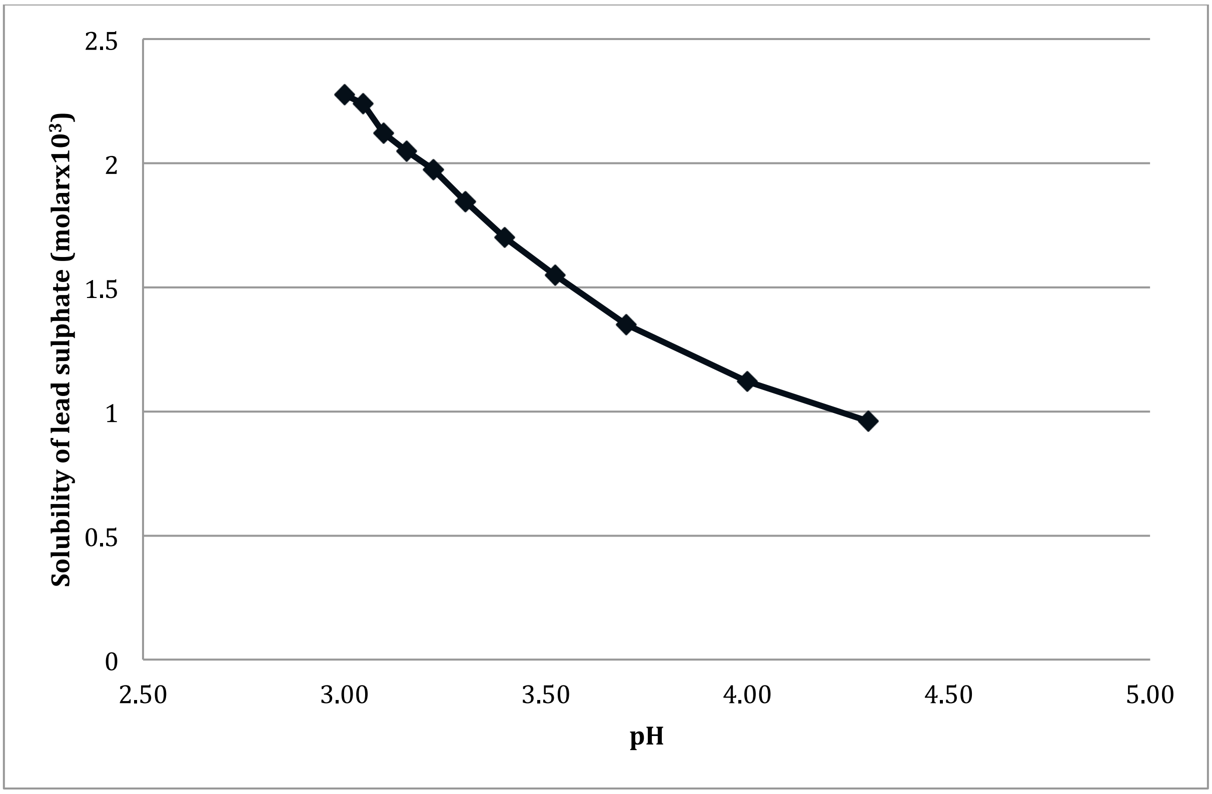


Figure 2-3: Effect of increased acidity on lead sulphate solubility by increasing perchloric acid concentration. Adapted from Ramette and Stewart (1961)

Role of ageing on the solubility of lead and pH of solution

Ageing is a process carried out as an extension of the precipitation process in order to mimic equilibrium conditions and to invoke pH changes, which would lead to conversion of a solid into a highly stable form. Ageing has been discussed throughout much of the research done on lead precipitation, with a number of authors employing different techniques to mimic ageing. Marani, Macchi and Pagano (1995) described the lead-sulphate system as being prone to kinetic limitations, therefore minimising the stabilising effect that ageing normally has to offer precipitation and crystallisation processes during which time solids are normally formed.

The period of time for an ageing process can vary, from several hours to several months, as can the procedure involved. Ageing can include simply standing samples for a period of time while other work on ageing has seen experiments conducted at fixed temperatures with constant stirring.

Marani et al. (1995) Investigated the relationship between ageing and pH where long-term ageing was carried out in sealed bottles at room temperature during which time pH measurements were taken. The results showed that the pH either increased or decreased with the ageing process depending on the starting pH of the solution: the pH trend is upwards when starting from a solution with initial pH of 4.8 and downwards when starting from a higher initial pH solution with the ageing period lasting anything from several days to several months. Solutions tested were 10 milligrams per litre, in the pH range of 3.9-11.3 resulting in a residual lead concentration as low as 0.1 milligrams per litre.

Figure 2-4 shows the trend in pH with the ageing process where the solution starts off at a pH of about 6.4 and a solubility of around 0.7 mg/l before dropping to a solubility of around 0.4 mg/l at pH 7, remaining constant. The figure demonstrates the change in solubility over an ageing period of 73 days, where it is apparent that the lengthy ageing process contributed little to the overall drop in solubility realised. Both the filterable lead concentration from the experimental results and the predicted solubility are seen here following the same trend, even with a difference of a few tenths of a milligram per litre in their starting points when starting from a pH 6.5 solution.

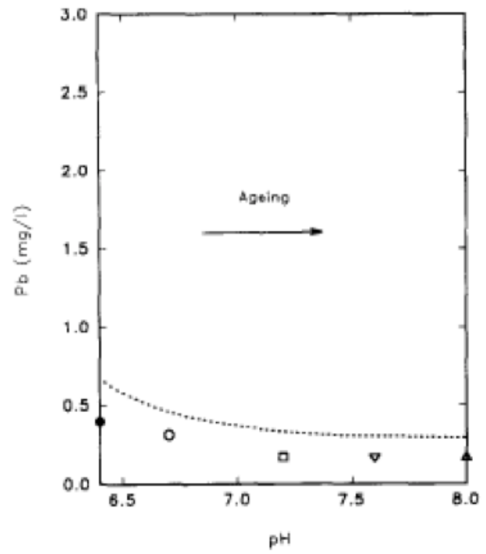


Figure 2-4: Profile showing effect ageing has on pH trend and lead solubility at room temperature in the case of a cerussite sample. Arrow denotes direction in which pH moves during ageing. ●, Filterable lead concentration 1 h after reagents blending; O, after 2 h; □,after 1 day; ∇,after 33 days; Δ, after 73 days; −−−, predicted cerussite solubility. (Marani et al., 1994)

Kolthoff and Von Fischer (1939) studied the ageing of lead sulphate precipitates produced by adding together lead nitrate and potassium sulphate. Their ageing method included:

1) digesting precipitate in nitric acid for the period of one week at a temperature of 94 °C and
2) storing the precipitate in distilled water for a period of four months

This enabled them to draw comparisons between a fresh precipitate and aged precipitates. Table 2-6 shows the marked difference between a fresh precipitate and an aged precipitate by reporting the lead values found in solution.

Table 2-6: Results of test work done on lead precipitates where Product B is a fresh precipitate of lead nitrate and potassium sulphate and Product C is an aged precipitate of lead nitrate and sulphuric acid digested in nitric acid. Adapted from Kolthoff and Von Fischer (1939)

SPEED OF SOLUTION OF PRODUCTS B AND C (CHEMICAL METHOD)				
Lead in solution, equiv. X 10^4 per litre				
Time of shaking,	Product B	Product C	0.1. g. each of B and C	

minutes				
0.5	3	0.81	2.76	
1	3.16	1.02	3.16	
2	3.41	..	3.40	
3	3.28	..	..	
5	3.21	..	3.12	
10	3.18	1.48	3.10	
30	3.14	2.00	3.09	
12	3.10	2.42	..	
1 day	3.09	2.7	3.09	
3 days	3.09	3.04	..	

Kolthoff and Van't Riet (1959) then looked at the ageing of lead sulphate from starting solutions of 1 molar lead in various backgrounds including perchloric acid or sodium sulphate from 4-32 hours with the experiments conducted at room temperature. They then reported how the sulphate concentration and the lead concentration of a solution affects the ageing while Kolthoff et al. (1939) during other work on lead sulphate precipitation chose to focus on the perfection process that takes place should solutions be concentrated enough.

Approaches used in determining solubility

The majority of work completed on the solubility of lead sulphate is based on a combination of both experimental work and theoretical modelling with more emphasis having been placed on experimental results in older publications, as compared with newer publications containing data from equilibrium models, where a good example can be found in Clever (1980) who reviewed various publications dealing with the solubilities of lead compounds, as well as the following more recent publications who were more inclined to discuss results around data from models.

- Paige et al. (1992) looked at modelling parameters for the uranium industry which deals with lead-bearing material

- Little & Nancollas (1970) mentioned the use of an electronic computer in kinetic analysis of the crystallisation of lead sulphate from combining lead nitrate and sulphuric acid
- Marani et al. (1995) modelled lead solubility in wastewater
- Powell, Brown, Byrne, Gadja, Hefter, Leuz, Sjoberg and Wanner (2009) used numerical methods to determine equilibrium constants involved in the formation of lead sulphate

2.3.2. Lead sulphate cake

Effect of pH on lead sulphate particle size

The effect of pH on the particle size of lead sulphate due to precipitation has not been clearly discussed. While discussing the processes, which often precede a filtration, Coulson and Richardson's Particle Technology and Separation Processes (2002) emphasised the importance of this information by saying that the particle size is often affected by the conditions of precipitation including the temperature as well as the pH of the reacting system. Furthermore Perry's (1999) stated that detrimental changes of this nature can then go on to affect filtration flow rates and therefore the cost of filtration equipment.

By collecting solubility data at different pH levels together with particle size information this study aims to provide an answer as to how the final pH of precipitation before solid–liquid separation affects the particle size of the cake, as well as associated filtration rates.

Effect of sodium sulphate on precipitated lead sulphate particle size

Much of the work completed on lead sulphate precipitation involves the mixing of lead nitrate solutions and in many cases sodium sulphate to precipitate out the lead sulphate. Some authors have therefore published data on lead sulphate solubility when varying sodium sulphate added. However, the other aspect to consider during this precipitation is the particle size which is produced in the presence of the sodium sulphate during reaction or when there is excess. In the case of this study, the researcher would consider the effects of excess sodium sulphate on particle size because while the sodium sulphate is not added it is produced during the precipitation.

Novosel and Ljubicic (1978) discussed the impact on lead sulphate crystal size with a variation in sodium sulphate concentration, as seen in Figure 2-5. In Figure 2-5 (a), a precipitate is shown subsequent to a mixing time of 2 minutes where there has been an excess of lead in the form of lead nitrate.

Figure 2-5(b) also displays a suspension after 2 minutes of mixing has been formed in the presence of an excess of sodium sulphate, and Figure 2-5(c) it formed in 1 minute as a consequence of equal amount of lead nitrate and sodium sulphate being added together.

These figures serve to emphasise how fast the reaction conditions are, such that visible material can be observed after only 1 minute of mixing the reagents together, with the reagents always being in low concentration. It would appear that varying the ratio of lead nitrate to sodium sulphate produces different sizes and shapes of crystals, where the difference between Figure 2-5 (a) and Figure 2-5 (b) demonstrates the role that adding an excess of sulphate has on the size of the crystals formed.

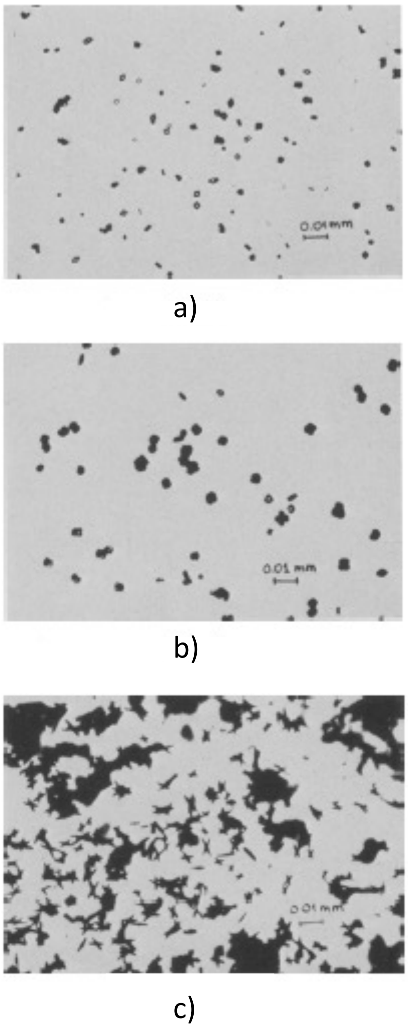


Figure 2-5 (from top to bottom): The crystals of precipitate of lead sulphate in water, 2 minutes after mixing: (a) 0.1N lead nitrate and 0.0025N sodium sulphate; (b) 0.1N sodium sulphate and 0.0025N lead nitrate; (c) 1 minute after mixing, 0.005N lead nitrate and 0.005N sodium sulphate. Magnification 610X (Novosel & Ljubicic, 1978)

2.4. Sodium sulphate

An additional complexity explored in this work is the sodium sulphate produced as a result of the high level of sodium hydroxide in the feed solution, which reacts with the sulphuric acid, causing the lead sulphate and sodium sulphate to be precipitated together.

2.4.1. Recovery of sodium sulphate from lead sulphate precipitation

As there has been little or no work found on the precipitation of lead sulphate from an alkaline leach solution, no data has been found on recovering sodium sulphate from such a solution. Lenz and Martins, (2007) who did test work on alkaline leaching of lead and zinc waste in the form of electric arc furnace dust, used sodium sulphide to remove lead sulphide from solution with no mention of using sulphuric acid as an alternative precipitant. This study looks at how to deal with the precipitation of these two products, one after the other. While the focus is on lead removal and containment into a saleable cake, every opportunity should be taken to recover resource and value from the other products, especially including the sodium sulphate produced *in situ*.

Theory of precipitation - crystallisation processes

There are three major steps involved in any crystallisation process. These are supersaturation, nucleation and growth. While some of these stages may only be on a molecular level and therefore not visible, it is important to include them in discussions around any crystallisation process. The difference between precipitation and crystallisation is how supersaturation is achieved. Precipitation processes reach supersaturation through reaction or a change in pH whereas crystallisation mainly sees a change in temperature to effect supersaturation.

Seeding, which is common to industrial processing, is capable of speeding up the nucleation initiation period, and for this reason it is often found that crystallisers may not be cleaned out between batches, leaving behind crystalline material which can be used as a basis for nucleation and growth.

Temperature, residence time and reagent addition are some of the key factors that play a role in the quality of the final solid produced. Mixing of reagents is known to have a significant effect on particle size, which ultimately affects the solids-handling and the purity of the crystals. For this reason, design of reagent addition points, speed of mixing, rate of addition and impeller design are often considered crucial parameters to the overall performance of a crystallisation unit. To create larger particles, reagents should be added at high intensity mixing zones.

Effect of temperature

By controlling the temperature during precipitation and filtration of lead sulphate, the co-precipitation of sodium sulphate can be decreased.

A study on the recovery of sodium sulphate by Reddy, Lewis, Witkamp, Kramer and Van Spronsen (2010) presented work done by Thomsen (2007) on determination of the transitional temperature for sodium sulphate in water. By exploiting these data in the form of a phase diagram for the sodium sulphate–water system, information can be gained as to what temperatures should be avoided in order to keep sodium sulphate dissolved in solution. This will then serve to facilitate the selective precipitation of lead–tin sulphate over sodium sulphate given suitable temperature control. Figure 2-6 shows the transitional temperature for sodium sulphate at 32.27 °C at a 33.13% weight of sodium sulphate. This minimum temperature can be referred to as the temperature of crystallisation for sodium sulphate, above which the sodium sulphate remains dissolved in solution as shown in Figure 2-6.

At the same time a maximum temperature should be implemented, so as to avoid an expected increase in lead solubility at higher temperatures. Crockford and Brawley (1934) show this increase in lead sulphate solubility with an increase in temperature given a sulphuric acid concentration of 20 % in Table 2-4.

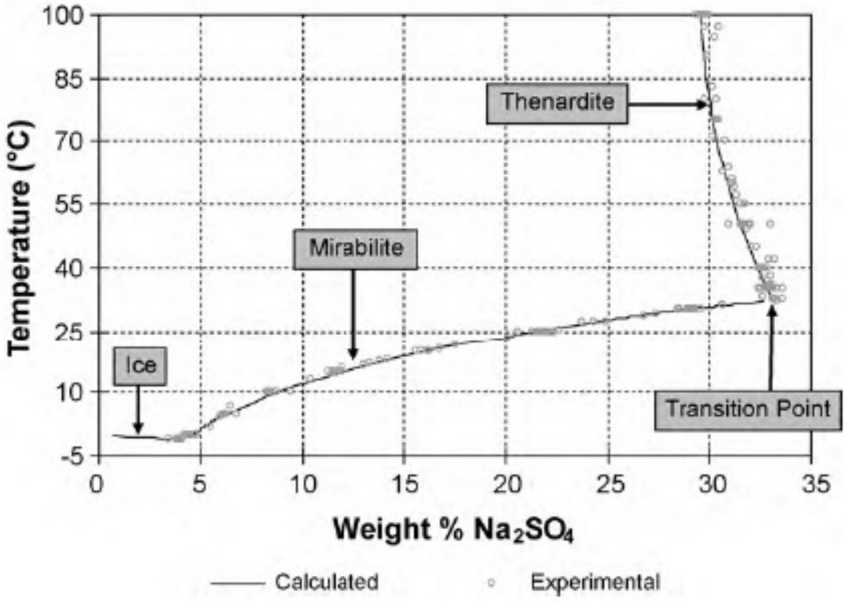


Figure 2-6: Binary phase diagram for Na2SO4-water showing regions of stable phases (Thomson, 2007)

This would then result in a) improved quality of lead–tin sulphate cake and b) increased recovery of sodium sulphate for sale.

2.5. Analysis of lead in solution

2.5.1. Experimental methods

Analytical methods for determining solubility

With solubility often considered as being a key parameter for precipitation processes, it is important to identify those methods which have been used and which are still current in determining solubility. Normally this requires filtering the solution to remove any solids before being analysed for lead. Various methods have been used in determining the residual lead concentration during experimental work on lead sulphate solubility, with the most current being the ICP-OES (Inductively coupled plasma optical emission spectrometer). Older techniques include measurements for lead concentration using conductivity, colorimetry, tyndallometry and titration, with the solid phase generally being determined through X-ray diffraction together with microscopy.

Authors Packter and Alleem (1980) and Novosel and Ljubicic (1978) focused on morphology from different crystal growth mechanisms of the lead sulphate crystals as a product of precipitation using microscopy.

2.5.2. Theoretical methods

Equilibrium models

When it comes to current publications, it is to be expected that a majority of the solubility data will be obtained from equilibrium models, as a result of the development in technology and the ease with which programmes can be developed to calculate solubilities. Marani et al. (1995) compared the solubility data obtained when using the equilibrium model vs. experimental data and found there to be major differences between the two sets of results. His explanation of this was that these differences can be eradicated should initial inputs to the model be refined to include educated assumptions on the dominant solid phases present in the lead sulphate suspension. An example of this can be seen in the MinteqA2 curve showing a significant drop in solubility in the pH range of 7-10 before increasing again, in comparison to the scattered points representing the filterable lead concentration from aged suspensions, showing the lowest solubility at a pH of around 9.5 and the highest at a pH of about 6.5. The MinteqA2 model shows the lowest solubility figure appearing at a pH around 10 and the highest at a pH around 6.5.

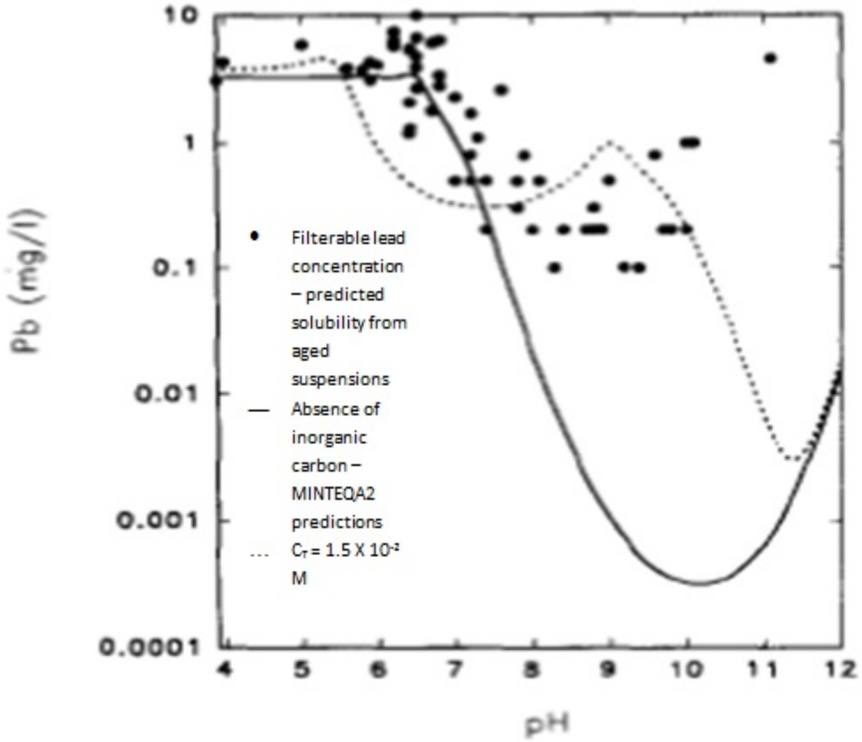


Figure 2-7: Graph showing difference between MINTEQA2 equilibrium model predictions and experimental results for lead solubility vs. pH (Marani, Macchi, & Pagano, 1995)

While predicting the lead sulphate solubility via equilibrium modelling will not be considered within the scope of work to be completed in the present study, the results of the comparisons between the modelled data and the experimental data will still be taken into account when reviewing the work done so far on lead sulphate solubility.

