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Investigation of the Conditions for Leaching of Gilding Metal from 5.56mm Projectiles

(Investigation Report)

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1. ABSTRACT

Analysis of the metals leached from the sheath (gilding metal) of 5.56mm projectile was carried out by Atomic Absorption Spectroscopic (AAS) and Mass Measurement methods. Mass measurement method was found to be the more reliable method of analysing the metals, namely copper and zinc, in the leaching solutions. pH plays a crucial role in maintaining solubility of the metal complexes in the leaching solution. The optimum conditions for the leaching of the gilding metal from 5.56mm projectiles were determined to be; composition of the leaching solution of 4M : 1M ($[NH_3]$: $(NH_4)_2CO_3]$); contact time of 10 hours; temperature of 40^0C. Increase in contact time and temperature produced marginal effects in the efficiency of leaching. Addition of oxygen to the leaching reaction also had marginal effect on the leaching efficiency. However, the effect is more pronounced if 2M : 1.5M ($[NH_3]$: $[(NH_4)_2CO_3]$) was to be used as the leaching solution at temperature of 40^0C.

2. Introduction

The 5.56 mm projectiles were supplied by Pentarch Pty Ltd from recovered obsolete small arms ammunition, composed of lead inner core and the sheath. The sheath is made up to approximately 32% of the projectile and the sheath in turns is comprised of gilding metal (90% of it is Cu and 10% of it is Zn) and thin layer of acetate materials coating the outside of the sheath. The main interest in this work is in the recovery of the gilding metal, namely the copper and zinc.

There are two most commonly used leaching solutions and in particular for the leaching of copper, by industries. They are sulphuric acid and ammoniacal carbonate solutions. It has been found that when sulphuric acid was used as the leaching solution at moderate pH, both Zn and Cu were simultaneously leached. However, the use of ammoniacal carbonate as a leaching solution offers many advantages including the ability to separate Zn from Cu *[1]*. Studies carried out by other investigators *[2, 3, 4]* also described the copper recovery by similar hydrometallurgical leaching process.

In the work carried out by Andersson and Reinhardt *[4]*, ammoniacal carbonate solution was used, known as the Am-MAR (Ammoniacal-Metals and Acids Recovery) processes *[4]*. These processes revealed that there were many factors that contributed to the efficiency of leaching of copper when an ammoniacal carbonate solution was used as the leaching agent. These factors include variation of the concentration of the ammonia and the ammonium carbonate, pH of the leaching solution, temperature and the addition of air into the reaction mixture. It was found that an increase of the NH_3 concentration increases the total 'leaching potential' of the system in respect to dissolved metals, in particular for copper, through a greater tendency towards the formation of metal amine complexes. It has been found that leaching times longer than 10 hours, or increased leaching temperatures have marginal effects on the "leaching potential" of the system.

Another work carried out by Andersson and Reinhardt *[4]* made use of sulphuric acid as the leaching reagent in a process known as H-MAR (Sulfuric acid – Metals and Acids Recovery). In this work both copper and zinc were leached from Swedish Steel and Brass Mill flue dusts and recovered by extraction and electrowinning processes. Both copper and zinc were successfully leached in a pH-controlled leaching at temperature of 60^0C. In the case of copper, the final pH was controlled at 2 to 2.5 while maintaining oxidising conditions with addition of MnO_2 to promote copper dissolution and prevention of copper cementation of metallic copper and for zinc, only mildly oxidising conditions was necessary.

