

# Ultrasound assisted crystallisation of synthetic gypsum from used battery acid

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**ABSTRACT:** The production and recycling of lead acid batteries, has a very important role in the lead industry. The entire lead consumption from battery production is about 60-70 % depending on a country, although recently the profitability is reducing due to environmental costs mostly in relation to waste generation and energy consumption. Very large amounts of toxic leachable soda slugs are produced for landfill from recycling spent batteries. Therefore developing a zero waste generating process to produce a new concept in the battery reprocessing industry is vital and which is the aim of this project.

In this project a scientific and rational model for the production of gypsum that was validated on a pilot plant scale. Therefore it was necessary to investigate how the variation in chemical composition will affect the synthetically produced gypsum quality, i.e. analyzing the gypsum produced for some trace metals, such as Pb, Fe, Cu, As, Sb, Zn, Ni, Cd and Na. Most of these metals can cause a serious hazard to humans through inhalation, skin contact, eye contact or ingestion [Rai and Amit ,Jan 2002].

Na is not toxic however it can cause efflorescence and Fe causes discolouration of the plasterboard. Synthetic gypsum can be produced by a simple chemical reaction between sulphuric acid ( $H_2SO_4$ ) and lime ( $Ca(OH)_2$ ) or limestone ( $CaCO_3$ ). The non-ferrous metallurgical industry produces large volumes of acidic effluents, or wastewaters, which are treated using lime neutralization in order to remove the acidity and heavy metals. The success of this research lead to investigating the possibility of making synthetic gypsum during the neutralization of acidic waste waters with lime or limestone. Gypsum samples were produced at different operational conditions (pH, temperature, mixer speed, residence time, etc.). The samples were analysed for trace metal content using flame atomic absorption spectroscopy and inductively coupled plasma spectrometry. Ultrasound assisted crystallisation during the synthesis of gypsum was performed to observe the possibility of obtaining a cleaner gypsum product. A 40 kHz ultrasonic bath and a 20 kHz ultrasonic probe were used in this investigation. All the experiments performed in this investigation were lasted for 4 hours and were carried out at room temperature. Different ultrasonic powers and different methods of sonication methods were carried out at pH 2 and pH 4 in order to obtain the cleanest gypsum product. Various sonication methods were also carried out using the 20 kHz ultrasonic probe at 25%, 50% and 75% sonication powers.

## 1 INTRODUCTION

Ultrasound is defined as the sound range to which a human ear cannot respond. The sound range for human hearing is from about 16Hz to 20kHz. This limit applies for humans and sound beyond this upper range limit is impossible to hear. Ultrasonic frequency has an upper limit of about 5MHz for gases and 500MHz for liquids and solids. Frequency (Hz) is the number of waves that pass a fixed point in unit time, whereas power is related to the intensity of the sound source ( $Wcm^{-2}$ ). This large frequency range leads to dividing the ultrasonic usage into two areas. The first area is concerned with the effect of a medium on the wave. It involves low amplitude and high frequency propagation. This type of ultrasound is known as low power or high frequency

ultrasound. It is also known as diagnostic ultrasound (1-10MHz). This type is very commonly used in medicine (scanning), physiotherapy and chemical analysis.

The second area is called power ultrasound and involves high energy, low frequency ultrasound. Power ultrasound ranges from 20 kHz-100 kHz. This type of ultrasound is used in cleaning, plastic welding and chemical reactivity.

The power and the production of the chemical effects of ultrasound are provided by a phenomenon known as cavitation. Cavitation is the production of microbubbles in a liquid which are formed when a large negative pressure is applied to the liquid [Mason, and Peters, 2002]. It is only at powers

above the cavitation threshold that sonochemistry can occur. That is because at only these powers, the great energies associated with cavitational collapse will be released into the liquid.

## 1.1 Ultrasonic equipment

### 1.1.1 Ultrasonic bath

Sonication with an ultrasonic cleaning bath is one of the easiest and cheapest methods of sonication. A typical ultrasonic cleaning bath consists of a stainless steel tank with a transducer at the base (see figure 1.1.1). Sonicating a chemical reaction is performed by immersing a glass beaker or vessel containing the reactants in an ultrasonic bath filled with a liquid medium and switching on the power.

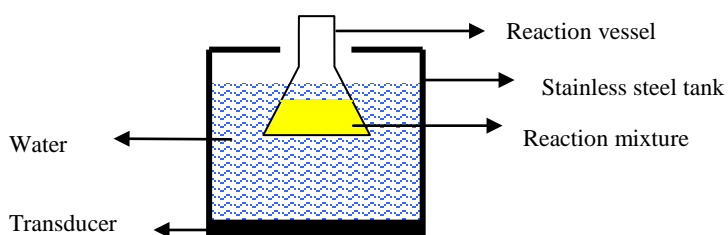


Figure 1.1.1. A systematic diagram of an ultrasonic cleaning bath

### 1.1.2 Ultrasonic Probe

In order to increase the power of sonication, a probe system was designed. A typical probe system consists of a horn with a detachable tip, a transducer and a generator (see figure 1.1.2). The length of the probe is an important point to take into consideration.