2.6. Concluding points

While a lot of experimental work has already been done on lead sulphate precipitation, the present study poses an interesting set of questions as it serves to solve problems encountered when precipitating lead from an alkaline lead solution rather than an acidic one, which is common in this field of study. Data published by the authors discussed in this chapter have contributed significantly to the researcher's knowledge around the solubility of lead sulphate systems. It is expected that newer work published on lead removal processes will entail using more unconventional materials and processes including adsorption, which has an ever increasing range of adsorbents.

The scope of this literature review was narrowed down to that material which would give the researcher a better understanding of the following:

- Recovery of sodium sulphate
- Solubility of lead sulphate
- Solids handling – particle size
- Operating conditions used to create an ideal environment for precipitation
- Methods of control/parameters to control

The focus of these authors was in producing solubility data for lead sulphate at different temperatures and concentrations in the case of sulphuric acid, or different temperatures when working in sodium sulphate. Another topic of great importance in this field of study was the particle shapes and sizes. More current work published by Reddy et al. (2010) showed the process of recovering 90% sodium sulphate from a reverse osmosis product and the importance of this work in the context of salt removal from brine solutions.

3. Methods and materials

3.1.Introduction

Due to the nature of the work completed for the benefit of the company's waste management plan, a sense of urgency for a viable solution to the problem meant that there was an unconventional take on the progression and implementation of the experimental plan. Rather than have an absolute baseline test, against which to compare other results, the results from using a specific set of conditions on one test led to doing further tests, sometimes changing more than one of the parameters concerned, from one test to another rather than changing one parameter at a time and being able to observe the effects of this variable. Care was taken not to change too many critical variables at once when completing one test after another, so as to be able to still identify the key conditions and variables responsible for the various results.

The effect various parameters play on lead removal from an industrial waste lead solution was investigated. These included the starting metal content, the feed concentration of the precipitant, the final pH of the precipitation and the temperature.

The work completed involved experimental test work on a laboratory scale, although it was expected that, subsequent to this study, the techniques and conditions employed would be translated into a larger-scale process to be operated in a manufacturing facility.

3.2Reagents

3.2.1 Feed solution

Feed solution from a leach process was used whereby lead was leached together with tin, using sodium hydroxide and hydrogen peroxide. Both the initial pH and lead concentration were determined for each solution (see procedure for lead analysis below). These were filtered on laboratory grade filter paper with a pore size of 80 microns. This solution was used so as to provide a representative source of material for the purpose of the test work. Both critical parameters were measured on this incoming material – pH and dissolved lead concentration in mg per litre solution – lead within the range of 175 ppm to 4000 ppm and tin between 1400 ppm to 2300 ppm. The lead was in the form of a plumbate, the oxidation state occurring as four and the lead complex being anionic. The sodium hydroxide in these solutions was approximately 200 grams per litre of solution, meaning that the pH could not be recorded as it was out of the pH scale range: in excess of 14. Table 3.1 shows a typical analysis of the feed solution. In most cases the solution was introduced to the precipitation at ambient temperature, except in the case of test number 9, where the solution was heated to 37 °C.

Table 3-1: Initial feed solution conditions

Test	Lead content in solution (mg/l)	Tin content in solution (mg/l)	Copper content in solution (mg/l)
T1	4416	1441	2007
T2	4416	1441	2007
T3	2005	2072	1374
T4	2005	2072	1374
T5	3109	1417	2377
T6	1655	1734	506.1
T7	1655	1734	506.1
T8	175.3	2713	not recorded
T9	3109	1417	2377
T10	3109	1417	2377
T12	3109	1417	2377
T13	175.3	2713	not recorded
T14	175.3	2713	not recorded
T15	1173	not recorded	not recorded
T16	806	not recorded	not recorded
T17B-C	1360.5	not recorded	not recorded
T18A-B	806	not recorded	not recorded

3.2.2 Sulphuric acid precipitant

The chosen reagent for the pH neutralisation and subsequent lead recovery was dilute sulphuric acid, a reagent already in use on-site. The initial concentration of this acid was 98% by mass as supplied by Protea Chemicals as a commercial grade. The MSDS (Material Safety Data Sheet) can be seen in Appendix C1.

This was then diluted to two different concentrations (20% and 63%) creating two different variations of acid to be tested. Deionised water was used to dilute the sulphuric acid.

Using a dilute solution of sulphuric acid would mean that the heat released would be lower than that produced by a concentrated sulphuric acid solution. This will lead to lower costs for the materials of construction for the equipment required for this reaction to take place. In these tests, the sulphuric acid solution was prepared for use at ambient temperature.

Table 3.2 shows the test conditions used for the precipitation tests and Table E 1 found in Appendix E shows the amount of acid added in each test.

Table 3-2: Inputs to precipitation tests

Test	Volume of lead solution added (litres)	Added H_2SO_4 concentration mass/mass %
T0	not recorded	63%
T1	1.25	20%
T2	1.65	20%
T3	1.5	20%
T4	1.45	20%
T5	1.5	20%
T6	0.8	20%
T7	0.8	20%
T8	0.8	20%
T9	0.8	20%
T10	0.7	20%
T12	0.67	63%
T13	2	63%
T14	2	63%
T15	0.61	20%
T16	1	20%
T17B-C	0.1	20%
T18A	1	20%
T18B	not recorded	20%

3.3Equipment

The lead sulphate suspensions were prepared using overhead agitators for mixing in open glass beakers with an agitation speed of 426 rpm and 490 rpm for the sodium sulphate crystallisation. Rubber tubing was connected to a funnel for acid addition under the surface of the solution at the point of agitation.

3.3.1 Measurement and control

The temperature and pH of the precipitation solution were measured and controlled through acid addition. The temperature was measured using a laboratory alcohol thermometer. The pH, was measured using a pH meter (Hanna Instrument, model number HI9025) calibrated daily using buffer solutions of pH 4 and pH 7 and stored in a storage probe solution specified for use with a pH meter. Measurements were taken throughout the precipitation process. Values taken when reading a standard buffer solution at regular intervals can be seen in Appendix D1.

3.3.2 Solid-liquid separation

Filtration was the chosen method for solid–liquid filtration due to the hazardous nature of the lead-containing suspension and therefore the requirement to maximise removal of dissolved lead as well as lead-containing solids from the solution. A laboratory size Buchner funnel and glass flask were used for the filtration with the same filter paper as mentioned above. A hand-held drier kept both the solution and the filter pad heated throughout filtration, in order to avoid a large drop in temperature to below 40 °C, the temperature of crystallisation for sodium sulphate.

3.4Experimental set-up

Batch precipitation experiments were done in open glass beakers (5 or 2 litres) or else volumetric flasks (250 ml) in the case of the smaller-scale tests.

Specific concentrations of sulphuric acid were added to the lead solution as both a neutralising agent and a precipitant. In most cases the sulphuric acid was added at the point of mixing, for good dispersion of the acid, through a piece of rubber tubing attached and positioned around the impeller shaft. This was the case with the exception of tests 0 and 13, where sulphuric acid was added to the surface of the solution in the beaker.

3.5Experimental Procedures

3.5.1 Precipitation process

Sulphuric acid was added to the reaction vessel at regular intervals (5-10 minutes) over a total period of 1 hour, throughout the precipitation process, while the solution pH and temperature were monitored. This allowed for the acid to be well mixed, giving enough time to affect the pH and allow for a reading to take place. The exception was test 1, where the acid was added slowly.

It should be acknowledged that besides the heat of reaction produced during addition, there is also heat of dilution expected during the addition of the sulphuric acid to the lead caustic solution. To avoid re-solubilising the lead, in most cases the temperature was controlled by slow addition of the sulphuric acid to ensure that there were no big temperature rises. This is important in terms of scale-up for an industrial process as it helps to keep the costs down by eliminating the need for excessive cooling and expensive materials of construction often associated with high-temperature process streams.

The temperatures reported in the following table represent the highest temperatures reached over the entire acid addition.

Table 3-3: Details of acid addition during precipitation tests

Test	Average rate of acid addition(ml/min)	Duration of acid addition (hours)
Test	Average rate of acid addition (ml/min)	Duration of acid addition (hours)
0	5ml/min	Not recorded
1	5ml/min	Added over period of two days - Stopped overnight
2	20 ml/min	1 hour 30 minutes
3	20 ml/min	1 hour 5 minutes
4	20 ml/min	40 minutes
5	20 ml/min	1 hour 5 minutes
6	50ml/min	20 minutes
7	40ml/min	35 minutes
8	20 ml/min	59 minutes
9	20 ml/min	57 minutes
10	20 ml/min	40 minutes
11	not recorded	not recorded
12	6.85 ml/min	20 minutes
13	10ml/min	49 minutes
14	10ml/min	40 minutes
15	20ml/min	25 minutes
16	not recorded	30 minutes
17B-C	not recorded	not recorded
18A	20ml/min	15 minutes
18B	20ml/min	15 minutes

Tests were done by obtaining lead sulphate suspensions at different final pH levels in order to assess the impact on lead recovery of pH using acid addition to affect the change. The solution was agitated and the sulphuric acid was added at regular intervals until the final intended pH level was reached.

Samples of the feed lead solution, lead–tin sulphate cake and filtrate solution were taken for analysis. Sampling took place either during sulphuric acid addition (see test 17) or at the end of this addition depending on how the experiment was done. In order to ensure that the samples were representative of what was happening, the contents of the vessel were mixed thoroughly to ensure that both the solid and liquid phases were represented in the sample.

3.5.2 Solid-liquid separation

Samples were filtered directly after sample collection using a laboratory grade filter paper rated 80 microns. Liquid samples were collected once acid addition was complete. However, during test 17, samples were taken during acid addition once specific pH levels had been reached.

Each of the test suspensions was filtered immediately after acid addition was completed. For tests number 8-18, the funnel was kept heated by blowing hot air onto its outside surface throughout the filtration process, to make sure that the temperature of the solution never dropped below 40 °C, the temperature of crystallisation for sodium sulphate. In the case of the tests where the final temperature was lower than 40 °C, these tests were heated to 40 °C or more on a gas-stove plate. The motivation behind choosing 40 °C was to have a safety margin of roughly 7 °C within which to operate so as to avoid precipitation of sodium sulphate as mentioned above, which takes place at 32.27 °C (Thomsen, 2007). It was taken into account when looking at the experimental results which tests exceeded a temperature of 40 °C, whether as a result of acid addition or in the case of Test 8 and 9, the solution being re-heated to 50 °C or above.

Appendix A can be referred to for a description of the conditions used during filtration.

It is important to note that the majority of the precipitation test work completed was done without temperature control which led to there being temperature rises during the acid addition. This temperature rise during experimentation can be expected to lead to inaccuracies in the data.

3.5.3 Washing

Table 3-4: Washing stages during various precipitation tests

Test number	No. of washes	Cake mass before wash (g)	Cake mass after wash (g)	Mass reduction %
Test 0 -1	none			
Test 2	single cold wash	23		
Test 3	single cold wash	34.5		
Test 4	multiple cold washes	36.1	35.3	2.2%
Test 5	One cold wash, one lukewarm wash	39.3	25.9	34.1%
Test 6	Single cold wash	79.6	20.9	73.7%
Test 7	None	49.5		
Test 8	single wash-hot	30.9		
Test 9	none	374		
Test 10	Multiple washes-hot	12.1		
Test 12	multiple hot washes	10		
Test 13*	none	537.3		
Test 14*	none	208.1		
Test 15	single wash-hot	17		
Test 16, 17B, 17C, 18A, 18B	None	unknown		

* The lead sulphate cake mass recorded in Test 13 and 14 comprised of lead sulphate with layers of sodium sulphate that had crystallised out in-between, creating a sandwich effect.

3.5.4 Drying

Solid samples collected were air dried for 24-48 hours separately after each test, therefore it can be assumed that there is a small error introduced into the cake masses as a result of there being residual moisture. This approach was taken as oven drying the lead sulphate cakes could possibly result in the volatilisation of the lead during the drying process when a convection oven is used.

3.5.5 Ageing process

Where it was necessary to age the cakes, the reaction beaker was left open, standing overnight, at room temperature, with the exception of test 15 which was aged under a constant temperature water bath at 40 °C with no stirring.

Table 3-5: Ageing time for various tests

Test number	Ageing (hours)
0	**12-24 hours**
1	**48 hours**
5	**1 hours**
9	**48 hours**
12	**88 hours**
14	**15 hours**
15	**286 hours**
18A	**1 hours**
18B	**48 hours**

3.5.6 Determining filtration rate

In order to assess the filterability of the lead sulphate precipitate, and be able to size and design a filter for this application, a test unit, supplied by a company called SLFC, was used with a precipitation solution from the test work based on how an industrial-scale Nutsch filter would work. The following procedures were carried out by the test unit in the following steps:

- Feeding

  Following precipitation, the resulting suspension (up to 2.5 litres) was poured into the feed chamber of a pressurized filtration rig.

- Washing

  After being filtered in a 15-20 mm chamber, the solids from the suspension, now in the form of a cake, were then washed with water while remaining in the filtration chamber.
- Blowing

  The cake was then air dried for 3-8 minutes in the chamber, depending on the volume of solution put through the filter chamber initially.
- Final squeezing

  The cakes were then squeezed for 3 minutes by pressurizing the filtration chamber to 600 kPa.
- Unloading

  The cake was then removed from the filtration chamber by unsealing the filtration rig letting the cake drop out.

The test unit was used together with three different solutions each from a different test. These were numbered 2,18A and 18B. The conditions can be found in the table below.

Table 3-6: Conditions used during filtration tests with test rig from SLFC

Conditions	Test 2	Test 18B-aged	Test 18A-fresh
Filter temperature (° C.)	ambient	40	40
Product temperature (° C.)	+/- 60	+/- 60	+/- 60
Volume filtered (litres)	0.1	2.5	1.82
Pressure (kPa)	500	600	400
Drying time(minutes)	1	8	3

3.6Analytical methods

3.6.1 Analysis using ICP-OES (Inductively coupled plasma optical emission spectrometer)

The ICP-OES was used as a means of determining the dissolved lead and tin concentration in solution. Both the lead feed solution and the lead filtrate, following filtration of the lead-sulphate suspension, were analysed this way.

The analyses were done on a Perkin Elmer ICP Optima, model number 3000. The ICP-OES is used as a means of determining the concentration of an element in solution. The calibration of this instrument involves the use of three calibration solutions, from 1000 ppm pre-prepared standard solution of lead with concentrations of 100, 150 and 200 ppm in lead, and 10, 20 and 30 ppm in tin. These were prepared according to the same background as the samples, thereby matrix matching the samples to the standards. Suggested limit of detection figures for analysing lead were obtained from software on the ICP-OES.

A programme was set up on the instrument that includes the necessary parameters required for analysis of the given samples.

Together with this program specific to lead analysis, the standard solutions were aspirated in ascending order so as to allow the spectral peaks to be viewed according to each wavelength specified on the instrument.

3.6.2 Analysis using XRF (X-ray fluorescence)

In order to analyse the lead–tin sulphate cake produced during this test work, XRF was used to determine, qualitatively, the elemental content of the cake. The XRF shows the elements reporting to the solid material, which are present in the highest proportion.

The XRF Minipal used was supplied by Panalytical and manufactured by Philips.

The XRF works on analysing solid samples using an x-ray tube as its source of power. No calibration was used here. Rather the instrument provides a mode of analysis called ‘standardless’ which it uses when no standard reference materials are provided. Once the instrument has moved out of the reference position and the samples are in position, analysis can take place. When analysis is complete, the results are shown in terms of percentages of each element present in the sample. The spectra or peaks for the sample can also be viewed.

3.6.3 Procedure for analysis: Analysis using the Malvern

A Malvern particle analyser, Scirocco 2000 model, was used to analyse the particle sizes of three different solid cake samples from precipitation tests.

Outlined below is a brief description of the procedure followed in preparing the samples for the Malvern analysis:

1. The wet cell unit was connected and the standard operating procedure (SOP) was configured specific for the material.
2. The cake was broken down manually into smaller pieces and thereafter the cone and quartering technique was used to obtain a sizeable sample for the analysis.
3. Using a glass crucible, the sample above (~15 g) was mixed with water to make a slurry.
4. A spatula was used to transfer the sample in slurry form from the crucible to the wet cell for size analysis.
5. The Standard Operating Procedure was performed and the data collected. This could then be used to plot the frequency and undersize curves. The above steps were repeated for all three different solids.

3.6.4 Effect of pH and lead concentration on lead removal

The role of pH on lead removal by sulphuric acid precipitation was determined both for low and high concentration lead solutions. Controlled volumes of sulphuric acid (either low or high concentration) at regular intervals were added to drop the pH. The pH was dropped by adding acid until a pH change of 1 unit was obtained, each time varying the targeted final pH and in so doing reaching all the values within the allowable pH range (6-10) stipulated by local government restrictions on industrial wastewater.

The pH’s covered ranged from 4-14. The volume sampled was under 1% of the overall solution volume.

The final samples were then filtered through filter paper with an 80 micron pore size and their lead concentration found by using a Perkin Elmer ICP-OES.

Table 3-7: Summary of modifications to test methods

Test	Modifications to test method
0	**Sulphuric acid added to surface of solution**
1	**Filtrate decanted off**
9	**First heated to 37 deg. Celsius before acid addition**
13	**Sulphuric acid added to surface of solution**
17	**Samples taken throughout precipitation test**
18A	**Filtration took place using test unit from SLFC as described**
18B	**Filtration took place using test unit from SLFC as described**

4. Results and Discussion

4.1. Introduction

Precipitation was investigated as a process for the recovery of heavy metals from a lead alkaline solution containing hazardous waste. This was done with the intention of treating a pre-selected stream containing primarily lead and tin in order to decrease the lead concentration to values legally permissible for discharge to municipal reticulation. The effect of this on lead removal is shown, including the role pH plays during this removal.

This chapter reports the outcome of the precipitation tests completed in the context of the reaction products, namely the filtrate for disposal as well as the valuable by-products for sale - the lead–tin cake and sodium sulphate. For maximum value gain and compliance, suitable operating conditions for the final processing steps should be chosen and implemented so that requirements of both downstream processors and environmental regulations are met.

Having motivated in previous chapters for the use of sulphuric acid as the precipitant, these results focus on precipitations of lead sulphate using sulphuric acid.

To determine the suitability of this process to the waste stream, batch scale laboratory tests were set up with conditions described in Chapter 3. Each test run can be assessed against a specific objective and compared with others in order to come to a conclusion about the various conditions used to bring about precipitation of the lead–tin sulphate using sulphuric acid. All the conditions used and the merits in each will be discussed further in this chapter.

4.2. Products of precipitation

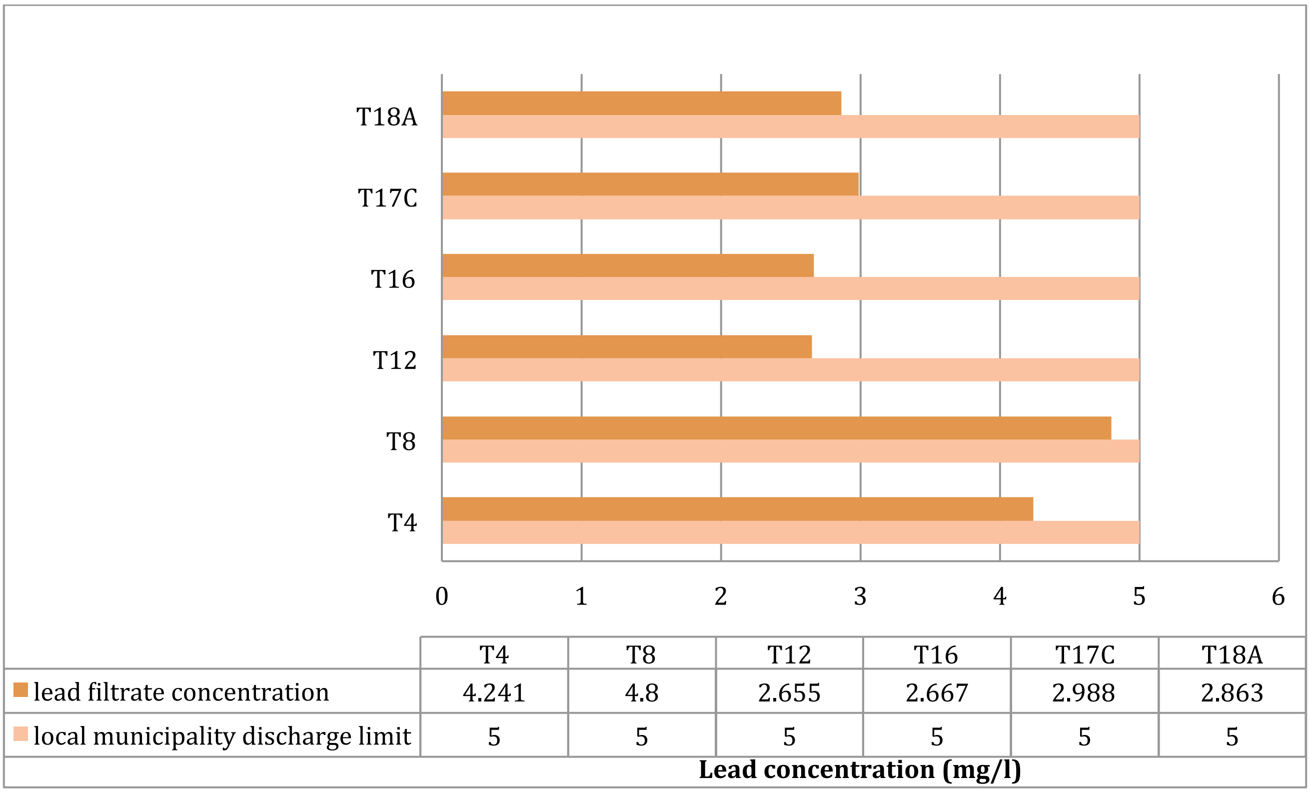
4.2.1. Filtrate following lead-sulphate precipitation – residual lead concentrations

In order to assess which conditions brought on a successful precipitation in removing lead to a low enough concentration, the final lead concentrations from all test filtrates were compared against one another relative to the stipulated local discharge limit for lead as seen in Figure 4-1 through to Figure 4-3.