Similar investigation was carried out by Bingöl et al. *[5].* They found that the main important parameters in ammoniacal leaching of malachite ore were determined as leaching time, ammonia/ammonium concentration ratio, pH, solid/liquid ratio, leaching temperature, and particle size. Optimum leaching conditions from malachite ore by ammonia/ammonium carbonate solution are found as ammonia/ammonium carbonate concentrations: 5 M NH_4OH + 0.3 M $(NH_4)_2CO_3$; solid/liquid ratio: 1:10 g/mL; leaching times: 120 min; stirring speed: 300 rpm; leaching temperature: 25 °C; particle size finer than 450 µm with more than 98% of copper was effectively recovered. During the leaching, copper dissolves as in the form of $Cu(NH_3)_4^{+2}$ complex ion. This is supported by the same complex formation of the Cu in the Am-MAR processes *[4]* mentioned above. The reaction proposed for Cu when the ammoniacal carbonate leaching solution is used, can be seen in equation (1). Similar reaction can be proposed in the case for Zn, as shown in equation (2)

$$Cu^0 + 2NH_3 + (NH_4)_2CO_3 + \tfrac{1}{2}O_2 \rightarrow Cu(NH_3)_4CO_3 + H_2O \qquad \text{..............................(1)}$$

$$Zn^0 + 2NH_3 + (NH_4)_2CO_3 + \tfrac{1}{2}O_2 \rightarrow Zn(NH_3)_4CO_3 + H_2O \qquad \text{..............................(2)}$$

According to these equations, the amount of the Cu or Zn complex formed is dependent on the amount of the ammonia and the ammonium carbonate present in the reaction mixture. The role of oxygen is also shown in these equations.

The main objective of this project is to fully recover the Cu and Zn from projectiles by firstly, investigating and determining the optimum conditions in which the Cu or Zn can be leached from the projectiles into an aqueous solution, prior to the recovery of these metals using hydrometallurgical processes of solvent extraction and electrowinning. Investigation carried out in this project involved ascertaining the optimum conditions in the leaching of Cu and Zn from the 5.56mm projectiles. The variables studied include leaching time, temperature, ratio of the concentrations of ammonia and ammonium carbonate, addition of oxygen and pH.

After Cu and Zn have been optimally leached, solvent extraction can be applied to the aqueous solution in order to recover both metals. Literature survey reveals that, solvent extraction has been applied extensively for the recovery of Cu(II) and Zn(II) using cost effective commercial extractants, including alkyl phosphorus reagents, viz., D2EHPA, PC 88A, CYANEX 272 and their equivalents and many of the hydroxyl oxime reagents, viz., LIX 84 I, LIX 84 N, LIX 87QN, LIX 54, LIX973, LIX 984 and LIX 34. The different extraction abilities of these LIX reagents are caused mainly by the various acidities of the phenolic group in these reagents. Of LIX reagents, LIX 84 *[6]* was used commercially for extraction and also for selective removal of copper ions from aqueous solutions. The solvents or the diluents that are commonly used are the commercially available solvents such as low aromatic kerosene *[7]* and distilled kerosene *[8]*.

Extraction work using LIX 84 I has shown that Cu(II), and Zn(II) can be selectively separated by adjusting the equilibrium pH of the aqueous phase *[8]*. It was found that the extraction of Cu(II) started at pH values around 0.5 and reaches quantitative extraction (≈100%) at equilibrium pH 4.0. Under these conditions, the extraction of Zn(II) was nil. The extraction of Zn(II) started at around pH 7.50 and reaches 99.5% at an equilibrium pH of 9.0 The $pH_{1/2}$ values calculated from 50% extraction of Cu(II) and Zn(II) are 0.9 and 8.0 respectively, demonstrating the possible quantitative separation of Cu(II) and Zn(II) *[8]* by adjustment of the pH of the aqueous solution. These results indicate the feasibility of separating the Cu(II) from Zn(II) in the ammoniacal carbonate leaching solution obtained from leaching of these metals from the projectiles using the LIX reagents.

The extraction of Cu(II) and Zn(II) from ammoniacal solution can be represented by the equation (3) shown below:

$$[M(NH_3)_4^{2+}]_{aq} + [2RH]_{org} \qquad [R_2M]_{org} + [2NH_3]_{aq} + [2NH_4^+]_{aq} \qquad \text{......................(3)}$$

where M = Cu(II) or Zn(II) and RH = LIX reagent.