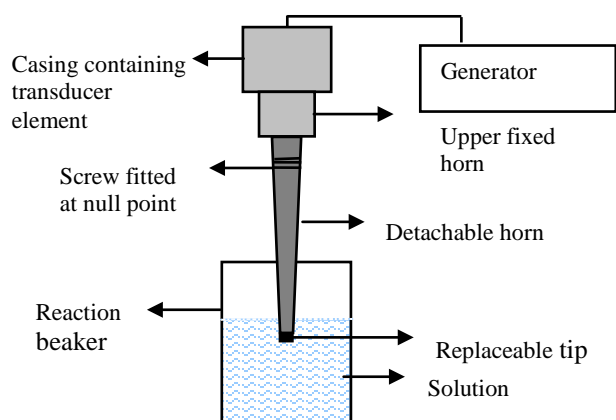


Figure 1.1.2 A systematic drawing of an ultrasonic probe system

## 2 GENERAL EXPERIMENTAL PROCEDURE

Before commencing the experiment, the pH meter was calibrated with pH 4 and pH 7 buffer solutions. Tables 2a, 2b and 2c illustrate the experiments performed in this research.

Table 2a. Experiments performed in the absence of ultrasound.

Experiment number	pH	Lime	Acid	Period/minutes
1	2	analytical	analytical	240
2	2	commercial	commercial	240
3	4	commercial	commercial	240

Table 2b. Experiments performed using a 20 kHz ultrasonic bath.

Experiment number	pH	Power	Sonication	Period/minutes
4	2	100%	continuous	120
5	2	100%	continuous	20
6	4	100%	continuous	15

Table 2c. Experiments performed using a 40 kHz ultrasonic probe.

Experiment number	pH	Power	Sonication method	period/minutes
7	2	25%	pulsed	240
8	2	50%	pulsed	240
9	2	75%	pulsed	240
10	2	25%	continuous	240
11	2	25%	pulsed on lime addition	5
12	2	50%	pulsed on lime addition	5
13	2	75%	pulsed on lime addition	5
14	2	50%	continuous to lime prior addition	5
15	4	25%	pulsed	240
16	4	50%	pulsed	240
17	4	75%	pulsed	240
18	4	25%	continuous	240
19	4	25%	pulsed on lime addition	5
20	4	50%	pulsed on lime addition	5
21	4	75%	pulsed on lime addition	5
22	4	50%	continuous to lime prior addition	5

### 2.1 Using the 40 kHz ultrasonic bath

A 5-litre reaction beaker was placed in the ultrasonic bath through a hole in the aluminium cover. The aluminium cover was designed in order to act as a template so that the 5-litre reaction beaker could be located in exactly the same position each time an experiment was performed.

The beaker was filled with 2-litres of sulphuric acid (analytical grade or battery acid). The agitator was

fitted on a metal stand and positioned centrally above the reaction beaker. The mixer blade was immersed in the acid (the distance between the blade and the bottom of the beaker was 1.5-2cm) and the agitator was turned on at a variable speed (see each experiment). About 5cm of the thermometer probe was immersed in the acid to obtain an initial temperature reading. The pH probe was also immersed in the acid to obtain the initial pH reading.

## 2.2 *Using the 20 kHz ultrasonic probe*

When the probe was used, the author decided to use a smaller reaction beaker (3L). The 3L reaction beaker was filled with 1.5L of the battery acid and placed in a fume cupboard. The ultrasonic probe was securely fitted on a metal stand and positioned over on the top of the reaction beaker (nearer the left edge of the beaker). 25mm of the tip of the probe was immersed into the acid. The pH and the temperature probes were also immersed in the acid in order to obtain a pH and temperature readings respectively. The sonication time, method, power and pH were varied.

The remainder of the experimental procedure is the same for both sonication methods.

While the pH probe was stabilising, a  $500\text{gL}^{-1}$  of analytical grade  $\text{CaCO}_3$  solution was prepared by the addition of 1kg of  $\text{CaCO}_3$  to 2L of distilled water into a 5L glass beaker ( $\text{CaCO}_3$  stock solution). A magnetic follower was used and the beaker was placed on a magnetic stirrer. The magnetic stirrer was turned on to provide a homogenous mix of calcium carbonate milk.

The time required to stabilise the pH reading varied from 30-60 minutes. When the reading was stabilised, the initial pH and temperature readings were recorded.