A majority of the filtrates from these test runs fell under a concentration of 40 ppm, with the exception of Test 15, which was aged for over 6 days having a final concentration of 120.7 ppm.

Regardless of whether filtrates are found to be acceptable according to the discharge limit of 5 ppm, it is imperative that a margin of safety be implemented to allow for discrepancies between on-site analyses and sampling methods and the local municipalities’ methods.

Figure 4-1 shows the precipitation tests, which produced favourable, lead concentrations, falling under the local discharge limit of 5 ppm.



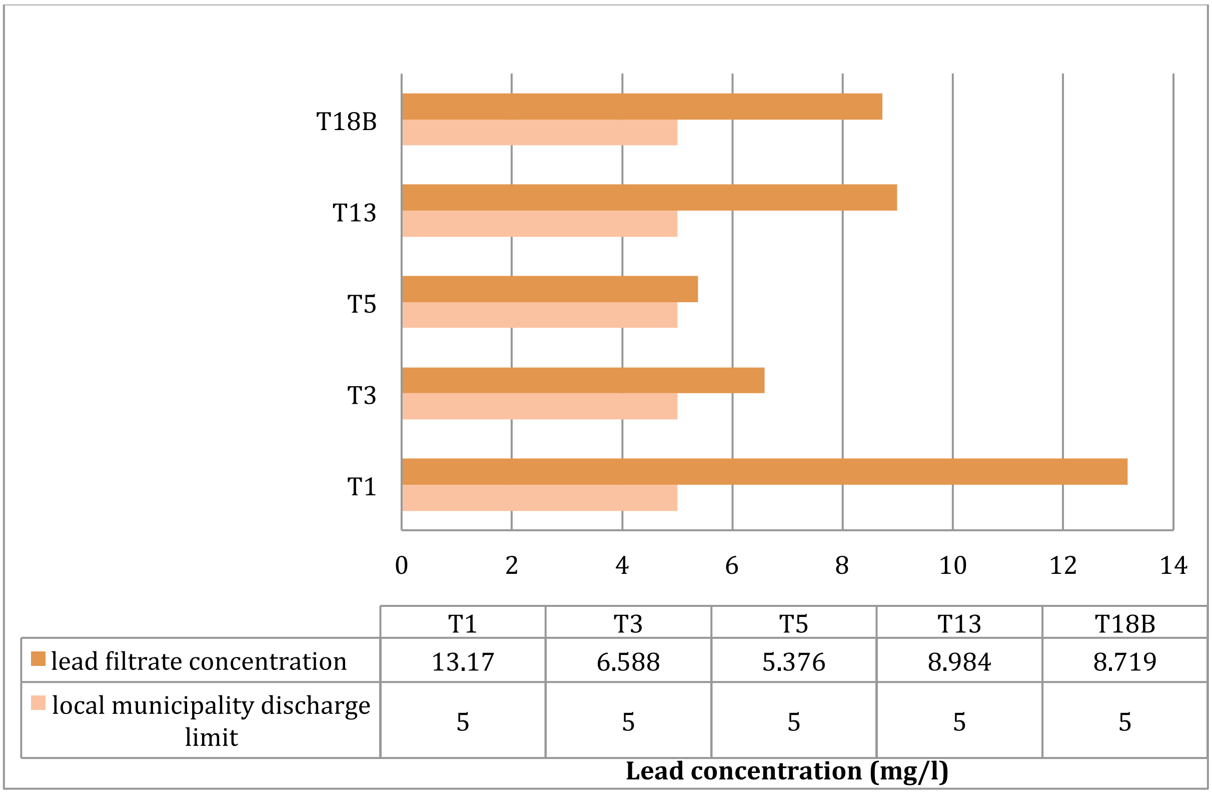
	T4	T8	T12	T16	T17C	T18A
lead filtrate concentration	4.241	4.8	2.655	2.667	2.988	2.863
local municipality discharge limit	5	5	5	5	5	5

Figure 4-1: Graph showing final lead concentration from precipitation tests, which would pass against local lead discharge limits

Table 4-1: Conditions used during precipitation tests giving final lead concentration below 5ppm

Test number	Test 4	Test 8	Test 12	Test 16	Test 17C	Test 18A
H_2SO_4 acid concentration (%)	20	20	63	20	20	20
Lead input (ppm)	2005	175	3109	1655	1360.5	806
Final pH	7.29	7.32	6.90	6.15	7.02	7.00
Ageing time (hours)	None	None	88	None	None	None
Max. temp. reached (°C)	44	49	58	unmeasured	unmeasured	unmeasured

Figure 4-2 shows the precipitation tests that produced lead concentrations falling above the local lead discharge limit of 5 ppm. Table 4-2 shows the corresponding test conditions that generated these particular results.



	T1	T3	T5	T13	T18B
🟧 lead filtrate concentration	13.17	6.588	5.376	8.984	8.719
🟧 local municipality discharge limit	5	5	5	5	5

Figure 4-2: Graph showing precipitation tests with final lead concentration above 5 ppm and less than 20 ppm compared with local lead discharge limits

Table 4-2: Conditions used during precipitation tests giving final lead concentration above 5 ppm and less than 20 ppm

Test number	Test 1	Test 3	Test 5	Test 13	Test 18B
H_2SO_4 acid concentration (%)	20	20	20	63	20
Lead input (ppm)	4416	2005	3109	1173	806
Final pH	9.09	7.00	8.00	6.77	7.30
Max. temp. reached (°C)	32	49	55	65	Not recorded
Ageing time (hours)	none	none	None	none	48
Acid addition	Into impeller	Into impeller	Into impeller	To surface of solution	Into impeller

Figure 4-3 shows the precipitation tests that produced lead concentrations falling above the local lead discharge limit of 5 ppm. Table 4-3 shows the corresponding test conditions that generated these particular results.

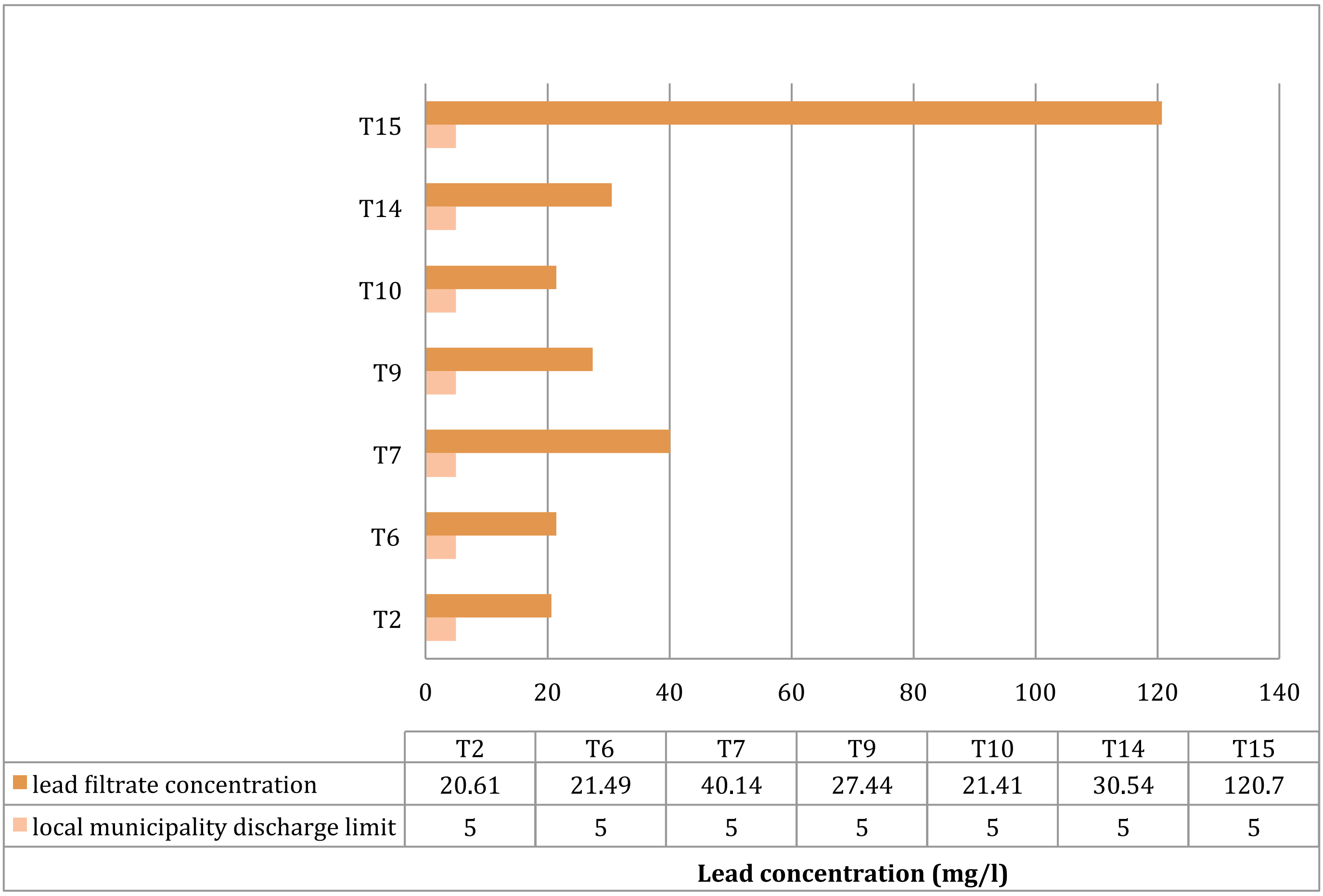


Figure 4-3: Graph showing precipitation tests with final lead concentration above 20 ppm compared with local lead discharge limits

Table 4-3: Conditions used during precipitation tests with final lead concentration above 20 ppm

Test number	Test 2	Test 6	Test 7	Test 9	Test 10	Test 14	Test 15
H_2S0_4 acid concentration (%)	20	20	63	20	20	63	20
Lead input (ppm)	4416	1655	1655	3109	3109	175.3	175.3
Ageing time (hours)	none	none	none	48	none	15	286 hours
Final pH and pH after ageing	4.59	6.62	6.09	pH_1: 6.15 pH_2: 7.70	6.48	pH_1 :5.44 pH_2: 5.96	pH_1: 6.97 pH_2: 7.39 pH_3: 8.12 pH_4: 8.85
Max. temp. reached due to acid addition(° C)	49	55	45	50	46	69	46

Solubility

Effect of pH on the final lead concentration

Besides having a stipulated lead discharge limit, there is also a pH range (6-10) to abide by when disposing of waste solutions to municipal sewer. It is therefore important to understand how much lead would be in solution at this particular pH range. The results in Figure 4-4 show the residual lead ion concentration at this pH range.

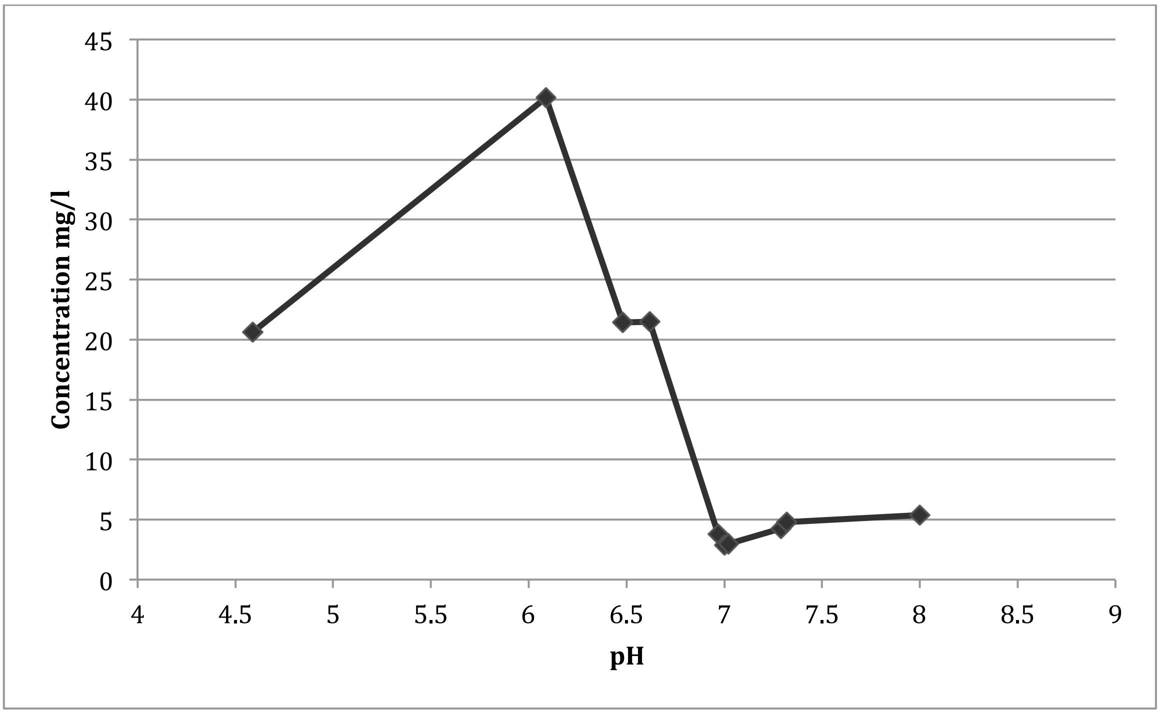


Figure 4-4: Effect of pH on final lead concentration in solution

This part of the report investigates the effect of pH adjustment via sulphuric acid addition on soluble lead sulphate concentration.

Precipitation tests were conducted under which the pH was controlled via sulphuric acid addition. The final pH ranged from 4.5 to 9.0 to get a good idea of the propensity for the lead to crystallise out in this region. The final pH measurements from each of these tests were plotted against the corresponding final measured lead concentration. This graph comprises of data from Tests 2, 4, 5, 6, 7, 8, 10, 17B, 17C and 18A.

Diluted sulphuric acid (20%) was prepared for addition to a measured volume of lead leach liquor at ambient temperature. This was added beneath the surface of the solution through plastic tubing to ensure thorough dispersion while the contents of the vessel were agitated. The temperature was not controlled during this addition and therefore was allowed to rise given the heat of dilution and neutralisation involved. pH measurements were taken, where initially the pH was between 13.8-14 and acid added up until the pH had changed by 1 unit. In the beginning of the precipitation, 100 ml of sulphuric acid was added (roughly 10% of the initial solution volume) every 5 minutes with continuous stirring up until the rate at which the pH was dropping started to increase significantly. At this point, smaller quantities of acid were added (several millitres) drop by drop. These suspensions where then filtered with a laboratory Buchner funnel and flask under vacuum. Any modifications to this method have been laid out in Chapter 3.

The data show the lowest lead concentration of 2.863 ppm was obtained at pH 7. At pH levels below 7, the residual concentration starts to increase before dropping off again at pHs below 6. Above pH 7, the concentration increases slightly to around 5 ppm, coming in close proximity to the discharge limit. These results are highly significant in displaying a) the optimum pH and b) whether the residual lead concentration is affected by pH. In dropping the pH, the solution could be neutralised quickly to a pH of 7.

Trend in lead concentration with pH through semi-batch test work

In order to look at the rate at which the concentration of lead and tin decreases in solution during and up to the point of suspension forming, the following tests were performed:

Tests 17B and C

20% sulphuric acid was added in increments to the point of agitation to decrease pH allowing for samples to be taken at the different pH levels. These tests are represented as Test 17B and C in Chapter 3. Figure 4-5 and Figure 4-6 depict the drop in pH and concentration of lead and tin from Test 17C where samples were taken at different pH measurements during these tests. This test was repeated and reference is made to Tests 17 B and C.

Figure 4-5 shows the effect of dropping the pH on lead concentration. It can be seen that at a pH of 14 and 86% of the total volume of sulphuric acid added during precipitation (0.1 litres), the lead concentration drops to 60.8 ppm. A further 0.016 l addition of acid takes the pH from 14 to 7 and the lead concentration to 3 ppm.

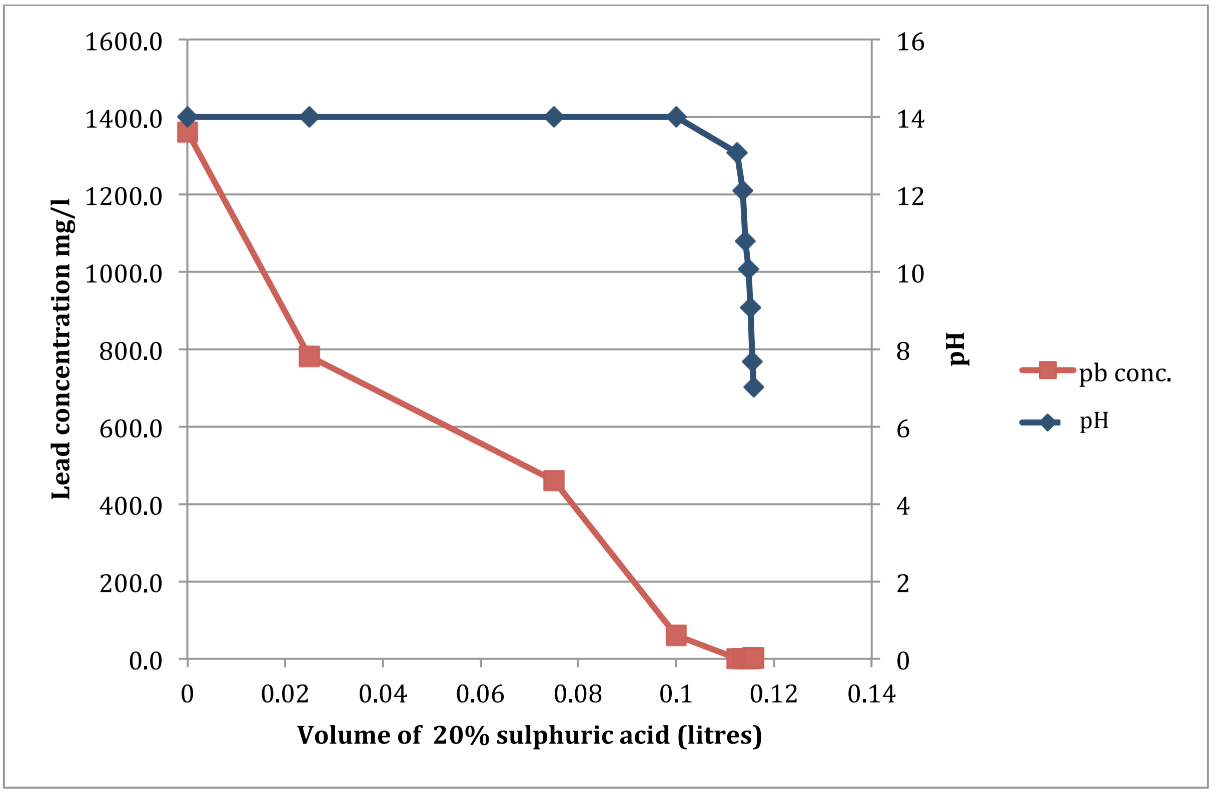


Figure 4-5: The instantaneous effect of acid addition on pH and lead concentration from Test 17C

The same analysis was done for the tin in the same solution. A similar trend was observed, showing that both the lead and the tin are removed and precipitated simultaneously from solution.

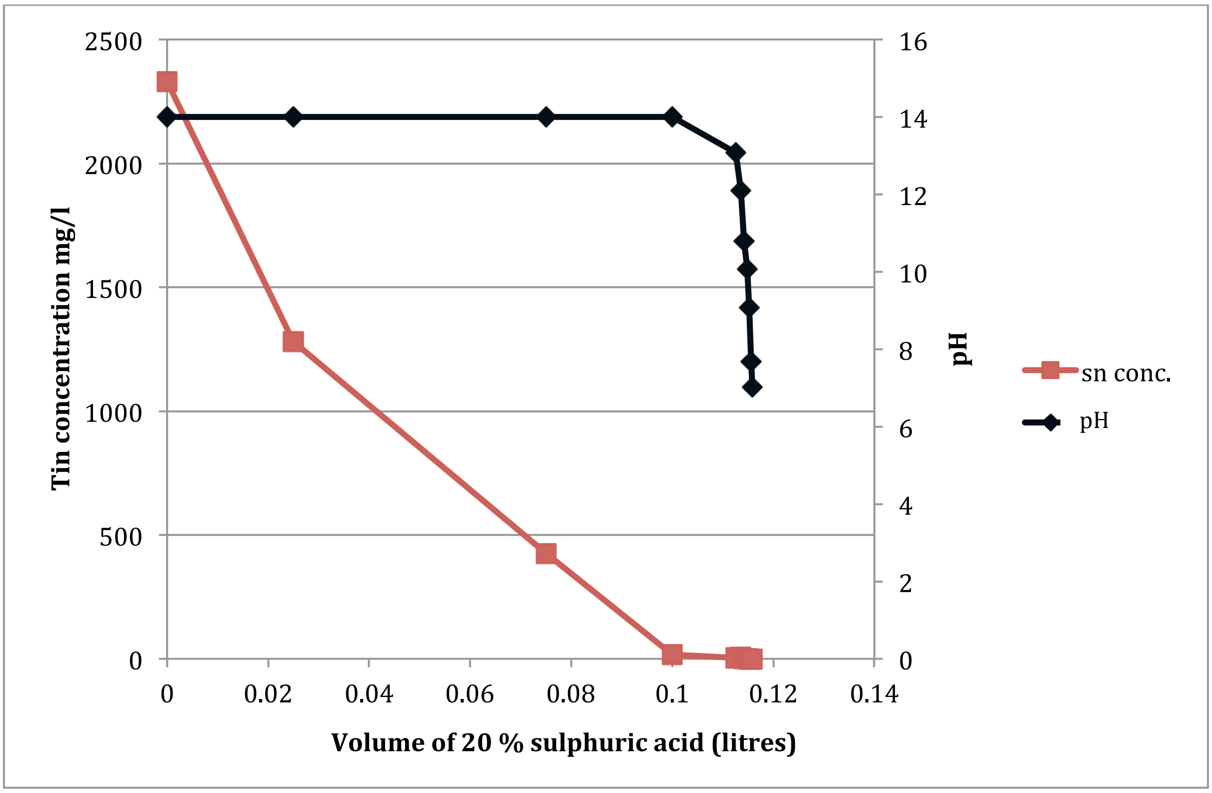


Figure 4-6: Graph showing effect of acid addition on pH and tin concentration from Test 17C

96% of the lead and 99% of the tin was removed while still at a pH of 14.

When comparing the tin to the lead profile, the tin can be seen behaving in the same way as the lead, leading to simultaneous removal of both the lead and tin with the addition of acid.

While it is important to mention that Test 0 did not involve *in-situ* sampling during precipitation of one solution from a starting pH down to a lower pH, the test did involve using exactly the same batch of lead solution each time therefore providing invaluable data. Each aliquot of this solution was precipitated down to a different pH unit and a sample thereof taken. For this reason, Tests 0 and 17 were plotted on the same set of axes for comparison. Figure 4-7 below is compiled from both the batch of solutions precipitated to different pH levels making up Test 0 and samples taken from one precipitation during Test 17C.

Deviations to the method during Test 0 include addition of a higher strength of sulphuric acid (63%) as well as feeding the acid to the surface of the precipitation.

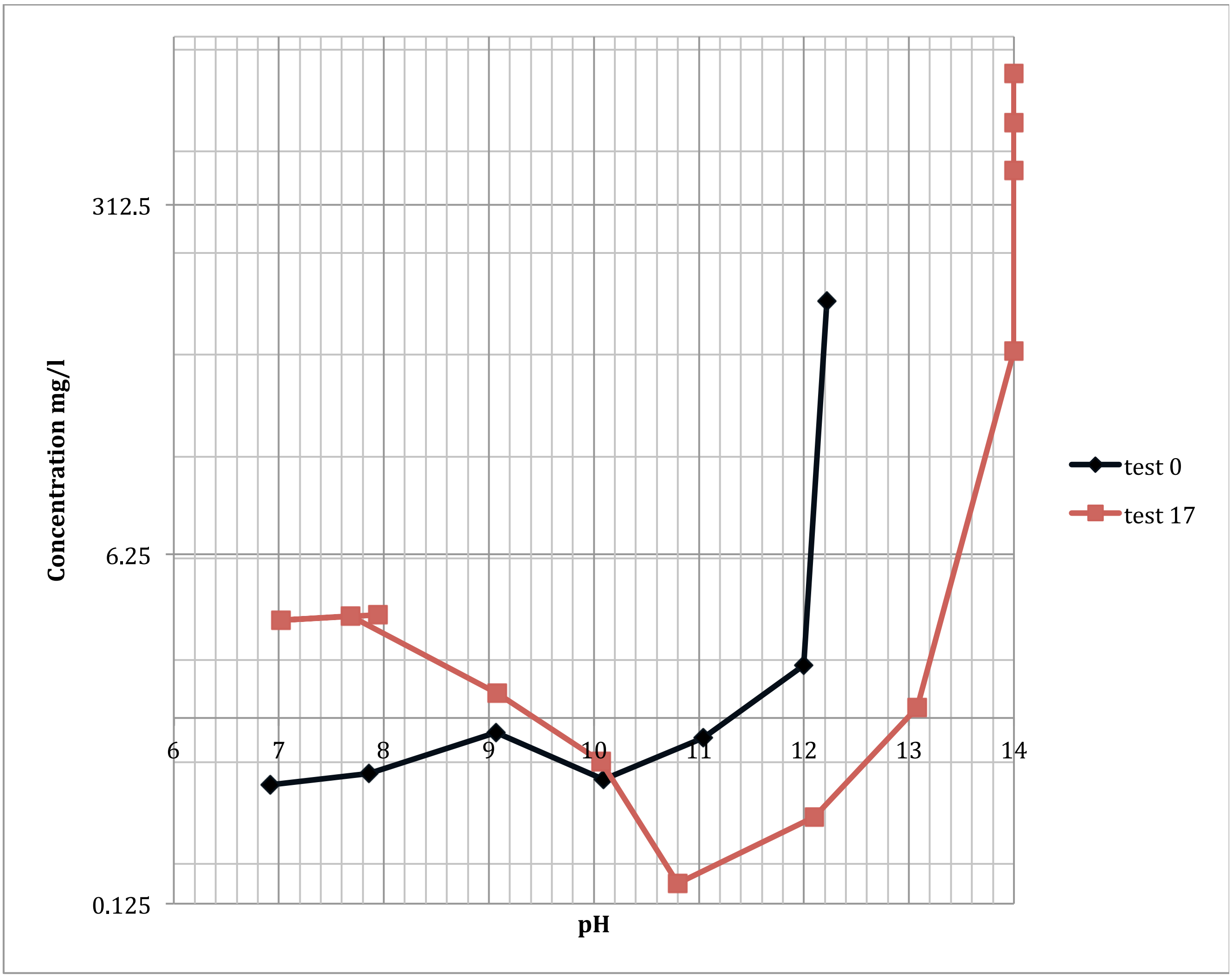


Figure 4-7: Semi-log plot showing comparison of lead concentration results from Test 0 and Test 17C at different pH levels (Test 0 – lead input 106 ppm, 63% H_2SO_4, addition at surface of solution, solution aliquots precipitated to different pH levels; Test 17c – lead input 1361 ppm, 20% H_2SO_4, addition at impeller, solution batches each precipitated to different pH levels)

Input

Role played by initial lead concentration in solution on final lead filtrate concentration

Lead solutions with different concentrations of lead were used in order to gauge the effect lead feed concentration has on precipitation of lead sulphate and removal efficiency. In the context of the problem being solved, it is important to determine process conditions, which are flexible enough to be used over a wide range of lead feed concentrations thereby forming a viable treatment solution. For this reason, tests were carried out to determine the effect of the initial lead concentrations on the lead sulphate precipitation and removal efficiency. The results are shown in Figure 4-8 and Figure 4-9.

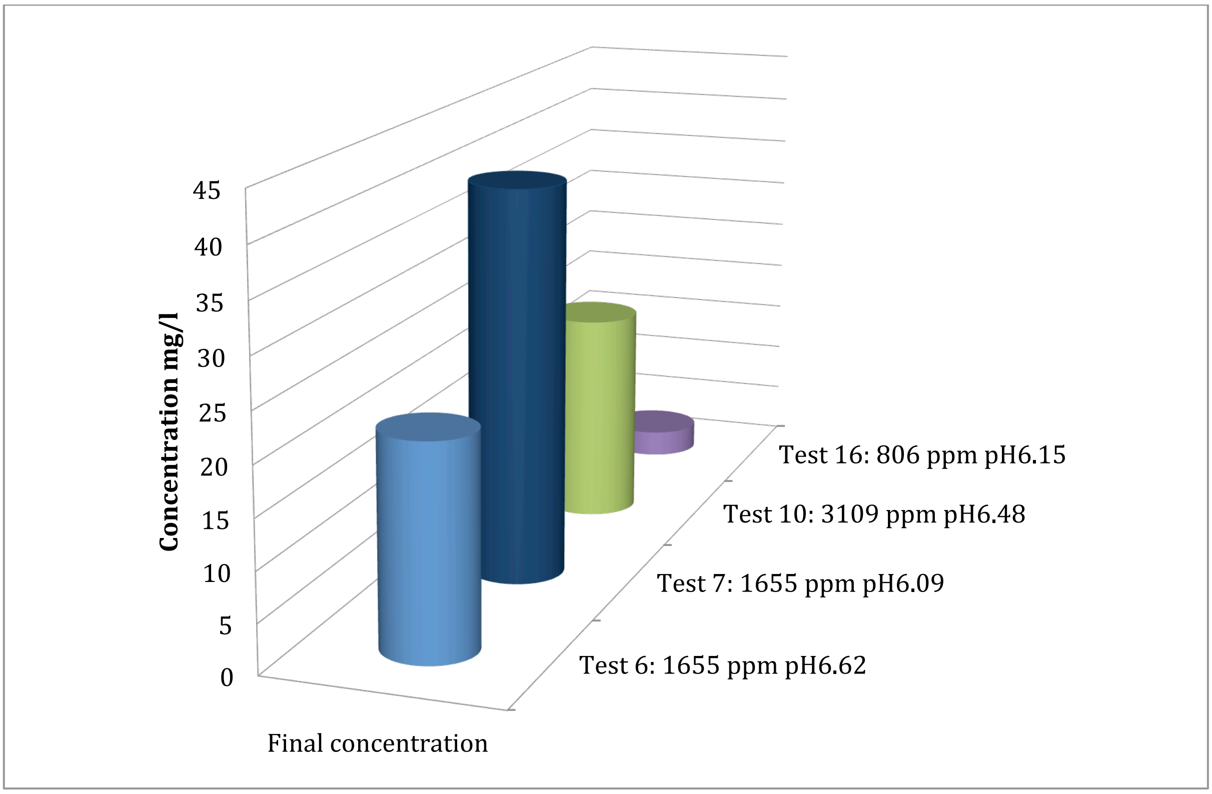


Figure 4-8: Plot of residual lead concentrations given their lead feed concentrations at a final pH of 6

Table 4-4: Test conditions used during the precipitation process

Test	**Test 6**	**Test 7**	**Test 10**	**Test 16**
Lead input (ppm)	1655	1655	3109	806
Final buffered pH	6.62	6.09	6.48	6.15
Max. temperature reached (°C)	55	45	46	unmeasured

The sulphuric acid concentration added for precipitation was 20% for all these tests.

When comparing Tests 6 and 7, the residual filtrate concentration more than doubles when the same solution is precipitated with Test 6 at pH 6.62 and Test 7 at pH 6.09. These two tests, which are 0.53 pH units apart, show a significant difference in final lead concentrations. Test 16 with half the feed concentration of Test 7 shows a major difference in final lead concentration. Similarly while Test 6 had a residual lead concentration of 21.49 and Test 10, 21.41 ppm , Test 6 had half the feed lead concentration.

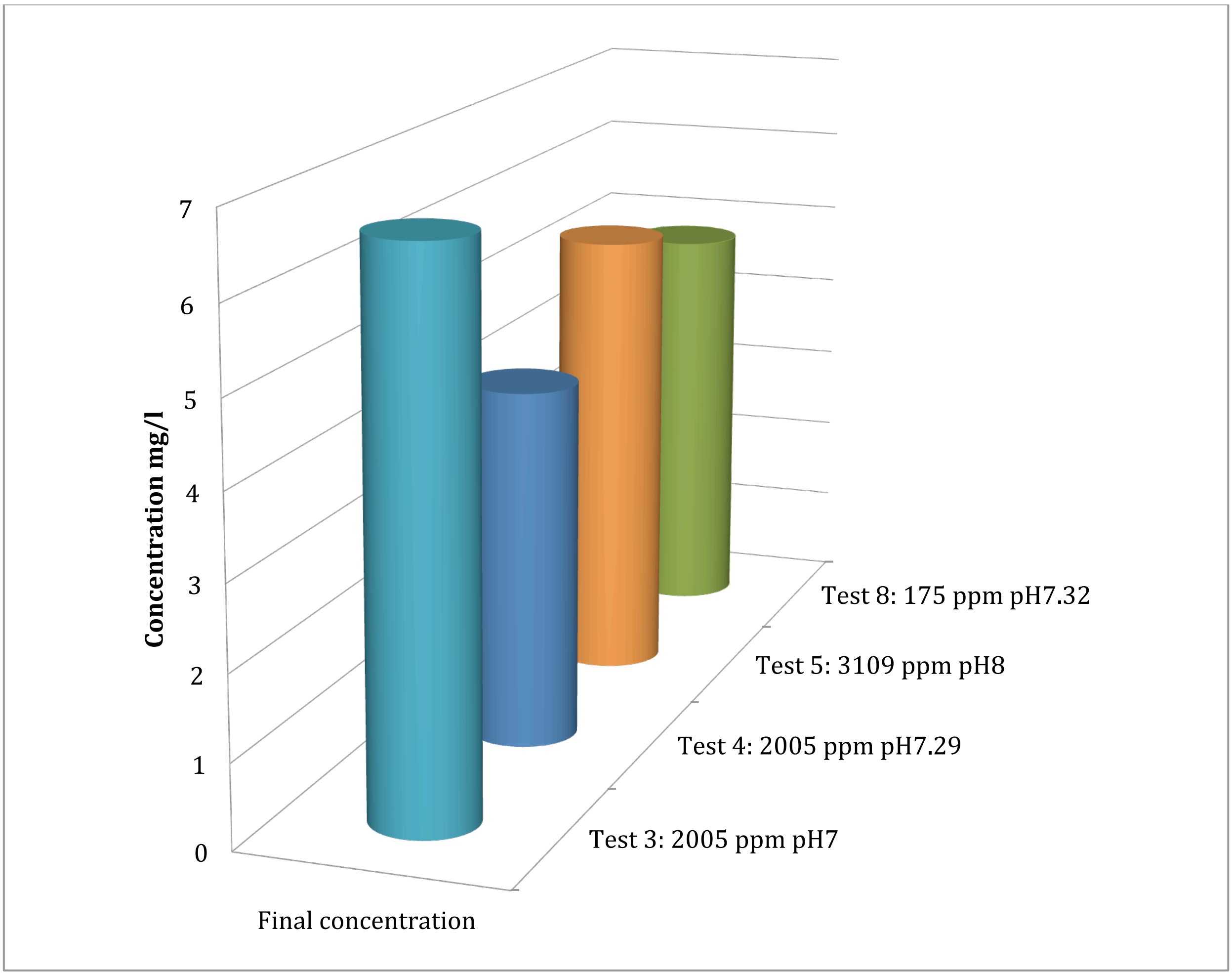


Figure 4-9: Plot of residual lead concentrations at a final pH of 7 given various lead feed concentrations

Table 4-5: Test conditions used during the precipitation process

Test	**Test 3**	**Test 4**	**Test 5**	**Test 8**
H_2SO_4 acid concentration (%)	20	20	20	20
Lead input (ppm)	2005	2005	3109	175
Final buffered pH	7.00	7.29	8.00	7.32
Max. temperature reached (°C)	49	44	55	49

The tests precipitated to pH 7, as well as Test 5 precipitated to a pH of 8 ,with lead feed concentrations in the range of 175 ppm to 3109 ppm all show similar filtrate concentration values of 3-6 ppm. While Test 5 was precipitated to pH 8, it showed a residual lead concentration in the same range of the other tests precipitated to pH 7. With the ten-fold increase in feed lead concentration between Test 3 and Test 8, the difference in filtrate concentration is 2 ppm. The reader should take into account the possibility of this being due to analytical error.

Figure 4-8 compares Tests 6, 7, 10 and 16 on the basis of their final pH being around 6 while the results from Tests 3, 4, 5 and 8 are displayed in Figure 4-9 and compared on the basis of their final pH being around 7. Regardless of lead input concentration, the required minimum residual lead concentration can be obtained when the pH is controlled carefully close to a value of 7.

Effect of feed sulphuric acid concentration on residual lead ion concentration

Effect feed sulphuric acid concentration has on lead filtrate concentration

Two variants of sulphuric acid were tested as a precipitant, a more dilute concentration of 20% and a more concentrated solution of 63% sulphuric acid. Taking into account the high heat generation, the addition rate was kept slow and controlled. Besides avoiding a steep temperature rise, the addition is controlled so as to maintain the pH buffer zone.

The final lead concentration results from the tests using 20% sulphuric acid (Tests 6 and 10) were compared with higher sulphuric acid (63%) feed tests (Test 0 and Test 13) in order to see whether changing the feed acid concentration had an impact on residual lead concentration. The choice of feed acid concentration is required to design the plant section housing the precipitation process when choosing materials of construction for tanks and pumps, storage capacity for the diluted acid as well as dosing pump capacities for delivering the sulphuric acid to the solution. It should be taken into account that the basis of this comparison is that the final pH of these filtrates is in the range 6.48-6.92 which could be considered to be of major importance. While the difficulty in this comparison is that the feed lead concentrations are significantly different, this may still be considered information worth noting.

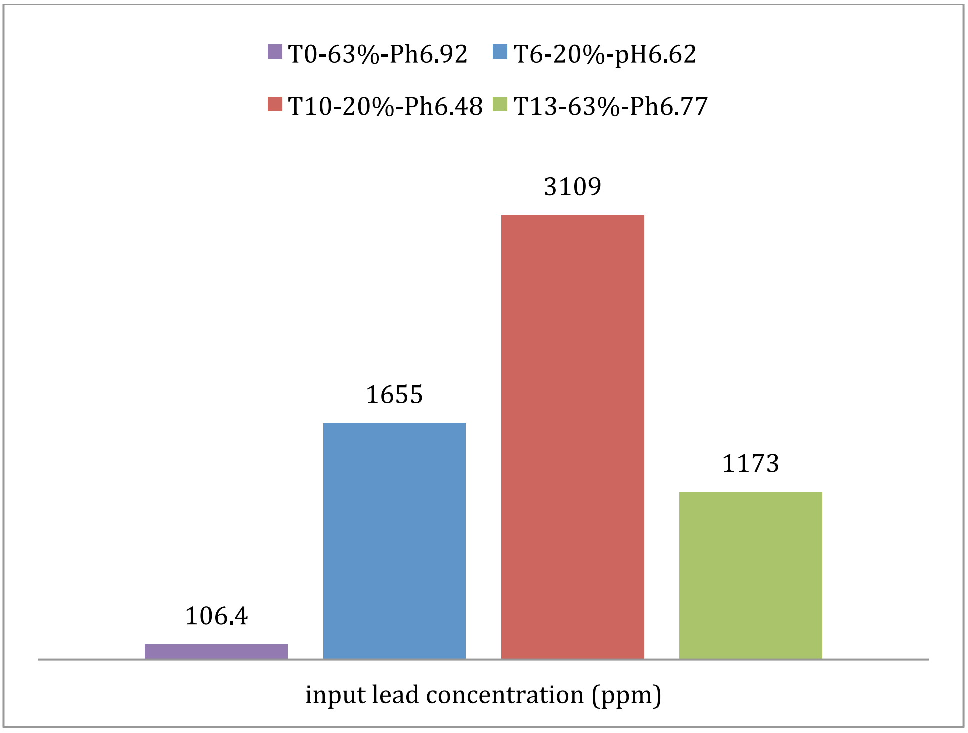


Figure 4-10: Lead input concentrations and feed acid concentrations during Tests 0, 6, 10 and 13

Table 4-6: Conditions used in precipitation tests during Tests 0, 6, 10 and 13

Test	Test 0	Test 6	Test 10	Test 13
H_2S0_4 acid concentration (%)	63	20	20	63
Sulphuric acid (kg) added per litre leach solution	0.229	0.229	0.239	0.211
Acid addition	To surface of solution	At point of agitation	At point of agitation	To surface of solution
Max. temperature reached (°C)	Unmeasured	55	46	65
Lead input (ppm)	106.4	1655	3109	1173
Final pH	6.92	6.62	6.48	6.77

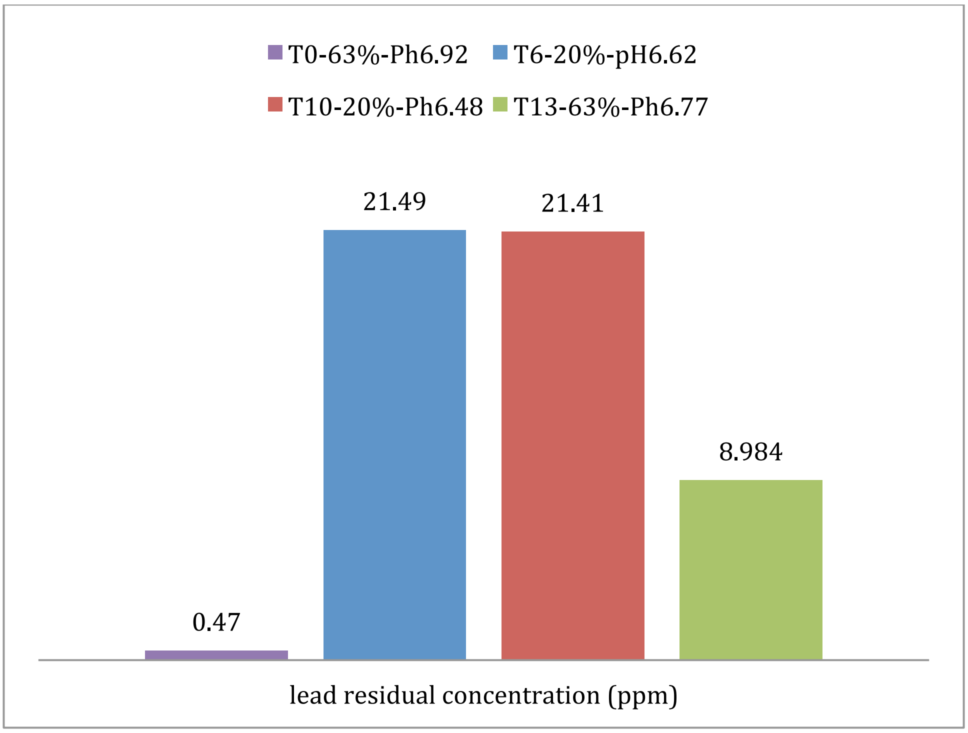


Figure 4-11: Residual lead concentrations during Tests 0, 6, 10 and 13 where feed acid concentration was varied

The results in Figure 4-11 show that Test 6 and 10 (20% acid addition) produced very similar residual lead concentrations of 21.49 ppm and 21.41 ppm respectively even with Test 10 having a feed lead concentration almost double that of Test 6.