The stopwatch was started when the first 50 ml of the  $\text{CaCO}_3$  milk was pipetted from the  $\text{CaCO}_3$  stock solution into the (3 or 5) litre reaction beaker.  $\text{CaCO}_3$  milk was added to the reaction beaker in different amounts but at regular intervals in order to reach and maintain the pH at approximately 2. All the experiments lasted for 4 hours. In some experiments, samples were taken from the reaction beaker during the experiment at different pH levels in order to investigate the impurity level change at different pH points (vary for each experiment). Each reaction ended when the time reached 4 hours and the agitator plus ultrasonic source was turned off. The final pH and temperature reading were recorded and a final gypsum product was obtained.

Up to six (75ml) samples were taken from the final gypsum product and placed into 100ml glass beakers in order to investigate the effect of extra sonication at different powers and times on the final product. The ultrasound was applied using a 20 kHz ultrasonic probe. The temperature of the solution was measured before and after sonication. The samples were “blasted” with continuous ultrasound as follows; a “blast” of 25% continuous ultrasound for 1 minute was applied to the first sample, and a “blast” of 25% continuous ultrasound for five minutes was applied to the second sample. The third sample was “blasted” with 50% ultrasound for 1 minute, and the fourth sample was “blasted” with 50% ultrasound for five minutes. The fifth sample was “blasted” with 75% ultrasound for 1 minute, and the sixth sample was “blasted” with 75% ultrasound for five minutes. The number of samples taken for this investigation varied for each experiment.

The final gypsum pulp was filtered, washed with two separate portions of 100ml of distilled water. The other samples taken (from the impurity level change & extra sonication investigations) were also filtered and washed with two separate portions of 20ml distilled water. The final gypsum product and all the samples were dried in a fan-assisted oven at  $40^\circ\text{C}$  for 24 hours.

## 2.3 *Experiments performed in the absence of ultrasound*

### 2.3.1 *Analytical grade reagents at pH 2*

The experimental technique for this experiment follows the general experimental details. 2L analytical grade sulphuric acid and  $500\text{gL}^{-1}$  analytical grade limestone were used in this experiment. The 40 kHz ultrasonic bath was used but not switched on. The experiment was run at pH 2, and the agitator was set at 900rpm. No samples were obtained for the impurity change investigation. At the end of the experiment, the gypsum product was washed, filtered, and dried according to the general experimental details section

### 2.3.2 *Battery acid and commercial grade $\text{CaCO}_3$ at pH 2*

The experimental technique for this experiment follows the general experimental details.

The 40 kHz ultrasonic bath was used (power switched off), 2L battery acid and  $500\text{gL}^{-1}$  commercial grade limestone were used. The

experiment was run at pH 2 and the agitator was set at 900 rpm. As in the previous experiment, no further samples were collected for extra investigation. Only one gypsum product was obtained and analysed. At the end of the experiment, the gypsum product was washed, filtered and dried according to the general experimental details section.

### 2.3.3 Battery acid and commercial grade $\text{CaCO}_3$ at pH 4

The experimental technique for this experiment follows the general experimental details.

1.5L of battery acid and  $500\text{gL}^{-1}$  commercial grade limestone were used. The experiment was run at pH 2 and the agitator was set at 756.8 rpm. In this experiment, a 3L glass reaction beaker was used and the reaction was carried out without any sonication. In this case the reaction beaker was placed directly on the base of the fume cupboard. No further samples were taken for extra investigation. Only one gypsum product was obtained and analysed

At the end of this experiment, six (75ml) samples were taken from the final gypsum product for the “extra sonication” investigation (see general experimental procedure). The final gypsum product and all the samples obtained in this experiment were filtered, washed and dried according to the general experimental details section.

### 2.4 Experiments performed using a 40 kHz ultrasonic bath

- Battery acid and commercial limestone at pH 2 for 4 hours
- Battery acid and commercial limestone at pH 4 with 15 minutes sonication
- Battery acid and commercial limestone at pH 2 with 20 minutes sonication

The experimental technique for this experiment follows the general experimental details. The experiment was run at pH 4 and the sonication lasted for 20 minutes.

Two 20ml samples were taken from the reaction beaker during the experiment at the following pH levels; pH 0.98 (at 10minutes), pH 1.60 (at 118 minutes). At the end of the experiment, the final gypsum product and all the samples obtained in this experiment were filtered, washed and dried according to the general experimental details section.

### 2.5 Experiments using a 20 kHz ultrasonic probe

In all the following experiments,  $1.5\text{L}^{-1}$  of battery acid and  $500\text{gL}^{-1}$  of commercial grade limestone were used.