Tests 6 and 13, which both had feed lead content in excess of 1000 ppm, showed a significant difference in their final lead concentration. Test 6 and 10 had very similar residual lead concentrations of 21.49 ppm and 21.41 ppm respectively even with Test 10 having a feed lead concentration almost double that of Test 6.

When evaluating these results, three of these tests produced a filtrate with a residual lead concentration over the stipulated lead discharge limit of 5 ppm. Only Test 0 showed a filtrate with an acceptably low lead concentration for disposal thereby confirming that the use of a higher acid feed concentration and surface addition is not detrimental to obtaining a filtrate low in lead.

To gauge the effect of acid concentration on the lead sulphate solubility, the rise in temperature during the addition of acid should be taken into account, with temperature considered a key parameter in the solubility of lead sulphate (Crockford & Brawley, 1934). With the higher sulphuric acid feed concentration, temperature rises are elevated with acid addition due to the increased heats of reaction released. Chapter 2 showed the effect temperature has on the solubility of lead sulphate given various acid concentrations according to work done by authors.

One of the other parameters controlled during precipitation besides pH was temperature. The temperature was measured and recorded regularly during precipitations before acid additions.

Table 4-7 shows the maximum recorded temperatures during the precipitation tests. The highest temperatures were recorded during Tests 13 and 14 showing temperatures above 60 °C. where the higher concentration variant of feed sulphuric acid was used. On the other hand Test 1 showed the lowest temperature recorded at 32 °C.

Table 4-7: Maximum temperatures recorded during precipitation

Test	Maximum temperature reached during precipitation (°C)
T1	32
T2	49
T3	49
T4	44
T5	55
T6	55
T7	45
T8	49
T9	50
T10	46
T12	58
T13	65
T14	69
T15	46
T16	49*
T17-T18	not recorded

* Only final temperature available and not maximum temperature that was recorded

The effect of Ageing on the precipitation process

Marani (1995), Kolthoff and Van't Riet (1959) and Kolthoff et al. (1939) are amongst some of the authors who have reported positive results when incorporating an ageing period into lead sulphate precipitation. Marani (1995) used low lead concentration samples, which were aged over several months to obtain an equilibrium state. During these experiments it was found that both pH and lead concentration changed with the ageing process. The pH value was seen to decrease from a solution with initial pH of 9.8 to a pH of 9.3 and increase in a solution with initial pH of 6.5 to a pH of 8 possibly indicating the difference between near neutral solutions and those more alkaline. However, in both cases lead concentration was found to decrease. Kolthoff and Van't Riet (1959) reported improvements in ageing results at higher sulphate concentrations while earlier work done by Kolthoff et al. (1939) showed how lead sulphate perfects itself in the earlier stages of ageing.

Effect ageing has on the lead filtrate concentration

Kolthoff and Van't Riet (1959) focused on the ageing process of lead sulphate given different sulphate and lead concentrations after its precipitation. Kolthoff et al. (1939) on the other hand reported on the perfection process in highly concentrated lead sulphate suspensions.

In order to test these theories, the following tests were done where the precipitate was aged for various lengths of time and the trend in pH monitored. The lead filtrate concentration was analysed either during or after ageing.

Below are the runs completed where ageing was incorporated into the test work.

Test 9: Heated solution precipitated to pH of 6.94 and thereafter aged for 48 hours

Test 12: Solution precipitated to 6.9 and aged for a total of 88 hours by standing at room temperature

Test 14: Aged for a total of 15 hours after solution precipitated to 5.44

Test 15: Suspension kept in water bath controlled to temperature of 40 °C for 286 hours following precipitation to 6.97 using 20 % sulphuric acid

Test 18B: Solution left standing for 2 days after lead solution precipitated to pH of 7 using 20% sulphuric acid

The choice of ageing time was based on time available within the constraints of the plant operating shifts and holding capacity. However during some tests, a longer ageing period was used in line with literature sources, in order to assess the benefit if any on the lead removal level achieved. Marani (1995) completed ageing test work on suspensions ranging from 30 minutes to 80 days while Kolthoff and Von Fischer (1939) looking at ageing periods from one week up to four months.

A summary of the ageing results can be seen in Table 4-8 with the measured lead concentration.

Table 4-8: Data from ageing tests

Test number	Total ageing(hours)	pH after acid addition	pH after ageing-measurement 1	pH after ageing-measurement 2	pH after ageing-measurement 3
0	**12-24 hours**	**pH6.92**	**No more measurements were taken**		
1	**48 hours**	**pH9.09**	**pH9.32**		
9	**48 hours**	**pH6.94**	**pH7.7-27.44ppm**		
12	**88 hours**	**pH6.9**	**pH7.96-17.51ppm**	**pH8.65-2.655ppm**	
14	**15 hours**	**pH5.44**	**pH5.96-30.54ppm**		
15	**286 hours**	**pH 6.97**	**pH 7.39**	**pH 8.12**	**pH 8.85**
18B	**48 hours**	**pH7**	**No more measurements were taken**		

The results of the ageing during Test 15 can be seen below.

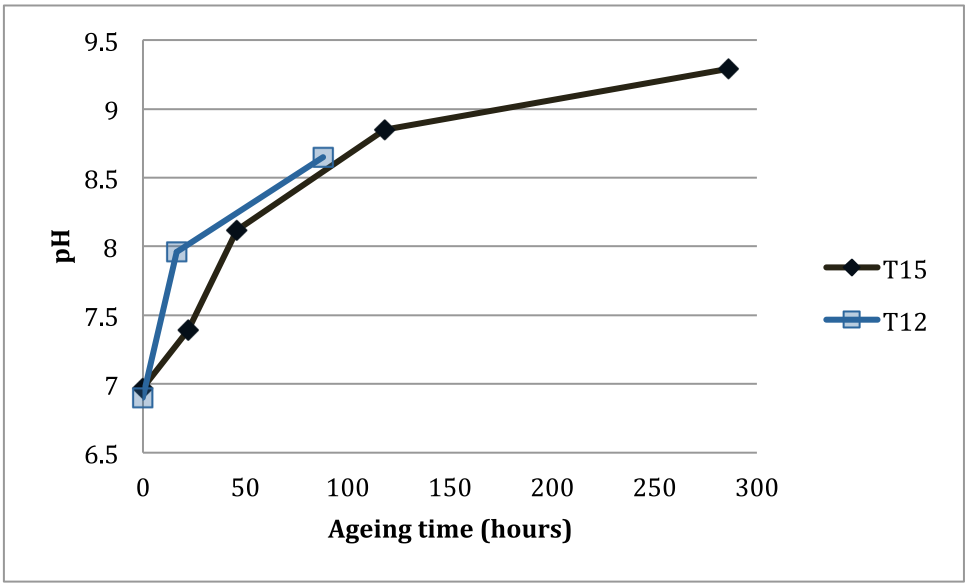


Figure 4-12: pH trend with time during ageing from Tests 12 and 15

Figure 4-12 shows how the suspension from test 15 shows a consistent rise in the pH of the suspension over the duration of 12 day ageing period. Test 12, shown here as three scattered points, similarly shows a rise in pH from 6.9 to 8.65 over a period of four days. Data from an ageing experiment published by Marani (1995) similarly showed a rise in suspension pH over 73 days, a significantly longer period of time in relation to the ageing experiments done as part of this study.

However, the change in pH measured and recorded during the Tests completed as part of this report saw an increase in lead concentration of 148% taking place over almost 12 days, This result can be seen in Figure 4-13 from the lead concentration analysed in solution after a 22 hour ageing period in a temperature controlled water bath at 40 °C.

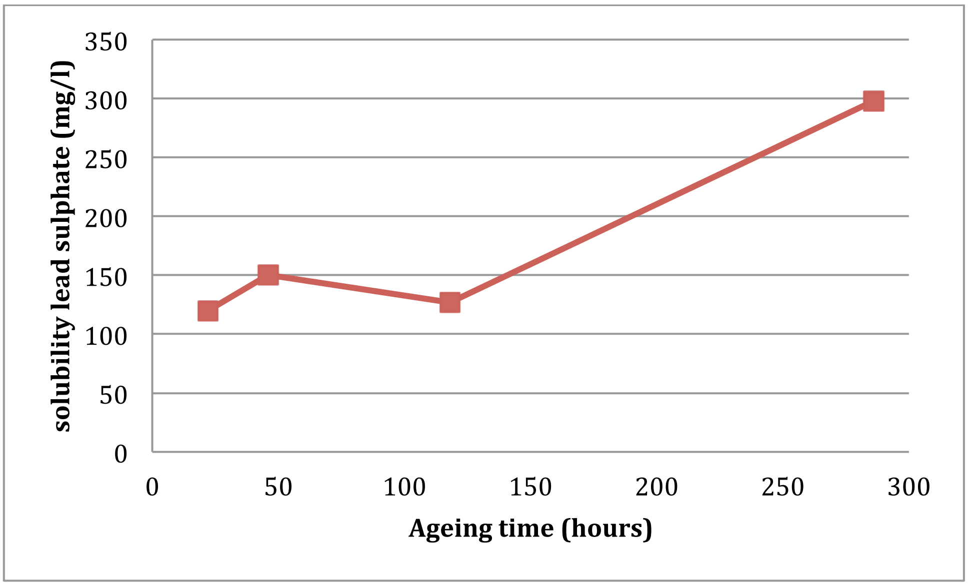


Figure 4-13: Solubility profile during ageing process in Test 15

Marani's results show how the rise in pH by one and a half units conversely had the lead concentration decreasing to lower than half a ppm.

Precipitation of copper present in lead feed solutions

The lead feed solutions presented to the precipitations also contained some dissolved copper ranging from 500 ppm to 2400 ppm in solution. In order to ascertain the effect this could potentially have on lead removal, the copper concentration was analysed before and after precipitation together with lead and tin.

Here the same solution was precipitated both times, to different pH levels. At both of these, all the metals, including the copper can be seen precipitating out into the lead-tin cake.

Figure 4-14: Lead-sulphate cake formed from solution with a high copper concentration (left) and cake formed from solution low in copper (right)

Table 4-9: Description of test conditions used during Test 6 and 7

Test	Test 6	Test 7
H_2S0_4 acid concentration (%)	20	20
Final buffered pH	6.62	6.09
Lead input (ppm)	1655	1655
Tin input (ppm)	1734	1734
Copper input (ppm)	506.1	506.1
Residual lead concentration (ppm)	21.49	40.14
Residual tin concentration (ppm)	0	0
Residual copper concentration (ppm)	62.22	94.77
Max. temperature reached (°C)	55	45

In order to see the effect the precipitation reaction had on the removal of copper present in the feed solution samples were taken from the feed solution and from the filtrate after precipitation and analysed for copper, lead and tin. Approximately 79% of the copper was removed during Test 6 while 70% was removed in Test 7. Even though the final lead concentrations are high, other tests done with copper-containing solutions also gave favourable results on the lead removal given suitable conditions, showing copper removal into the lead–tin cake. This test was done to determine the removal percentage of copper. High copper in the feed solutions did not demonstrate a noticeable effect on lead removal.

4.2.2. Lead sulphate cake

In order to gain perspective on the effect pH has on the solids-handling of the lead–tin cake, it is necessary to find ways of characterising both the lead–tin suspension produced as well as the lead–tin cake following filtration. Particle size, which plays a large role in both solid-liquid handling and cake density, should be determined in order to have a benchmark for operating conditions.

Suspension

Once the lead sulphate has been precipitated, the suspension formed requires solids handling in the form of solid–liquid separation creating a lead sulphate cake. In order to have a high rate of lead sulphate production, the filtration rates are required to be of a reasonable level so as to keep the size of the filter units low to save costs.

Effect final pH has on solids handling: particle size

The particle size distribution of two different dried lead cakes was determined using the Malvern^{TM} particle analyser. These cakes were produced from suspensions of different pH.

This effect was determined by obtaining the particle size distribution of two sets of lead–tin sulphate cakes that had been taken to two different pH values during precipitation. Malvern^{TM} particle analysers are often used to optimise crystallisation processes. Here a Malvern^{TM} size analyser was used to analyse cakes from Test 1 and Test 3.

Results from the Malvern^{TM} in the form of a frequency plot of these three cakes can be seen below in Figure 4-15. The frequency represents the volume of particles present for a set range of particle sizes.

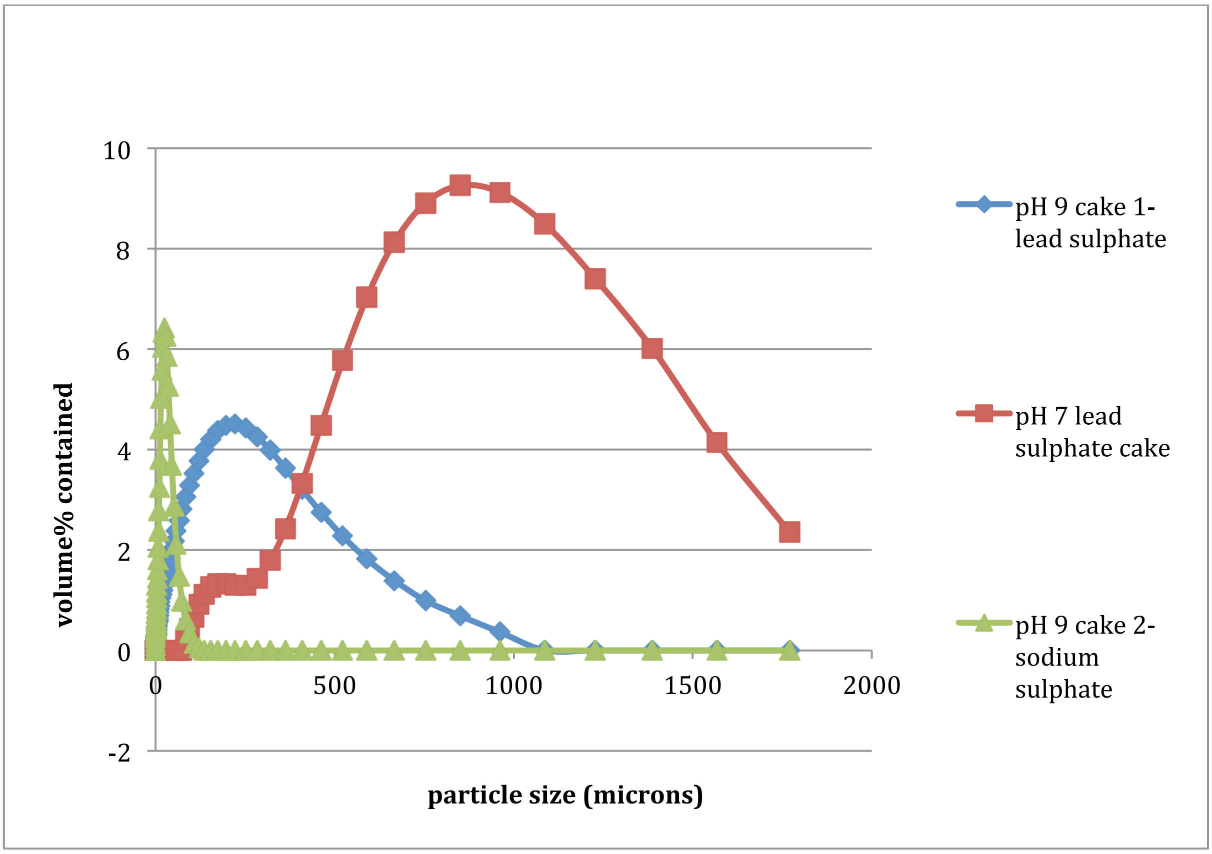


Figure 4-15: Frequency distribution obtained by analysing pH 9 and pH 7 cakes using the Malvern™

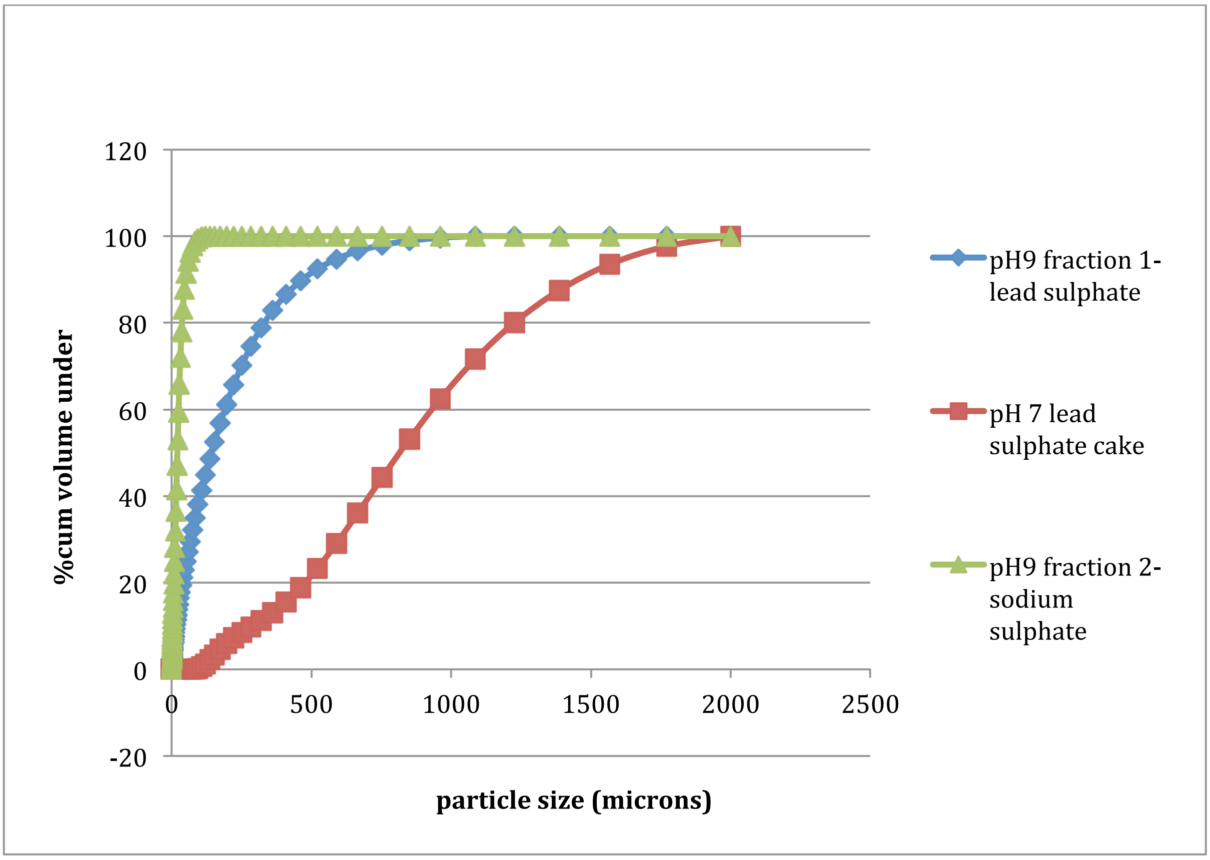


Figure 4-16: Undersize plot for pH7 and pH9 cakes

Figure 4-15 shows the particles from the pH 7 cake represented by a broad size distribution within the 500-1700 micron size range when compared with the pH 9 cake that had particles characterised into a narrower distribution with smaller particles in the 0-500 micron range. The cake with the smallest particles of all three cakes analysed was the sodium sulphate fraction, showing a high frequency of its particles occurring at the lower left of the axis, showing a high frequency of small particles making up the cake.

The major shift in frequency range between these cakes suggests that pH has a considerable effect on particle size distribution of the suspension.

Effect final pH has on solids handling: settling rate

In order to explore the extent to which pH affects the solids handing and other final characteristics of the lead–tin cake it is necessary to find ways of characterising the suspension produced from different pH levels. The results from the settling tests will be put against other results pertaining to characterisation of the suspension.