- Pulsed 75% ultrasound at pH 2

The experimental technique for this experiment follows the general experimental details. This experiment was identical to experiment 4, except that in this experiment 75% pulsed sonication was applied. At the end of the experiment, six (75ml) samples were taken from the final gypsum pulp and “extra sonication” was applied to them at the following ultrasonic powers 25%, 50%, 75% (see general experimental details).

- Pulsed 75% ultrasound at pH 4

The experimental technique for this experiment follows the general experimental details. Four 50ml samples were taken from the reaction beaker during the experiment at the following pH levels; pH 0.91 (at 15 minute), pH 1.29 (at 45 minutes), pH 2.61 (at 90 minutes), and pH 3.60 (at 160 minutes). As the previous experiment, six samples were taken from the final product and “extra sonication” was applied at the following ultrasonic powers; 25%, 50%, 75%.

- Continuous 25% ultrasound at pH 2

The experimental technique for this experiment follows the general experimental details (see the ultrasonic probe section). In this experiment, 25% ultrasound was applied, i.e. the reaction was sonicated continuously for four hours. The experiment was run at pH 2. When the reaction was terminated after 240 minutes, six samples from the final gypsum pulp were taken and sonicated at different powers (25%, 50%, and 75%).

- Continuous 25% ultrasound at pH 4

The experimental technique for this experiment follows the general experimental details (see the ultrasonic probe section). Four 50ml samples were taken from the reaction beaker during the experiment at the following pH levels; pH 0.93 (at 20 minutes), pH 1.39 (at 45 minutes), pH 2.46 (at 75 minutes), and pH 3.37 (at 150 minutes). At the end of the experiment, six samples from the final

gypsum pulp were taken and sonicated at different powers (25%, 50%, and 75%).

- Pulsed 25% ultrasound at pH 2
- Pulsed 25% ultrasound at pH 4
- Pulsed 50% ultrasound at pH 2
- Pulsed 50% ultrasound at pH 4
- Pulsed 25% ultrasound for 5 minutes on CaCO<sub>3</sub> addition at pH 2
- Pulsed 25% ultrasound for 5 minutes on CaCO<sub>3</sub> addition at pH 4
- Pulsed 50% ultrasound for 5 minutes on CaCO<sub>3</sub> addition at pH 2
- Pulsed 50% ultrasound for 5 minutes on CaCO<sub>3</sub> addition at pH 4
- Pulsed 75% ultrasound for 5 minutes on CaCO<sub>3</sub> addition at pH 2
- Pulsed 75% ultrasound for 5 minutes on CaCO<sub>3</sub> addition at pH 4
- Sonicating limestone milk at 50% for five minutes prior to addition at pH 2
- Sonicating limestone milk at 50% for five minutes prior to addition at pH 4

### 3 RESULTS AND DISCUSSION:

#### 3.1 Experiments in the absence of ultrasound

##### 3.1.1 Analytical grade reagents at pH 2

Table 3.1.1: Trace metal analysis in ppm (without US)

Element	mg/kg
Pb	23.5
Cd	<1
Cu	<1
Sb	<1
Na	87.1
Fe	<3
Zn	4.8

Note: "US" is an abbreviation for ultrasound.

#### Discussion:

Since this experiment was carried out using analytical grade sulphuric acid and limestone and performed at pH 2, low impurity levels were expected. However the Pb level seem to be higher than expected which could have risen from cross contamination. As the reagents used in this experiment were all analytical grade and the acids used in the digestion procedure were also analytical

grade, therefore the contamination could have either originated from the reaction beaker or the filtration funnel.

#### 3.1.2 Battery acid and commercial grade CaCO<sub>3</sub> at pH 2

Table 3.1.2. Trace metal analysis in ppm (without US)

Element	mg/kg
Pb	70.1
Cd	14.9
Cu	50.1
Sb	13.6
Na	837.2
Fe	334.6
Zn	86.5

Note: "US" is an abbreviation for ultrasound.

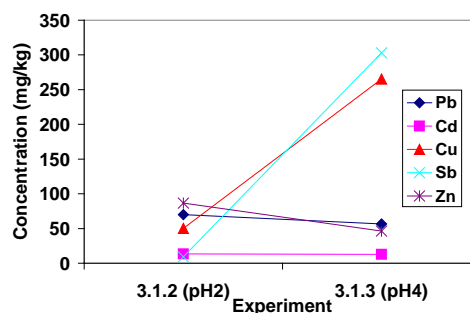
#### Discussion:

This experiment shows a significant increase in impurity levels in comparison with the previous experiment. This is due to the fact that this experiment was carried out using contaminated battery acid and commercial limestone.