The suspensions from 3 tests were used to determine the settling rate as a precursor to obtaining the particle size distribution.

Three of the tests (Tests 1, 3 and 5) discussed above were used in settling tests which involved shaking up the suspension prepared through precipitation and timing the volume and distance travelled in settling the suspension as described in Chapter 3.

The results of these tests demonstrated the effect pH has on the settling of the different precipitates. The three different rates obtained were as follows:

Table 4-10: Settling data from 3 suspensions

Test number	Litres settled per hour	Final pH
1: 20% $\mathbf{H_2S0_4}$, max. temp. reached during precipitation 32 ° C, lead input 4416ppm	0.38	9
3: 20% $\mathbf{H_2S0_4}$, max. temp. Reached during precipitation 49 ° C, lead input 2005ppm	0.97	7
5: 20% $\mathbf{H_2S0_4}$, max. temp. reached during precipitation 55 ° C, lead input 3109ppm	0.95	8

Less than half the volume of suspension was seen settling out in the same amount of time during Test 1 in comparison with Test 3. The difference between Test 3 and Test 5's settling rate was 0.02 litres per hour indicating that

a) The lower pH suspensions settle out faster than the higher pH suspension indicating the effect pH has on particle characteristics

b) When dropping the solution from pH 9 to pH 8, there was a significant increase in the volume settled, showing a 60% drop during an adjustment of 1 pH unit from pH 9 relative to the drop from pH 8 to pH 7 which showed only a difference of 2%

Effect of filtration temperature on filterability of material and final cake produced

With the filtrate concentration being the main criteria for evaluation for disposal, the criteria when it comes to manufacturing a by-product for sale can be seen as the consistency and density of the cake.

In order to look at the effect of filtration temperature, some tests were filtered in cold conditions and others in heated conditions to see the impact if any which this had on the cake.

Tests 3, 4, 5 and 7 were filtered at ambient and Tests 8, 9, 10, 12-16,18A and 18B were filtered at various temperatures above the temperature of sodium sulphate crystallisation. These conditions can be referred to in Appendix B1.

These tests produced cakes with two different consistencies when dried at the different temperatures, above or below the temperature of sodium sulphate crystallisation. An example of a cake filtered at a temperature below crystallisation is pictured on the left in Figure 4-17 with a very light and fluffy material occluding the lead–tin sulphate cake. The cake filtered at a temperature constantly above 40 °C, the sodium sulphate temperature of crystallisation, is shown on the right as part of Figure 4-17.

Figure 4-17: Picture of cake from Test 6 (top) and cake from Test 12 after being filtered hot (bottom)

In order to determine the effect of temperature on solids-handling – in terms of cake density and filtration throughput, a laboratory scale filter press was tested using three different suspensions from the following runs:

1

Solution precipitated to pH of 9

18A

Solution precipitated to 7.3

18B

Final pH of 7, aged for 2 days

The following results were collected during and after the filtration tests.

Table 4-11: Conditions and results from SLFC filtration test work

Conditions	Test 2: 20% H_2SO_4, max. temp. reached during precipitation 32 ° C, lead input 4416ppm, final pH 9	Test 18A: 20% H_2SO_4, input 806ppm, final pH 7, no ageing	Test 18B: 20% H_2SO_4, lead input 806ppm, final pH 7.3, aged for 2 days
Cake thickness(mm)	~6	Not measured	Not measured
wet cake weight(g)	7.6g	60.5g	79.1g
dry cake weight(g)	3.8g	20.1g	25g
Moisture content (%)	100%	201%	216%
Filtration flow rate (l/m^2/hr.)	112	±415	±350
Filtration Temperature (°C)	50-60	40	40
Filter recommendation	Nutsch/Filter press	Nutsch/Filter press	Nutsch/Filter press

The method of calculation for moisture content can be seen in Appendix B2.

With all the cakes being filtered in the temperature range of 40-60 °C, representative of the temperature range expected of the final precipitation suspension, the effect of final suspension pH on filtration can be noted here. Test 18 shows a considerable improvement in the filtration rate from the rate obtained in Test 2, creating more favourable conditions for filtration for industrial use. The filtration rate recorded for Test 18A as 415 l/m^2/hour and for Test 18B as 350 l/m^2/hour can be compared to a rate of 112 for that of Test 2, showing a trebling or quadrupling of the filtration rate in Test 2.

This information can be used further to confirm the data obtained above in Figure 4-15 from the analysis using the Malvern^{TM} where we saw earlier that the particle sizes of the pH 9 cake comprised of smaller particles unlike the pH 7 cake which consisted of larger particles.

Elemental analysis of solids

An X-ray fluorescence analyser (XRF) was used for a qualitative analysis of the solid lead-tin sulphate cakes produced during three different precipitation tests, namely Test 10 and Tests 18A and 18B.

Cakes produced from these tests were analysed using XRF for percent mass of major elements. The results of the analysis of these cakes from the Malvern^{TM} can be seen below in Table 4-12, confirming the presence of lead and tin.

Table 4-12: Results from XRF of Test 10, 18A and 18B

Element	Mass % T10 : lead 3109ppm, final pH 6.48	Mass % T18A: 20% H2SO4, lead 806ppm, final pH 7	Mass % T18B: 20% H2SO4, lead 806ppm, final pH 7.3, aged for 2 days
Ca	0.6	4	3.1
Fe	0.67	0.78	0.64
Cu	33.7	4.4	2.6
Zn	10.5	7.87	4.49
As	0.5	0.1	0.09
Sb		5	
Ag			2
S			30
Tb	0.06	0.1	
Dy	0	0.4	
Ta		0.1	
Os	1.2		
Sn	7.5	36	31
Pb	45.3	41.4	25.9

The lead and tin concentrations in the cakes were compared where it was observed that in Test 10, the tin appeared to be lower than normal, when comparing all 3 cakes. In the aged cake, the lead appears to be lower in comparison with the other cakes and higher in sulphur (30%), contributing a high percentage to the weight of the cake.

4.2.3. Sodium sulphate

With the high feed content of sodium hydroxide in the lead feed solution the potential exists for the recovery of a significant amount of sodium sulphate as a valuable by-product. So as not to be to the detriment of the lead sulphate precipitate, its co-precipitation should be avoided and rather controlled to follow solid-liquid removal of a lead sulphate mostly free of sodium sulphate, leaving it behind in solution to be crystallised out at room temperature from the filtrate solution.

The presence of sodium sulphate can be easily determined by identifying its characteristic shapes produced at different stages of growth. Figure 4-18 illustrates these crystal shapes at the later stages of growth.

The effect sodium sulphate has on the solids-handling of lead-tin sulphate cake

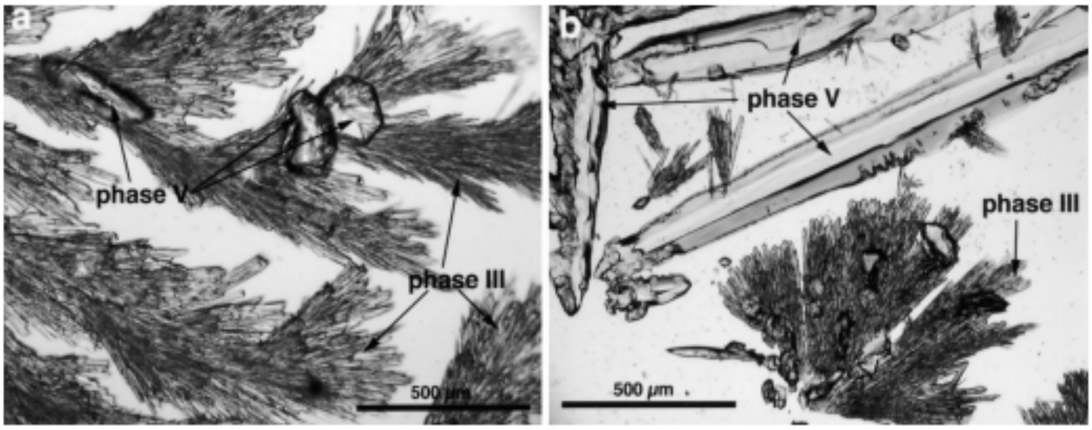
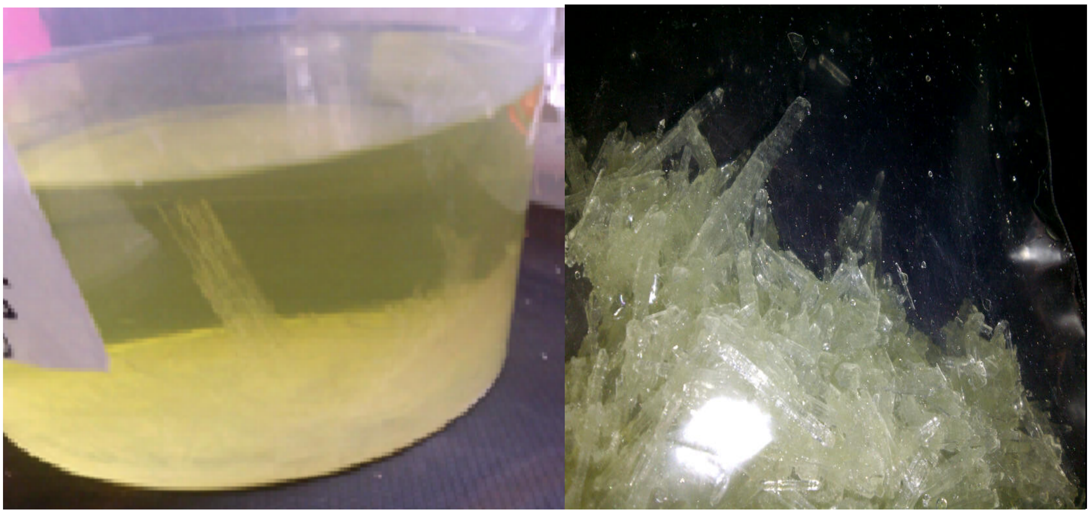


Figure 4-18: Sodium sulphate crystals at various stages of growth (Rodriguez-Navarroa, Doehnea, & Sebastian, 2000)

Figure 4-18 shows sodium sulphate crystals at different stages of growth. These images point out the difference in appearance between phases 3 and 4 of crystal growth.



a) b)

c)

Figure 4-19: Picture taken of cooled suspension where sodium sulphate had crystallised out. a) Test 9 b) Test 7 c) Test 12

In figures (a) and (b), needle-like crystals of sodium sulphate are shown clearly representing phase four growth according to Figure 4-18 while in figure (c), phase three crystals can be seen in the suspension.

Table 4-13 shows the tests where the mass of sodium sulphate recovered was recorded and the conditions used in each case. The highest amount of sodium sulphate recovered is from Test 12 at 260 g. The lowest amount of sodium sulphate recovered was during Test 10 with 34 g.

Table 4-13: Sodium sulphate weight recovered per litre of leach solution

Test	Na_2SO_4 (grams per litre filtrate)
Test 8:acid concentration 20% H_2SO_4, lead input 175ppm, final pH 7.32	88.3
Test 9: acid concentration 20% H_2SO_4, solution heated to 37 ° C, ageing 48 hours, final pH 6.94*	87.4
Test 10: acid concentration 20% H_2SO_4, ageing 0 hours, final pH 6.48	34.1
Test 12: acid concentration 63% H_2SO_4, ageing 88 hours, final pH 6.9	259.6
Test 14: acid concentration 63% H_2SO_4, ageing 15 hours, final pH 5.44	151.7
Test 15: acid concentration 20% H_2SO_4, ageing 120 hours, final pH 6.97*, constant temp. water bath used during ageing	82.1

Cake washing

Following filtration, several cakes were washed for removal of sodium sulphate. For this wash to be efficient, the temperature needed to be controlled to within a few degrees of the transition temperature of 32.27 °C for sodium sulphate. This would allow the sodium sulphate to dissolve in solution while keeping the temperature low enough so as not to solubilise any lead sulphate into solution. In the case of Test 4, 5 and 6, the cakes were re-weighed where it was found that the weights were reduced by only 2% in the case of Test 4, 34% in Test 5 and 74% in Test 6.

The lead-tin cakes selected for washing showed sodium sulphate crystallised out on the surface following a filtration at a temperature lower than 32.27 °C. In order to remove and separate more of the sodium sulphate from the lead-tin cake, a heated wash step was added subsequent to the filtration of these cakes in order to dissolve and remove the sodium sulphate into the wash water. More about the conditions used during these washes can be seen in Chapter 3. By removing the sodium sulphate, there are improvements not only in the quality and consistency of the lead-tin sulphate cake but also the quality of the sodium sulphate.

Table 4-14: Information on washing stages during various precipitation tests

Test number	No. of washes	Cake mass before wash (g)	Cake mass after wash (g)	Mass reduction %
Test 0	none			
Test 1	none			
Test 2	one	23		
Test 3	one	34.5		
Test 4	multiple washes	36.1	35.3	2.2%
Test 5	multiple washes	39.3	25.9	34.1%
Test 6	one	79.6	20.9	73.7%
Test 7	None	49.5		
Test 8	one wash-hot	30.9		
Test 9	none	374		
Test 10	Multiple washes-hot	12.1		
Test 12	multiple washes	10		
Test 13*	none	537.3		
Test 14*	none	208.1		
Test 15	single wash-hot	17		
Test 16	none	unknown		

* The lead sulphate cake mass recorded in Test 13 and 14 comprised of lead sulphate with layers of sodium sulphate that had crystallised out in-between, creating a sandwich effect.

The biggest reduction in mass seen above was during Test 6. The higher this reduction, it can be assumed that the more sodium sulphate is recovered into the filtrate by staying dissolved during washing of the lead sulphate cake. On the other hand there was an insignificant change during Test 4 where multiple washes were done.

Sodium sulphate crystallisation

Once filtration of the lead–tin sulphate cake had taken place, the filtrate could then be processed further in order to recover sodium sulphate. Crystallisation of the sodium sulphate took place in two different ways

a) Through leaving the filtrate standing and allowing the crystals to form naturally and sporadically. An example of the crystals formed in this way can be seen in the picture below from Test 5:

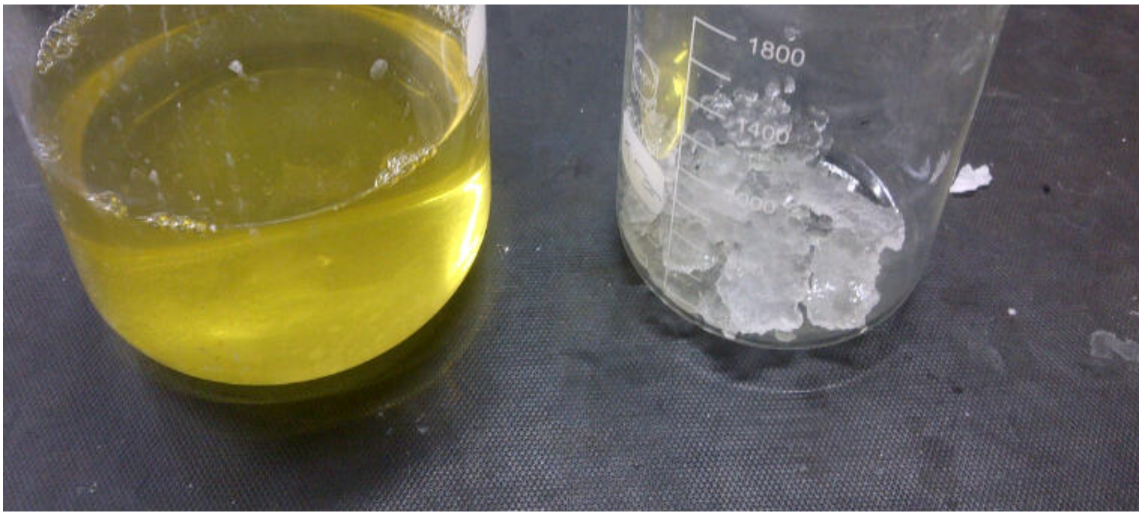


Figure 4-20: Sodium sulphate crystals (right) and filtrate solution remaining (left) formed after standing filtrate solution from Test 5

Alternatively

b) A controlled method was used to recover the sodium sulphate crystals. This was achieved by agitating the filtrate solution at ambient temperature at a rate of 426 rpm for a period of 1 hour until very small, divided crystals of sodium sulphate could be observed in the solution. These were then vacuum filtered, well distributed in a glass tray and air-dried taking into account that due to the hygroscopic nature of the crystals, oven drying was not an option to consider. This meant allowing for some residual moisture in the sodium sulphate crystals. This was done for Tests 10, 12 and 15. The crystal produced had significantly lower moisture content due to less moisture being trapped in the crystal.

-

Figure 4-21: Sodium sulphate cake made by controlled agitation from Test 10

Over all the test work done, Tests 12 and 16 showed the best results in terms of their final lead concentrations, having filtrates with concentrations of 2.655 ppm (Test 12) and 2.667 ppm (Test 16) in lead given final pH values of 6.9 (Test 12) and 6.15 (Test 16) precipitated over 30 minutes with no ageing. The filtration was done at a constant temperature of 40 °C giving a lead-tin sulphate cake mass of 10 grams (Test 12) from 0.67 litres of lead solution. The maximum temperature reached during Test 12 was 58 °C; the temperature reached during Test 16 was unmeasured.

The next chapter will eliminate any conditions from above considered detrimental and ineffective to the precipitation process in terms of filtrate concentration or quality of the lead–tin sulphate and sodium sulphate to be sold as products. This will lead to conclusions on the relationships if any between some or all of the conditions used and described in this chapter.

5. Conclusions and discussion

The effectiveness of sulphuric acid as a precipitating agent in removing lead and tin from an alkaline leach solution was determined through batch tests using a variety of conditions. The author came to do this investigation after having encountered numerous problems ranging from solids handling to ineffective precipitation and decided to do small-scale laboratory tests.

This chapter will familiarise the reader with the chosen inputs to the process as well as the conditions, which were chosen based on these batch tests. The overriding objective was to consolidate the outputs of the precipitation into saleable products: lead-tin sulphate cake and crystalline sodium sulphate as well as a low concentration lead filtrate solution suitable for disposal to municipal sewer.

The writer found that certain parameters affected the lead recovery as well as the solids handling of the lead-tin sulphate produced. The concluding thoughts on the relevance of these parameters can be found below.

5.1. Chosen parameters for precipitation of lead-tin sulphate

5.1.1. Temperature control

Laboratory test work on the precipitation of lead and tin has been done up until now with the only temperature control being the rate of sulphuric acid addition, leaving the precipitation to proceed towards its equilibrium temperature with no heating or cooling. The results shown indicate that temperature control should be included to avoid a) a drop in temperature below the critical temperature of 32.27 °C (Reddy S. T., Lewis, Witkamp, Kramer, & van Spronsen, 2010) which would lead to the sodium sulphate crystallising out, or b) the temperature rising too high causing lead to solubilise. Effect of temperature was investigated on both the solubility of the lead–tin sulphate and the sodium sulphate in solution. The test work shows the need for temperature control during precipitation as well as filtration to minimise lead sulphate solubility and to limit sodium sulphate precipitation during its filtration. At a sulphuric acid concentration of 20%, Crockford and Brawley (1934) report lead sulphate solubilities of 1.2 ppm at 25 °C and 8 ppm at a temperature of 50 °C showing the effect temperature has on the solubility of lead sulphate.

5.1.2. Sulphuric acid feed concentration

There were a number of factors to consider when making the choice between a more dilute sulphuric acid and a stronger sulphuric acid. These included:

a) water consumption, something to consider when operating on an industrial scale where excess volume translates to higher capital expenditure and higher waste volumes.
b) heat of dilution; this is expected to be higher in the case of a more concentrated sulphuric acid. If this translates into a temperature rise, which is not controlled, lead solubility is expected to increase. This will mean that acid addition rate will be low and cooling coils should be fitted to the tank in the case of runaway temperatures.
c) solubility of sodium sulphate.
d) With a higher concentration of sulphuric acid, the more aggressive the conditions are which the tank and agitator materials need to be able to handle.

To reach a pH of 14 from the initial solution, which had an undetectable pH due to it being highly alkaline, 86% of the acid was added to the lead solution, with the balance of the acid added to drop the pH to 7.

With pH control after the buffer zone becoming harder as smaller amounts are added to drop the pH from the higher alkaline pH levels to a neutral pH, the more dilute the acid mixture, and the more easily this addition regime can be controlled.

5.1.3. Lead concentration in feed solution

A variety of alkaline lead and tin leach solutions, differing in the concentration of lead and tin, were tested with the sulphuric acid precipitation process described in this report. The results showed that the two metals are removed successfully from both low and high initial concentration lead and tin solutions when put through the same precipitation process.

5.1.4. The roles played by sulphate concentration and pH

One of the research problems identified during this study was two possible effects on lead sulphate removal.

One of these effects was the role that increasing sulphate concentration plays on the lead sulphate solubility arising from the use of sulphuric acid as opposed to another acid without the sulphate ion presence.

The other possible effect was the part played by the change in pH resulting from the addition of hydrogen ions to the solution.

There is not much evidence to show the isolated role played by increasing the sulphate concentration.

Ramette and Stewart (1961) who investigated the effect on lead sulphate solubility with increasing perchloric acid concentration, showed how increased acid concentration affects the lead sulphate solubility, covered the pH range 2.5–4.5. The solubility dropped the lower the acid concentration, but as this data only covers a small range of the acidic pH region, it is not possible to assume the same trend applies to the alkaline region. Therefore these data are not entirely helpful in uncoupling the role of increased sulphate concentration from that of increasing pH, which could both potentially play a role in the precipitation of lead-tin sulphate.