#### 3.1.3 Battery acid and commercial grade CaCO<sub>3</sub> at pH 4

Graph 3.1.3:

A comparison between impurity levels in experiment 3.1.2 and Experiment 3.1.3 both carried out without US



#### Discussion:

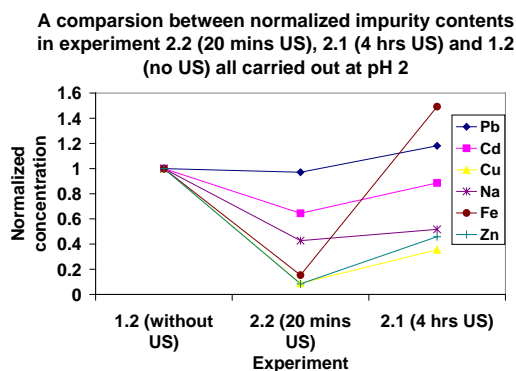
The solubility of most metal ions and salts generally decreases as the pH of the solution increases [Qingyum, Louis, McDonald, Jeffrey and Skousen]. In other words they become less soluble at higher pH levels. Since experiment 3.1.3 was performed at pH 4, higher impurity levels were expected in the product. Graph 3.1.3 show that the lead levels in experiment 3.1.3, which was performed at pH 4, are lower than the lead levels in experiment 3.1.2 which

was performed at pH 2. Since that the most dominant form of Pb is likely to be  $\text{PbSO}_4$ , the solubility of  $\text{PbSO}_4$  increases as the concentration of the sulphuric acid decreases [Blaskett and Boxall, 1990]. In other words as the pH of the solution rises, the solubility of  $\text{PbSO}_4$  increases leaving less to be co-precipitated in the gypsum product.

### 3.2 Experiments using a 40kHz ultrasonic bath

#### 3.2.1 Battery acid and commercial limestone at pH 2 with 20 minutes sonication

Graph 3.2.1:



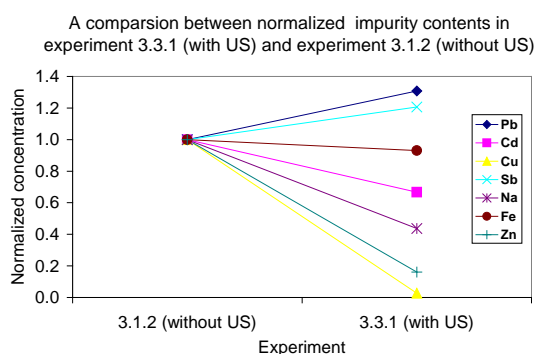
Discussion:

This experiment was carried out using a 40 kHz ultrasonic bath. The sonication commenced when the first 50ml of  $\text{CaCO}_3$  was added to the reaction and stopped after 20 minutes. The remainder time of the reaction was carried out without sonication and the experiment lasted for four hours. The final pH of the reaction was approximately pH 2. When the final product of this experiment was compared with the final product from experiment 3.1.2 (no US), it was found that there was a decrease in impurity levels when ultrasound was applied for 20 minutes (see table and graph 3.2.1). The product from this experiment provided the cleanest gypsum produced in this investigation.

### 3.3 Experiments using a 20 kHz ultrasonic probe

#### 3.3.1 Pulsed 75% ultrasound at pH 2

Graph 3.3.1:



Discussion:

In this experiment, a 20 kHz probe was used for the sonication. The reaction was sonicated with 75% pulsed power throughout the duration of the experiment (4 hours). The final pH of the experiment was approximately pH 2. When the final product of this reaction was compared with the product from experiment 3.1.2, which was carried out without any sonication, it was found that there was a significant reduction in impurity levels with the exception of Pb, Sb and Fe. As previously discussed, sonication can cause particle size to decrease by fragmenting the crystals [Perez-Rodriguez, Carrera, Poyato, Perez-Maguedu, 2002] [Franco, Perez-Mqueda, Perez-Rodriguez, 2004]. The fragmentation and the breakage of the crystals could cause the impurities to go into solution rather than precipitating on the surface of the crystals. Since the sonication was pulsed, the crystals could be continuously breaking which would allow minimum coprecipitation of impurities on the surface or even as part of the crystal matrix.

On the other hand, Pb and Sb levels increased when ultrasound was used in the reaction.

As previously mentioned the free radicals formed in the course of sonication could have caused the oxidation of  $\text{Pb}^{+2}$  to  $\text{Pb}^{+4}$ , consequently forming  $\text{Pb}_3\text{O}_4$  which is insoluble in water.

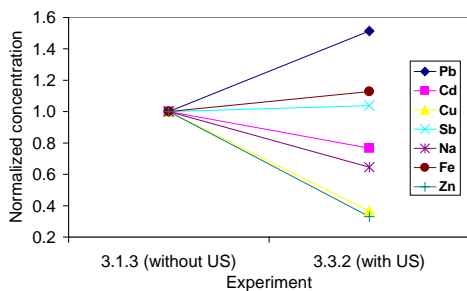
$\text{Sb}_2(\text{SO}_4)_3$  is insoluble in water but soluble in acid [West, Robert 1972-1973]. Therefore as the experiment continues and the acid concentration decreases, the level of Sb increases due to the precipitation of  $\text{Sb}_2(\text{SO}_4)_3$ .

As mentioned earlier, ultrasound causes the crystals to break, which leads to larger surface area [Chatakundu, Green, Thompson, Suslick, 1987] [Perez-Rodriguez, Carrera, Poyato, Perez-Maguedu, 2002]. Therefore as the surface area is increasing it is possible that  $\text{Sb}_2(\text{SO}_4)_3$  is precipitating on the surface of the crystals. All the other metal sulphates included in the analysis are soluble in water [West, Robert. 1972-1973]. Another factor worth mentioning is that the temperature of the solution also increases when ultrasound is used [Suslick, Kenneth, 1989] [Mason and Lorrimer, 1988] consequently leading to better dissolution. As for Fe, it can be oxidised to  $\text{Fe}_2\text{O}_3$ , which is insoluble in water [West, Robert. 1972-1973].

### 3.3.2 Pulsed 75% ultrasound at pH 4

Graph 3.3.2:

A comparison between normalized impurity contents in experiment 3.3.2 (with US) and experiment 3.1.3 (without US) both carried out at pH 4



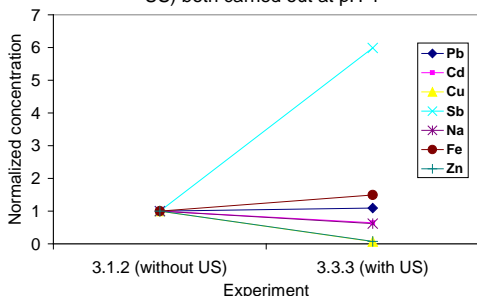
#### Discussion:

In this experiment, a 20 kHz probe was used for the sonication. The reaction was sonicated with a 75% pulsed power throughout the duration of the experiment (4 hours). The final pH of the experiment was approximately pH 4. When the final product of this reaction was compared with the product of experiment 3.1.3, which was carried out without any sonication, it was found that there was a significant reduction in impurity levels with the exception of Pb, Sb and Fe which mirrored results found at pH 2. The discussion given in experiment 3.3.1 is also valid for this experiment as the metal ions in both experiments are behaving in the same manner.

### 3.3.3 Continuous 25% ultrasound at pH 2

Graph 3.3.3:

A comparison between normalized impurity contents in experiment 3.3.3 (with US) and experiment 3.1.2 (without US) both carried out at pH 4



#### Discussion:

In this experiment a 20 kHz ultrasonic probe was used for the sonication. Continuous 25% sonication was applied to the reaction for the entire duration of the experiment (4 hours). The pH of the solution was approximately pH 2. When the product of this experiment was compared to the product of

experiment 3.1.2, which was carried out without any sonication, it was found that there was a significant decrease in impurity levels with the exception of Pb, Sb and Fe. Since the sonication was continuous, there was continuous “damage” being applied to the surface of the crystals, which caused any clusters to de-agglomerate and fragment releasing impurities trapped within or on the surface of the crystals.

As previously mentioned the free radicals formed in the course of sonication could have caused the oxidation of  $Pb^{+2}$  to  $Pb^{+4}$ , consequently forming  $Pb_3O_4$ , which is insoluble in water.

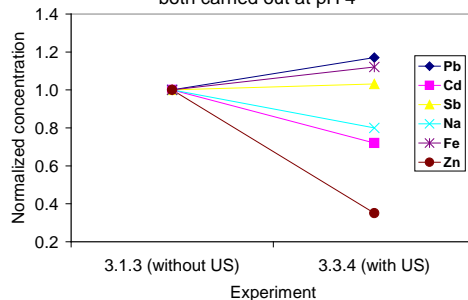
$Sb_2(SO_4)_3$  is insoluble in water but soluble in acid, therefore as the experiment continues and the acid strength decreases, the level of Sb increases due to the precipitation of  $Sb_2(SO_4)_3$ .

In addition the temperature increase of the solution due to sonication also helps dissolution in general. As for Fe, it could have oxidised to  $Fe_2O_3$ , which is insoluble in water.

### 3.3.4 Continuous 25% ultrasound at pH 4

Graph 3.3.4:

A comparison between normalized impurity contents in experiment 3.3.4 (with US) and experiment 3.1.3 (no US) both carried out at pH 4



#### Discussion:

In this experiment a 20 kHz ultrasonic probe was used for the sonication. Continuous 25% sonication was applied to the reaction for the entire duration of the experiment (4 hours). The pH of the solution was approximately pH 4. When the product of this experiment was compared to the product of experiment 3.1.3, which was carried out without any sonication, it was found that there was a significant decrease in impurity levels with the exception of Pb, Sb and Fe mirroring the findings at pH 2. Since the sonication was continuous, there was continuous damage being applied to the surface of the crystals, which caused any clusters to disintegrate and fragment releasing impurities trapped within or on the surface of the crystal.