One of the mechanisms through which precipitation can occur is a change in pH.

Lead filtrate concentrations precipitated at higher pH values showed higher lead solubilities. However as more acid was added, the lead solubility dropped as the pH approached values between 7 and 8. Thereafter, the solubility at pH levels below 7, experienced an increase before dropping off again.

Crockford and Brawley (1934) show a 35% drop in lead solubility when doubling the sulphuric acid concentration from 20% to 40% at a temperature of 35 °C. These data show a sudden increase of 88% in solubility at an acid concentration of 80%.

It is evident that while there is little or no change in pH in the initial stages of precipitation, the increasing sulphate concentration takes on a dominant role of dropping the lead solubility. When the pH did drop, which took place after the buffer zone, there was a further drop in lead solubility, with the continued addition of sulphuric acid and its associated drop in pH.

This investigation found a minimum in the lead solubility values of 2.7 ppm at a pH between 6 and 7. This is comparable with the value of 2.8 ppm given by Crockford and Brawley (1934) also recorded at a temperature of 35 °C in a sulphuric acid concentration of 20%.

Apart from looking at pH in terms of the lead removal, the solids handling and quality of the lead-tin sulphate cake is also important. Therefore the impact on particle size caused by pH was investigated as well.

Besides having an effect on lead removal, the particle size is also affected by the pH. Experimental work evaluating the particle size distributions was done using suspensions with different pHs. The results showed a significant difference in the particle sizes. It was shown that the pH 7 lead sulphate cake had larger particle sizes than the pH 9 cake. Therefore it can be concluded that acid addition to neutral pH promotes both high removal of lead and faster filtration rates as a result of the larger particle size produced. This is evident by looking at the improvement in the filtration rate, which increased from only 112 litres/m^2/hour to 415 litres/m^2/hour by dropping the pH of the suspension from 9 to 7.

Based on the conclusion that precipitation to neutral pH promotes high lead removal, this fact can be used as a means of control for the precipitation process by signalling the end of sulphuric acid addition.

5.1.5. Ageing

While it was thought that ageing of the solution following acid addition would achieve maximum conversion to lead sulphate crystals, test results on the suspensions showed that lead concentration in solution actually increased with time. Not only was this the case, but it was also discovered that the filtration rate when compared with a fresh, unaged solution was lower, at a rate of 350 litres/m^2/hour. Another observation made was that the pH level recorded after acid addition was seen to rise with the ageing process by anything from 1 to 3 pH units in a matter of 24 hours, as shown by Test 15.

While ageing is expected to support the growth and stability of the crystal structure in suspension, the ageing technique used during this study only added unnecessary time to the process, which would translate into metal lock-up on an industrial scale. It is important to keep in mind overall processing times to see whether they are acceptable for manufacturing purposes.

5.1.6. Filtration temperature for lead-tin sulphate cake

In order to avoid the sodium sulphate from being precipitated out with the lead-tin sulphate cake, a minimum filtration temperature was required. Local lead processors encountered problems with this cake, where they found that there was a lot of light mass making up the cake, which did not convert effectively during the smelting process.

Besides the problem of having the sodium sulphate occluded in the lead-tin sulphate cake, low filtration rates were encountered when the temperature dropped below the 32.27 °C.

For these two reasons, the suspension should be temperature controlled above the temperature of crystallisation for sodium sulphate, at the same time ensuring that the temperature does not increase far beyond this value to avoid pushing up the solubility.

In the event that the temperature did drop during filtration, causing the sodium sulphate to come out of solution, a heated wash step was required to dissolve any sodium sulphate from the lead sulphate cakes. This served to increase the percentage of lead sulphate in the final product stream thereby improving the final dried form of the lead sulphate cake. The sodium sulphate occluded in the lead-tin sulphate cake makes it an undesirable product for downstream lead processors who go on to feed the material into a lead smelting process.

Controlling when the sodium sulphate is crystallised out of solution is therefore important for ensuring product quality.

5.1.7. Conditions for crystallisation of sodium sulphate from filtrate

As a result of the high sodium hydroxide concentration in the feed leach solution, a major part of the overall precipitation process is the recovery of sodium sulphate from solution. The motivation for its recovery is threefold:

1) The sodium sulphate can be easily removed from the filtrate by precipitation – low processing costs involved
2) The sodium sulphate has an anticipated commercial value
3) The process requires that the lead sulphate be free of sodium sulphate suggesting selective precipitation
4) For purposes of disposal, the final solution will have a lower salinity.

Sodium sulphate was effectively crystallised out from the lead filtrate solution using a flat blade impeller at a stirrer speed of 500 rpm. To promote cooling following the heated precipitation, the crystallisation took place in a flat-bottomed open vessel at ambient conditions, therefore allowing natural cooling to take place. The solution was agitated for 1 hour before being removed for filtration at ambient temperature.

5.2. Discussion

5.2.1. Reaction mechanisms - Reduction of lead IV to lead II state

With the lead being in the form of a plumbate, the lead is initially a lead (IV) complex. With the conversion to lead sulphate, a reduction as well as sulfation reaction is required. The test work proved that this did not mean the kinetics were in any way unfavourable. It might be interesting to model these two stages of crystallisation through the use of population balance modelling.

5.2.2. Removal of tin

While this study does not focus on the removal of tin, the tin has a high concentration in the leach solution, which is fed to the precipitation. However, because of the chemical similarities between lead and tin, the tin is removed with acid addition as an insoluble sulphate, not adding significantly to the cost of processing. Results from test work have shown that the tin concentration drops down to concentrations as low as near zero ppm during precipitation tests where there have been significantly high levels of lead in solution. This shows the more favourable kinetics involved in its crystallisation.

5.3. Limitations of work

While every attempt was made to control the experimental programme, there was a sense of urgency in terms of collecting the data required to set up the unit processes involved with the precipitation of the lead-tin sulphate. These resulted in

- Inadequate temperature control during precipitation causing temperature fluctuations
- Qualitative rather than quantitative analysis of cake
- Cakes not oven-dried but rather air-dried to prevent the volatilisation of the lead and the sodium sulphate crystals from deliquescing . This could mean the weight of the cakes include some moisture in the reported weights
- No definite conclusion on the method of acid addition; at source of agitation or surface of liquid. This is because when comparing data between tests where each of these two options were used, it was found that the filtration conditions were different. However, there is some evidence to suggest that the addition should take place at the source of agitation in order to optimise the precipitation and particle size produced. As a result of this, the design of crystallisers often takes into account the design of addition points.

5.4. Recommendations for further test work to be done

5.4.1. Reaction pathways

Collect and analyse the thermodynamic data in the form of temperatures measured during the precipitation tests, which can then be used to determine the heat effect, if any, from the conversion of lead (IV) to lead (II) in producing lead nitrate. This would then show the heat generation from the reduction of the lead relative to the heat generated from the neutralisation and what the differences are, if any, produced by adding different acids to the same lead solution each time. If the reduction reaction is a slow reaction, this will be demonstrated by a noticeable heat effect since reduction reactions are usually associated with significant heats of reaction.

5.5. Acid effect

Look at the use of different acids to precipitate out the lead and what improvements, if any, these could bring to the process. This study has only managed to do experimental test work using sulphuric acid and theoretical investigation to some extent into perchloric acid. It will be useful to look at any other improvements to lead removal, which a change in acid type could bring.

5.5.1. Common ion effect

Further test work can be done to investigate the benefits that a sodium sulphate wash has in lowering the solubility of the lead sulphate cake. Currently this study only focuses on a lead sulphate precipitation and filtration followed by a sodium sulphate crystallisation and filtration, with no wash in-between.

5.5.2. Copper in solution

It should be noted that there was a high starting level of copper in the lead feed solution to the precipitation. It is not clear from the test work completed whether this had a positive or negative effect on the removal of lead. Copper sulphate, which is expected to have a low solubility, was removed and precipitated out into the lead-tin sulphate cake. Further work should be done to come to a conclusion on whether the presence of copper in any way is to the detriment of the lead removal percentage.

5.5.3. Two stage precipitation

Taking the research further, once the lead filtrate has been collected following sodium sulphate crystallisation, it is expected that the lead concentration in the remaining solution would have increased (test work showed that the lead concentration more than doubled following crystallisation). This should be sent for a second stage of lead sulphate precipitation should the lead concentration be above the stipulated concentration level.

5.5.4. Alternatives to treatment method of disposal for lead filtrate

Rather than disposing the filtrate to sewer, an alternative is to find other methods of treating this water further in order to remove the residual lead in solution and in so doing, serve the water requirements on the plant. As there are increasingly more environmental restrictions placed on processing plants, an alternative outlet for this water should be considered in terms of water and resource security. This may include optimising the process so as to further reduce the residual lead filtrate concentration. Other, more rigorous treatment methods could be employed for the residual, low-level concentration of lead in solution. These include membrane technology as well as wastewater ion exchange where treatment at this level of lead is economically feasible and successful.

5.5.5. Improvements to crystallisation and recovery of sodium sulphate

The crystallisation technique should be relooked at and refined to improve sodium sulphate product quality. This investigation should start with the current crystal size distribution in order to see what can be done to narrow down this profile. These trials should include trying out different impeller geometries as well as speed settings to optimise particle shape and size.

With industry's focus on lead-acid battery recycling, a lot of the available data for lead sulphate precipitation deals with the acidic pH scale. This investigation was fuelled by the need for lead solubility data at alkaline pH levels.

While globally there is the drive to reduce the use of lead, there is still a significant amount of lead-containing material requiring robust and low-cost treatment methods to prevent this toxic metal from entering our ecosystems and damaging the environment. The paint industry has completely removed lead from its products while the electronics industry is in the process of completely phasing it out. The car battery industry remains a key source of lead, with the production of anodes a small user of lead in comparison. The process solution recommended in this report is intended for translation to industrial scale with low capital expenditure.

This study has been successful in outlining a simple yet effective process for the precipitation of lead-tin sulphate as a mixed cake from a caustic leach solution. Data from this report will be translated into a process flow diagram for use on an industrial scale. Based on the information contained in this study, tanks will be designed and built for both the precipitation of the lead-tin sulphate and the crystallisation of the sodium sulphate. The same has been done in the case of the filter press for filtration of the lead-tin sulphate and the sodium sulphate.

Future research done by analysing plant data will enable process optimisation and further improvements in terms of cost, process efficiency and product quality. These laboratory tests proved that the lead can be removed with control of pH to neutral via addition of sulphuric acid. More test work will follow in order to further streamline the production of lead-tin sulphate and sodium sulphate.

This investigation has come up with a solution to the processing of the lead leach stream, which produces outputs that satisfy the environmental regulations as well as the market/commercial demand for a secondary source of lead.

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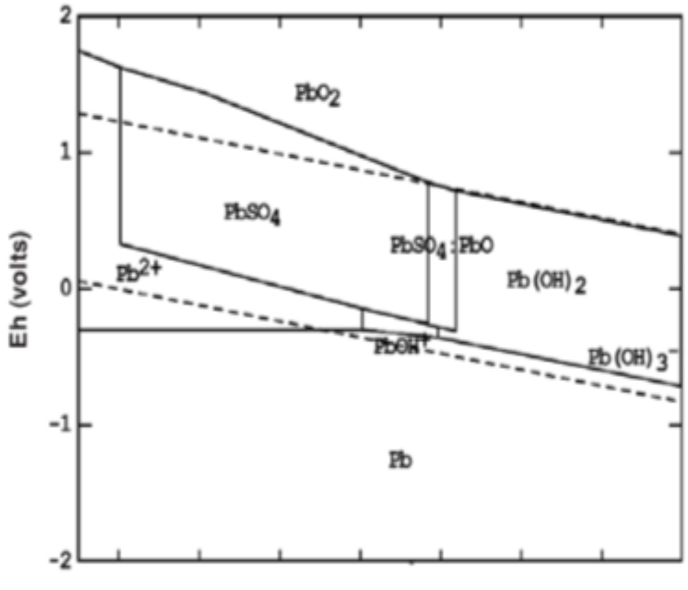
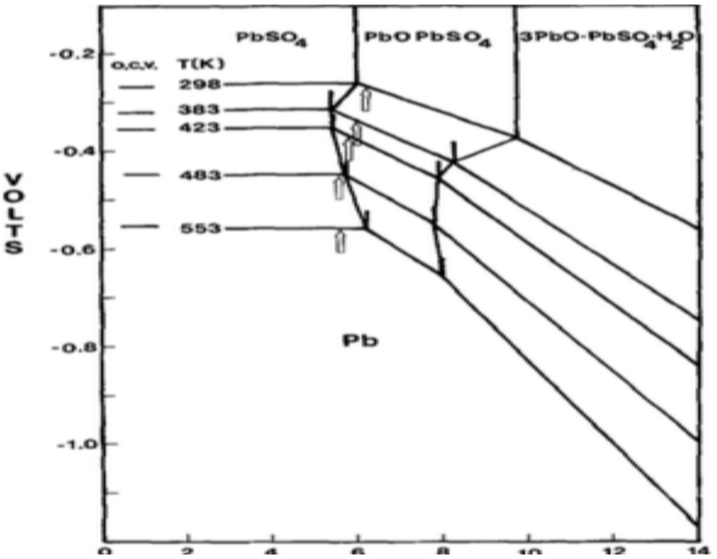
Appendix A: Pourbaix diagrams

When studying a precipitation system, it is worthwhile discussing the associated Pourbaix diagram to gain more information on the stability of different compounds formed at various pH levels and redox potentials. This case is no different and three teams of authors can be mentioned here for their extensive work on lead Pourbaix diagrams. While Delahay, Pourbaix & Van Rysselberghe (1951) and McMahon, Ruther and Melendres (1988) focused on lead corrosion in the field of lead storage batteries, the latter studied the lead system in sodium sulphate as opposed to sulphuric acid. Groot & Van der Linde (2009), who also looked at the corrosion and passivation of lead in sulphuric acid, were interested in the leaching characteristics of lead from electronic waste. Furthermore, McMahon, Ruther and Melendres (1988) add another level of information by incorporating temperature dependency into the Pourbaix diagram.





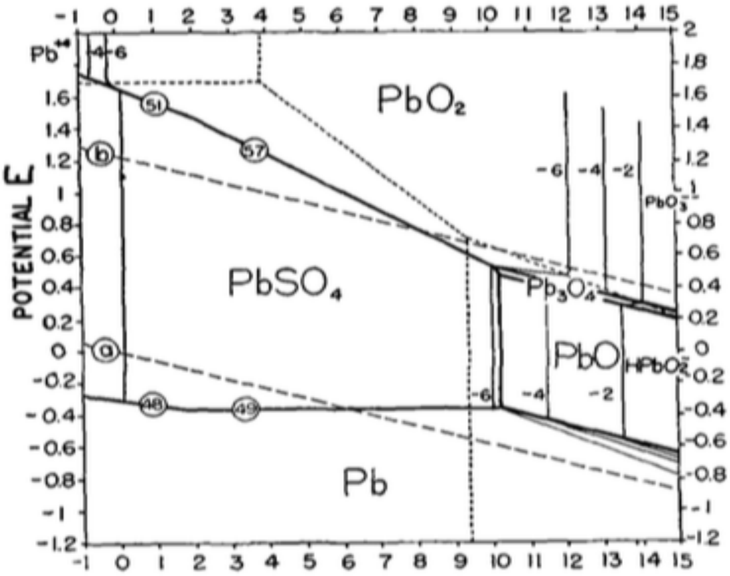


Figure A 1: Pourbaix diagrams for the lead system. From top to bottom: McMahon, Ruther & Melendres (1988) , Groot & van der Linde (2009) and Delahay, Pourbaix & Van Rysselberghe (1951)

Appendix B1

Test number	Temp. of filtration (^{O}C)	Solids wash
0	**Ambient**	**None**
1	**N/A**	**1 litre cold, deionised water added to decanted solids**
2	**Exit temperature precipitation – around 49**	**Washed with 0.2 litres of cold, deionised water on the surface of the Buchner funnel pad**
3	**Ambient**	**Washed with 0.2 litres of cold, deionised water on the surface of the Buchner funnel pad**
4	**Ambient**	**Washed with 0.3 litres of cold, deionised water on the surface of the Buchner funnel pad**
5	**Ambient**	**Wash 1:Slurry washed with 1 litre of cold deionised water** **Wash 2: Slurry washed with a further litre of deionised water slightly heated**
6	**Exit temperature precipitation – around 49**	**Wash 1:Slurry washed with 0.1 litres of cold deionised water** **Wash 2: Washed with another 0.1 litres of cold deionised water**
7	**30 - solution was left to cool before being filtered**	**None**

Table B 1: Temperature of filtration for tests 0-7

Test number	Temp. of filtration (^{O}C)	Solids wash
8	**Heated to 54 before being filtered**	**Wash 1: 1 litre of hot water poured in with filtrate during initial filtration – filtered in two parts producing two cakes** **Wash 2: Both cakes slurry washed in 3 litres of hot water (54 ^{O}C.)**
9	**Heated to 50 before being filtered**	**None**
10	**Hot-kept above 40**	**Wash 1:Washed with 1 litre of boiling deionised water on surface of Buchner filter pad** **Wash 2: Further 0.5 litres of boiling water poured onto surface of Buchner**
11	**N/A**	**N/A**
12	**Hot-above 40**	**Wash 1:Slurry washed with 1 litre of deionised water** **Wash 2: 0.5 litres hot water** **Wash 3: 0.5 litres of hot water**
13	**Exit temperature precipitation – around 63**	**NONE**

Table B 2: Solid-liquid separation for tests 8-13

Test number	Temp. of filtration (^{O}C)	Solids wash
14	**Hot-above 40**	**NONE**
15	**39**	**Washed at 43 ° C. 1 litre deionised water Washed on surface of Buchner filter pad**
16	**Exit temperature precipitation – around 49**	**NONE**
17	**N/A**	**NONE**
18A	**40**	**NONE**
18B	**40**	**NONE**

Table B 3: Solid-liquid separation for tests 14-18

Appendix B2

Filtration results

$$moisture\ \ content\ on\ a\ dry\ basis\ (\%) = \frac{weight\ of\ wet\ material\ (grams) - weight\ of\ dry\ material\ (grams)}{weight\ of\ dry\ material\ (grams)} * 100$$

Appendix C1

MSDS for sulphuric acid (received at 98% strength)

Omnia - SULPHURIC ACID 98 % Page 1 of 4

SULPHURIC ACID 98 %

Material Safety Datasheet

CAS No 7664-93-9
Date Issued: 2008/08/14
SULPHURIC ACID 98 %

Company Details

Name	Protea Chemicals - Cape	Emergency Tel	082-490-5011
Address	54 Killarney Avenue Killarney Gardens Milnerton 7441 Email: rfyfe@proteachemicals.co.za	Tel Fax	021-550-8100 021-550-8180

1.Product and Company Identification

Trade / Commercial Name	**SULPHURIC ACID 98 %**		
Chemical Name	Sulphuric acid		
Formula	H2SO4		
Chemical Family			
Synonyms	Oil of vitriol; BOU; Dipping Acid; Vitriol Brown Oil; Sulfuric; Acid Mist;		
Un No	1830	Hazchem Code	2p
ERG No	137	EAC	59

2. Composition

Hazardous Components	Sulphuric acid 98%

3. Hazards Identification

Corrosive
Skin contact poisonous.
Contact wil cause severe burns to skin and eyes.
Fire could produce irritating or poisonous gases.
Runoff from fire-control or dilution water could cause pollution.
Breathing high concentrations may cause coughing or sneezing.
Ingestion: Serious burns of mouth.