The impurities in this experiment are behaving in the same manner as the previous experiment.

#### 4 CONCLUSION:

Refer to tables 2a, 2b and 2c for the following experiment numbers. Some of the results of the experiments discussed are not included in the paper due to the length of the paper, however they can be found in reference [Abdul-Jabber, 2005].

All the gypsum samples produced in this investigation are not suitable for manufacturing plasterboard since that the levels of the trace metals analysed remain elevated in all the gypsum samples and exceed the maximum limits provided by Lafarge plasterboard. The only suitable gypsum product obtained from this investigation was the gypsum produced in experiment 1 (pH 2), which used analytical grade reagents.

This investigation showed that sonication could either increase or decrease impurities in the gypsum product. This depends on the source of sonication, the method of sonication, power, frequency, length of sonication. However this effect varies from one metal ion to another. For example the levels of Pb is always increased when ultrasound was introduced, this is due to the solubility of  $\text{PbSO}_4$  in sulphuric acid as discussed before.

Experiments 2 and 3 which were carried out without any sonication and used commercial grade limestone (provided by Lafarge plasterboard) and battery acid (provided by BRM), carried out at pH 2 and pH 4 respectively. The gypsum produced in both of these experiments were not suitable for plasterboard manufacturing since most of the elements analysed exceeded the maximum limits with the exception of Sb and Fe in experiment 2 (pH 2) and Pb in experiment 3 (pH 4).

The gypsum produced in experiment 2 (pH 2) has Pb content that is higher than experiment 3 (pH 4). Since the most dominant form of Pb in gypsum is likely to be  $\text{PbSO}_4$ , the solubility of  $\text{PbSO}_4$  increases as the concentration of the sulphuric acid decreases [Blaskett and Boxall, 1990]. In other words as the pH of the solution rises, the solubility of  $\text{PbSO}_4$  increases leaving less to be coprecipitated in the gypsum product.

When (pH 2, 4 hours US, using the bath) experiments were compared with experiment 2 (no US, pH 2), it was observed that ultrasound had a positive effect on the gypsum produced, since the levels of Cd, Cu, Na, Fe and Zn were decreased after the sonication with the exception of Pb and Sb. However the gypsum obtained from the sonicated

experiment had impurity levels which exceeded the maximum levels for FGD.

(pH 4, 15 minutes US, using the bath) experiment had lower Pb, Cd, Na, Fe and Zn levels when compared with experiment 3 (pH 4, no US) with the exception of Cu and Sb. However the final product obtained from the sonicated experiment did not meet the requirements for plasterboard manufacturing with the exception of Zn (13.9ppm) since the maximum limit is 50ppm.

When (20 minutes US) experiment, (4 hours US) experiment and experiment 2 (no US) were compared, it was observed that the lowest impurity levels reported were for 20 minutes sonication at the beginning of the experiment. Some of these levels such as Cu, Sb, Fe and Zn were within specification whereas Pb, Cd and Na were higher than the specified levels.

Using the probe, the following experiments were compared; (pulsed 25% US) experiment and experiment 2 (no US), both experiments were carried out at pH 2. It was observed that ultrasound has increased the impurity content in the gypsum produced. This is due to that the power used in this experiment was only  $3.4705 \times 10^{-3}$  kW. Perhaps the power was not sufficient to break the crystals but instead "pitted" the crystals, consequently the impurities could have penetrated into the crystal and become part of the crystal structure which has led to higher levels of impurities in the product. Therefore this sonication method is not recommended and the metal ions analysed in the final product exceed the maximum limits specified for plasterboard.

When experiment 15 was compared to experiment 3 which was carried out without any sonication, it was found that there was a significant increase in impurities when ultrasound was used perhaps due to the low power used as mentioned earlier.

When experiment 8 (pulsed 50% US) and experiment 2 (no US) were compared, it was observed that there was a significant increase in impurities when ultrasound was introduced with the exception of Cd and Zn.

Experiment 16 was identical to experiment 8, except that it was carried out at pH 4.

When experiment 16 was compared to experiment 3 which was carried out without any sonication, it was found that there was an increase in the levels of Pb, Sb, Na and Fe with a slight reduction in the levels of Cd and a significant reduction in the levels of Cu and Zn.

When experiment 9 (pulsed 75% US) with experiment 2 (no US), it was found that there was a



general significant decrease in impurity levels with the exception of Pb and a slight increase in the levels of Sb when sonication was introduced. This is due to the solubility of Pb and Sb as previously mentioned in this chapter. However the final product is not suitable for plasterboard manufacturing since only Sb, Fe and Zn levels are within specification.

Experiment 17 was identical to experiment 9, except that it was carried out at pH 4.

When experiment 17 was compared to experiment 3 which was carried out without any sonication, it was found that there was a general significant decrease in impurity levels with the exception of Pb, Sb and Fe. The final product is not suitable for plasterboard.

When experiments 11 (Pulsed 25% US for 5 minutes on lime addition) and experiment 2 (no US) were compared, it was observed that there was a slight decrease in the levels of some metal ions such as Cd, Cu, Zn with a significant reduction in the levels of Na. whereas there was an increase in the levels of some metal ions such as Pb, Sb and Fe.

The final product is not suitable for plasterboard manufacturing.

Experiment 19 was identical to experiment 11, except that it was carried out at pH 4.

When experiment 19 was compared to experiment 3 which was carried out without any sonication, it was found that there was a slight decrease in the levels of Cd and a significant decrease in the levels of Cu, Na and Zn when sonication was used. The levels of Pb, Sb and Fe were increased significantly after the sonication.

When experiment 12 (pulsed 50% US for 5 minutes on lime addition) was compared to experiment 2 (no US), it was found that there was an overall increase in impurity levels with the exception of Na when ultrasound was used. The final product is not suitable for plasterboard manufacturing.

Experiment 20 was identical to experiment 12, except that it was carried out at pH 4.

When experiment 20 was compared to experiment 3 which was carried out without any sonication, it was found that there was an overall increase in impurity levels with the exception of Na. the final product is not suitable for plasterboard manufacturing.

When experiment 13 (pulsed 75% US for 5 minutes on lime addition) and experiment 2 (no US), were compared, it was found that there was a significant reduction in the levels of Cd, Cu, Na and Zn when ultrasound was used, whereas there was an increase in the levels of Pb, Sb and Fe after the sonication. The levels of Cu, Sb, Fe and Zn are within specification and the levels of Pb, Cd and Na

are outside the specified limits for manufacturing plasterboard.

Experiment 21 was identical to experiment 13, except that it was carried out at pH 4.

When experiment 21 was compared to experiment 3 which was carried out without any sonication, it was found that there was a significant decrease in the levels of Cd, Cu, Na and Zn and an increase in the levels of Pb, Sb and Fe when ultrasound was used. However the final sonicated products not suitable for making plasterboard because all the metal ions analysed exceed the maximum limits with the exception of Zn.

When experiment 14 (sonicating CaCO<sub>3</sub> for 5 minutes before addition) and experiment 2 (no US) was compared, it was found that there was a significant reduction in the levels of Cu, Sb, Na, Zn and a small reduction in the levels of Cd when ultrasound was introduced. the levels of Pb and Fe were increased after the sonication. Despite the low levels of Cu, Sb, Fe and Zn obtained after the sonication, the final product remains unsuitable for manufacturing plasterboard due to the high levels of Pb, Cd and Na.

Experiment 22 was identical to experiment 14, except that it was carried out at pH 4.

When experiment 22 was compared to experiment 3 which was carried out without any sonication, it was found that there was a small decrease in the levels of Cu, Sb, Na and Fe, however this reduction in the impurity levels is not very significant if experimental errors were taken into consideration. The levels of Pb and Zn were significantly increased and Cd was slightly increased after the sonication and the final product is not suitable for plasterboard manufacturing.

When experiment 10 (continuous 25% US) was compared with experiment 2 (no US), it was found that there was a significant decrease in the levels of Cd, Cu, Na and Zn whereas the levels of Pb and Fe were slightly increased and the levels of Sb was increased significantly after the sonication. Despite the low levels of Cu, Fe and Zn, the final product remains unsuitable for making plasterboard due to the elevated levels of Pb, Cd, Sb and Na.

Experiment 18 was identical to experiment 10, except that it was carried out at pH 4.

When experiment 18 was compared to experiment 3 which was carried out without any sonication, it was found that there was a decrease in the levels of Cd, Cu, Na and Zn after the sonication, whereas the levels of Pb, Sb and Fe were slightly increased when ultrasound was used. The final

product is not suitable for manufacturing plasterboard.

The author recognises experiment 5 (20 minutes US/bath) as the best sonication method that gives the lowest impurity content. Experiments 9 (pulsed 75% US), 13 (75% US on lime addition) and experiment 10 (continuous 25% US) as the next best experiments that gives low impurity content results at pH 2. However non of the products produced in these experiments are suitable for manufacturing plasterboard as they have elevated levels of unwanted metal ions even when sonication was proved to be effective.

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