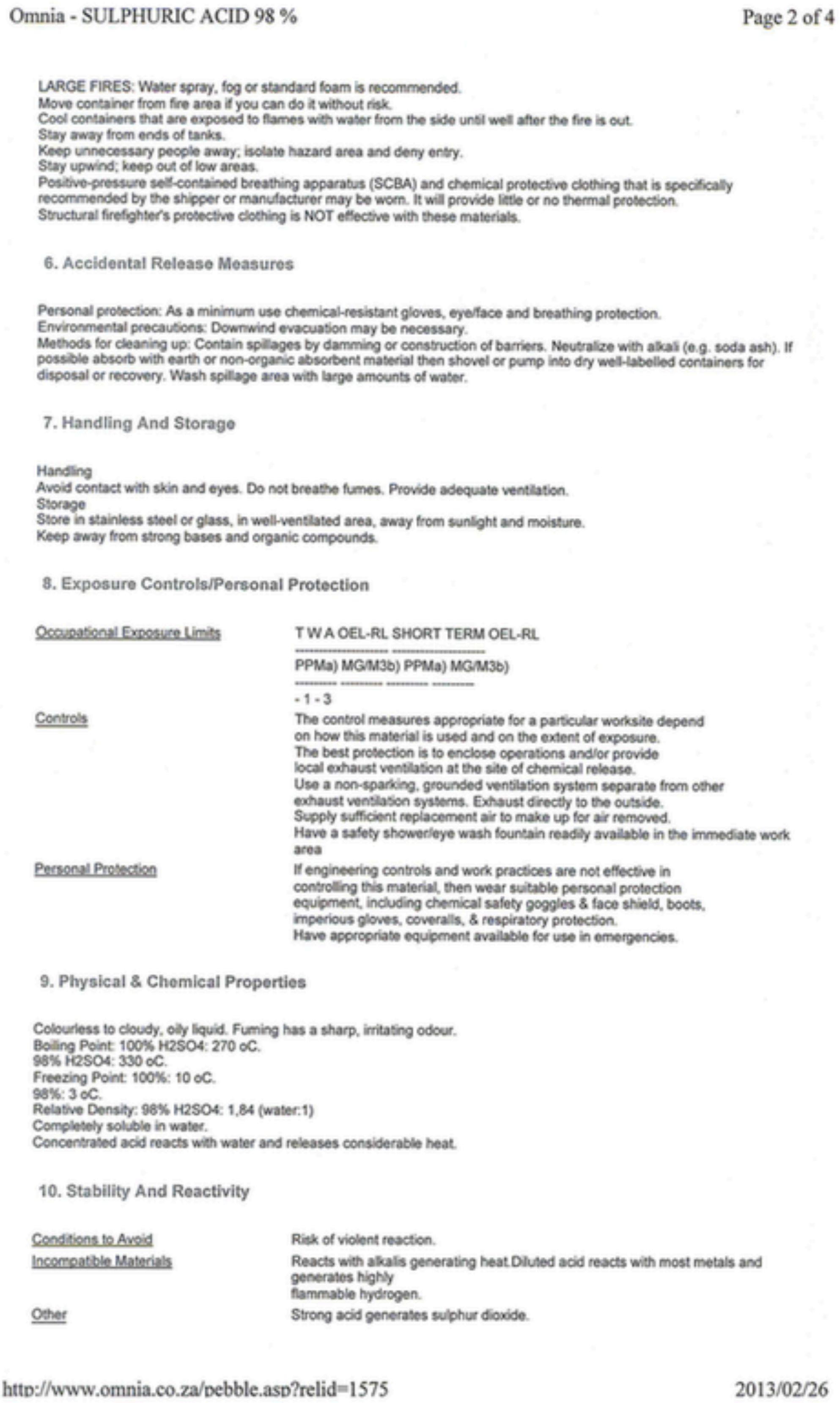
4. First Aid Measures

First Aid Skin	Wash off with water. Remove clothing. Shower thoroughly. IMMEDIATELY remove contaminated clothing and drench affected area with running water for 20 minutes.
First Aid Eyes	Flush eyes with water for 15 minutes. Hold eyelids open while washing.
First Aid Ingested	Do not induce vomiting. Rinse mouth. Immediately give plenty of water to drink. Prompt medical attention is vital.
First Aid Inhalation	Remove from contaminated area. Give oxygen. CPR if indicated. Move to fresh air.

5. Fire Fighting Measures

Some of these materials may react violently with water.
SMALL FIRES: Dry chemical, CO2, Halon, water spray or alcohol foam.

http://www.omnia.co.za/pebble.asp?relid=1575 2013/02/26



LARGE FIRES: Water spray, fog or standard foam is recommended.
Move container from fire area if you can do it without risk.
Cool containers that are exposed to flames with water from the side until well after the fire is out.
Stay away from ends of tanks.
Keep unnecessary people away; isolate hazard area and deny entry.
Stay upwind; keep out of low areas.
Positive-pressure self-contained breathing apparatus (SCBA) and chemical protective clothing that is specifically recommended by the shipper or manufacturer may be worn. It will provide little or no thermal protection.
Structural firefighter's protective clothing is NOT effective with these materials.

6. Accidental Release Measures

Personal protection: As a minimum use chemical-resistant gloves, eye/face and breathing protection.
Environmental precautions: Downwind evacuation may be necessary.
Methods for cleaning up: Contain spillages by damming or construction of barriers. Neutralize with alkali (e.g. soda ash). If possible absorb with earth or non-organic absorbent material then shovel or pump into dry well-labelled containers for disposal or recovery. Wash spillage area with large amounts of water.

7. Handling And Storage

Handling
Avoid contact with skin and eyes. Do not breathe fumes. Provide adequate ventilation.
Storage
Store in stainless steel or glass, in well-ventilated area, away from sunlight and moisture.
Keep away from strong bases and organic compounds.

8. Exposure Controls/Personal Protection

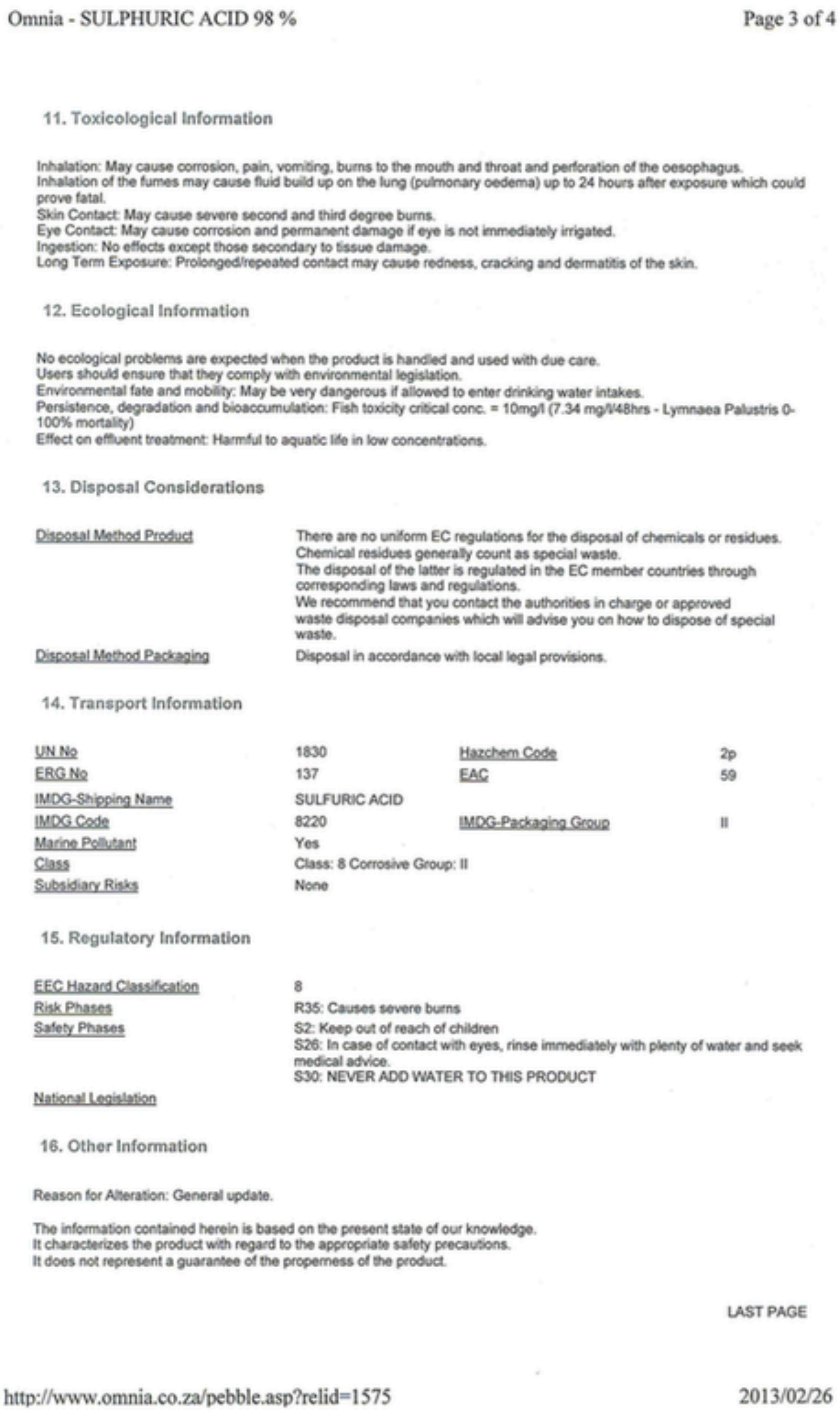
Occupational Exposure Limits	T W A OEL-RL SHORT TERM OEL-RL -------------------- -------------------- PPMa) MG/M3b) PPMa) MG/M3b) --------- --------- --------- --------- - 1 - 3
Controls	The control measures appropriate for a particular worksite depend on how this material is used and on the extent of exposure. The best protection is to enclose operations and/or provide local exhaust ventilation at the site of chemical release. Use a non-sparking, grounded ventilation system separate from other exhaust ventilation systems. Exhaust directly to the outside. Supply sufficient replacement air to make up for air removed. Have a safety shower/eye wash fountain readily available in the immediate work area
Personal Protection	If engineering controls and work practices are not effective in controlling this material, then wear suitable personal protection equipment, including chemical safety goggles & face shield, boots, imperious gloves, coveralls, & respiratory protection. Have appropriate equipment available for use in emergencies.

9. Physical & Chemical Properties

Colourless to cloudy, oily liquid. Fuming has a sharp, irritating odour.
Boiling Point: 100% H_2SO_4: 270 oC.
98% H_2SO_4: 330 oC.
Freezing Point: 100%: 10 oC.
98%: 3 oC.
Relative Density: 98% H_2SO_4: 1,84 (water:1)
Completely soluble in water.
Concentrated acid reacts with water and releases considerable heat.

10. Stability And Reactivity

Conditions to Avoid	Risk of violent reaction.
Incompatible Materials	Reacts with alkalis generating heat.Diluted acid reacts with most metals and generates highly flammable hydrogen.
Other	Strong acid generates sulphur dioxide.



11. Toxicological Information

Inhalation: May cause corrosion, pain, vomiting, burns to the mouth and throat and perforation of the oesophagus.
Inhalation of the fumes may cause fluid build up on the lung (pulmonary oedema) up to 24 hours after exposure which could prove fatal.
Skin Contact: May cause severe second and third degree burns.
Eye Contact: May cause corrosion and permanent damage if eye is not immediately irrigated.
Ingestion: No effects except those secondary to tissue damage.
Long Term Exposure: Prolonged/repeated contact may cause redness, cracking and dermatitis of the skin.

12. Ecological Information

No ecological problems are expected when the product is handled and used with due care.
Users should ensure that they comply with environmental legislation.
Environmental fate and mobility: May be very dangerous if allowed to enter drinking water intakes.
Persistence, degradation and bioaccumulation: Fish toxicity critical conc. = 10mg/l (7.34 mg/l/48hrs - Lymnaea Palustris 0-100% mortality)
Effect on effluent treatment: Harmful to aquatic life in low concentrations.

13. Disposal Considerations

Disposal Method Product	There are no uniform EC regulations for the disposal of chemicals or residues. Chemical residues generally count as special waste. The disposal of the latter is regulated in the EC member countries through corresponding laws and regulations. We recommend that you contact the authorities in charge or approved waste disposal companies which will advise you on how to dispose of special waste.
Disposal Method Packaging	Disposal in accordance with local legal provisions.

14. Transport Information

UN No	1830	Hazchem Code	2p
ERG No	137	EAC	59
IMDG-Shipping Name	SULFURIC ACID		
IMDG Code	8220	IMDG-Packaging Group	II
Marine Pollutant	Yes		
Class	Class: 8 Corrosive Group: II		
Subsidiary Risks	None		

15. Regulatory Information

EEC Hazard Classification	8
Risk Phases	R35: Causes severe burns
Safety Phases	S2: Keep out of reach of children S26: In case of contact with eyes, rinse immediately with plenty of water and seek medical advice. S30: NEVER ADD WATER TO THIS PRODUCT
National Legislation	

16. Other Information

Reason for Alteration: General update.

The information contained herein is based on the present state of our knowledge.
It characterizes the product with regard to the appropriate safety precautions.
It does not represent a guarantee of the properness of the product.

LAST PAGE

Appendix D

Appendix D1: Readings taken for pH 10.01 standard buffer solution over interval of time using pH meter used for test work

Date	29.08.14	01.09.14	02.09.14	03.09.14	04.09.14	05.09.14	08.09.14	09.09.14	10.09.14
Reading1	10.16	10.26	10.16	10.26	10.18	10.26	10.16	10.26	10.19
Range		0.10	0.10	0.10	0.08	0.08	0.10	0.10	0.07
Intensity	10.16	10.26	10.16	10.26	10.18	10.26	10.16	10.26	10.19

Table D 1: Readings taken using pH meter with pH 10.01 standard buffer solution

Date	11.09.14	12.09.14	15.09.14	16.09.14	17.09.14	18.09.14	19.09.14	22.09.14
Reading1	10.12	10.18	10.21	10.15	10.21	10.18	10.18	10.25
Range	0.07	0.06	0.03	0.06	0.06	0.03	0.00	0.07
Intensity	10.12	10.18	10.21	10.15	10.21	10.18	10.18	10.25

Table D 2: Readings taken using pH meter with pH 10.01 standard buffer solution

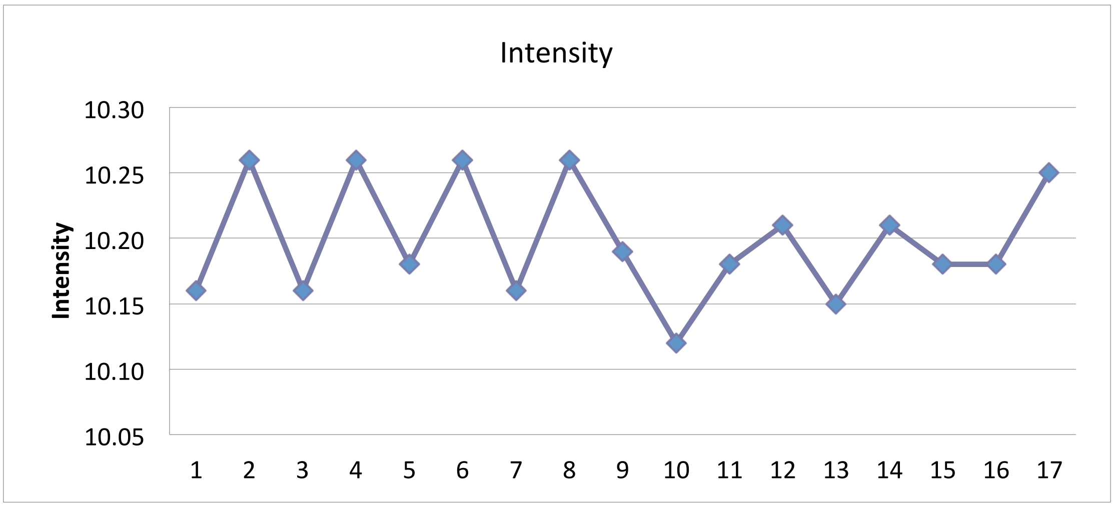


Figure D 1: Chart of readings taken daily from pH meter using pH 10.01 standard buffer solution

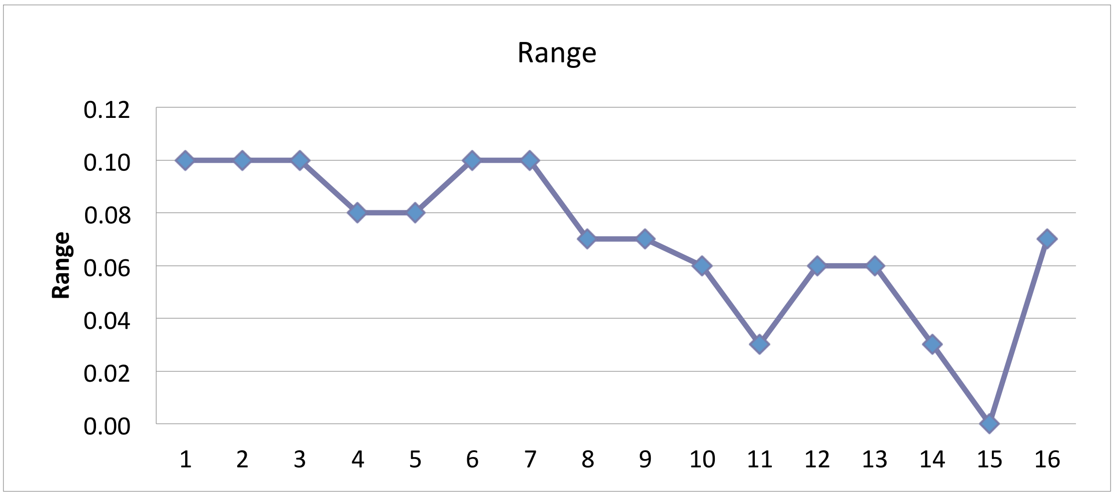


Figure D 2: Chart of calculated range values from readings taken

Where Range = pH Value read on the day - pH value read the previous day

Appendix E

Appendix E1: Mass balance calculations

Test	Vol. of acid-litres (20%)	Sulphuric acid used - kg	Vol. of leach liquor - litres
1	1.215	0.268	1.250
5	1.122	0.248	1.500
3	1.22	0.269	1.500
4	0.9	0.199	0.145
8	0.8165	0.180	0.800
15	0.5	0.110	0.610
9	0.905	0.200	0.800
12	0.137(63%)	0.126	0.670
13	0.459(63%)	0.422	2.000
6	0.83	0.183	0.800
10	0.758	0.167	0.700
7	0.94	0.208	0.800
14	0.45(63%)	0.414	2.000
2	1.7	0.375	1.65
16	0.83	0.183	1
17C	0.116	0.026	0.1
18A	not measured	not measured	1
18B	not measured	not measured	not measured

Table E 1: Mass balance inputs

Test	Analysed lead in feed - grams	Moles of plumbate in feed	Analysed tin in feed - grams	Moles of stannate in feed
1	5.520	0.02664	1.80125	0.01518
5	4.664	0.02251	2.1255	0.01791
3	3.008	0.01451	3.108	0.02619
4	2.907	0.01403	3.0044	0.02531
8	0.140	0.00068	2.1704	0.01829
15	0.7155	0.00345	not measured	not measured
9	2.487	0.01200	1.1336	0.00955
12	2.083	0.01005	0.94939	0.00800
13	0.351	0.00169	5.426	0.04572
6	1.324	0.00639	1.3872	0.01169
10	2.176	0.01050	0.9919	0.00836
7	1.324	0.00639	1.3872	0.01169
14	0.351	0.00169	5.426	0.04572
2	7.286	0.03517	2.37765	0.02003
16	0.806	0.00389	not available	not available
17C	0.13605	0.00066	0.233025	0.00196
18A	0.806	0.00389	not available	not available
18B	not available	not available	not available	not available

Table E 2: Lead and tin contained in feed solution

Test	Filter cake produced - grams	Sodium sulphate produced - grams	Sodium sulphate expected from neutralisation - grams
1	not available	not available	106.0587972
5	**35.300**	not available	97.79680139
3	34.500	not available	106.5983103
4	**35.300**	not available	77.89262048
8	30.900	169.500	72.00430874
15	17.000	not available	not available
9	374.000	107.500	79.76591852
12	10.000	129.800	49.95626738
13	537.300	not available	168.4175506
6	**20.900**	not available	73.29075111
10	12.100	40.580	66.74492339
7	49.500	not available	83.1956392
14	208.100	264.000	165.0408842
2	23.000	not available	148.6598872
16	not available	not available	not available
17C	not available	not available	10.23557161
18A	20.1	not available	not available
18B	25	not available	not available

Table E 3: Masses of lead sulphate cakes and sodium sulphate produced during precipitation tests

Bold font indicates that filter cake mass recorded was subsequent to multiple washes.

Test	Mass of sulphuric acid required by plumbate - grams	Mass of sulphuric acid required by stannate - grams
1	5.22588417	2.976941613
5	4.415020077	3.512832421
3	2.847254826	5.136618755
4	2.752346332	4.96539813
8	0.132767753	3.587039043
15	0.677405236	not available
9	2.354677375	1.873510624
12	1.972042301	1.569065148
13	0.331919382	8.967597607
6	1.253454826	2.29263756
10	2.060342703	1.639321796
7	1.253454826	2.29263756
14	0.331919382	8.967597607
2	6.898167104	3.929562929
16	0.763054826	not available
17C	0.128801004	0.385122453
18A	0.763054826	not available
18B	not available	not available

Table E 4: Sulphuric acid required for precipitation of lead and tin based on mass balance figures (excl. neutralisation reaction)

Test	Sulphuric acid required for neutralisation -grams
1	260.0691742
5	239.8097475
3	261.3921264
4	191.0022555
8	176.5633932
15	not available
9	195.595812
12	122.4988926
13	412.980483
6	179.7179076
10	163.6667355
7	204.0059076
14	404.700483
2	364.53227
16	not available
17C	25.09887654
18A	not available
18B	not available

Table E 5: Sulphuric acid to neutralise sodium hydroxide in feed solution worked out by difference – total sulphuric acid added to the feed solution less the calculated required acid for the contained lead and tin

Test	Mass of sodium sulphate from neutralisation - grams
1	106.0587972
5	97.79680139
3	106.5983103
4	77.89262048
8	72.00430874
15	not available
9	79.76591852
12	49.95626738
13	168.4175506
6	73.29075111
10	66.74492339
7	83.1956392
14	165.0408842
2	148.6598872
16	not available
17C	10.23557161
18A	not available
18B	not available

Test	Mass of lead sulphate expected from plumbate-grams	Mass of tin sulphate expected from stannate-grams
1	8.078861004	3.259065107
5	6.825320343	3.845742059
3	4.401662042	5.623413935
4	4.254939973	5.435966804
8	0.205249903	3.926981212
15	1.047222358	not available
9	3.640170849	2.051062432
12	3.048643086	1.717764786
13	0.513124759	9.817453029
6	1.937755792	2.509909849
10	3.185149493	1.794679628
7	1.937755792	2.509909849
14	0.513124759	9.817453029
2	10.66409653	4.301965941
16	1.179630792	not available
17C	0.19911758	0.421620345
18A	1.179630792	not available
18B	not available	not available

Table E 6: Lead and tin sulphate expected based on contained lead and tin in solution