The number of ammonia molecules coordinated to the metal (represented by $[M(NH_3)_4^{2+}]$) will vary depending on the conditions; four being a favoured number. In this process, the tendency of the metal extraction is to decrease with increasing ammonia concentration. This can be explained in terms of the lone pair of electrons on the nitrogen atom in ammonia, competing with the extractant for the metal ion. This reaction is reversible and stripping with ammonia might be practical in some situations which will produce copper-rich and zinc-rich strip aqueous phase *[9]*. Further purification of the metals can be carried our using electrowinning process of the aqueous solution containing these metals. Solvent extraction and electrowinning processes will be the subject for future works.

3. EXPERIMENTAL

3.1 Materials

Ammonia (NH_3, molecular weight: 17.034 g/mol) of Analytical Reagent grade obtained from Merck was used as received. The solution concentration used was 25:75 (v/v%) NH_3: H_2O.

Ammonium Carbonate ($(NH_4)_2CO_3$, Molecular Weight: 96.09 g/mol) of 99% purity was obtained from Sigma and used as received. Traces of ammonium carbamate were indicated to be present.

5.56mm projectiles were supplied by Pentarch Pty. Ltd. These 5.56 mm projectiles were from recovered obsolete small arms ammunition.

3.2 Sample Preparation

Four 5.56mm projectiles were randomly selected from a 2kg jar of 5.56mm projectiles supplied and were placed into a disposal 50mL test tube. 15mL of acetone was added to the test tube then shaken vigorously for 60 seconds. The acetone was than decanted and this process was repeated until all the grease was visibly removed from the projectiles. The projectiles were then washed with 15mL of deionised water for 30 seconds, and this process was repeated twice before they were left to dry on a paper towel.

3.3 Weight Distribution

Each 5.56mm projectiles were weighed using analytical balance and the weight distribution is presented in ***Figure 7.1*** (see Appendix, Section 7.1). The weight ranged between 4.031 g to 4.087 g. A total of sixty-eight 5.56mm projectiles were weighed and the average weight was determined to be 4.059 ± 0.002g.

3.4 Experimental Set-up and Conditions

Each leaching solution was made up with various concentrations of both ammonia and ammonium carbonate. The following concentration ratios of the leaching solutions were used in this experiment: $[NH_3]$: $[(NH_4)_2CO_3]$, 4M:1M, 4M:2.5, 3M:2M, 2M:1.5M, 2M:2M, 1M:1M, and 1M:2.5M. In each experiment, 200mL volume of each of these leaching solutions was used.

In the experiments where oxygen was used, the oxygen was introduced into the reaction vessel using Instrumental air gas (similar to atmospheric air; 72% Nitrogen, 27% Oxygen and traces of other gases). A rubber tube was connected to this air cylinder and the air was supplied to the reaction vessel via a disposal glass pipette attached to the end of the rubber tube which was immersed into the leaching solution.

Air was introduced into the reaction mixture for the duration of the experiment and in most cases for a period of 10 hours. The volume of air was determined by measuring the volume of water displaced by air in a measuring cylinder. This measuring cylinder was firstly filled with water, inverted into a beaker containing water and passing air through it. The amount of water displaced was measured over a period of 30 seconds. This was repeated 5 times. The average rate of the volume of air delivered was measured to be 694 ± 2mL per second. Making use of the above assumption that air contains 27% oxygen, the average rate of volume of the oxygen delivered was calculated to be 187 ± 2mL per second.

Figure 3.1 shows the experimental set-up for the leaching of the copper and zinc from the projectiles. The solution mixture and the projectiles were placed in an 'indented' round bottom flask. "Indented' round bottom flask was used in order to minimise the 'whirlpool' effects of stirring. Stirring was carried out for 10 hours using an overhead stirring unit, IKA RW20 digital, and at stirring rate of 1000-1015rpm. The flask containing the reaction mixture was placed in an oil bath of a constant fixed temperature. Two temperatures were used and they were 40^0C and 60^0C. Temperature of the experiment was monitored by placing a thermometer in the oil bath.

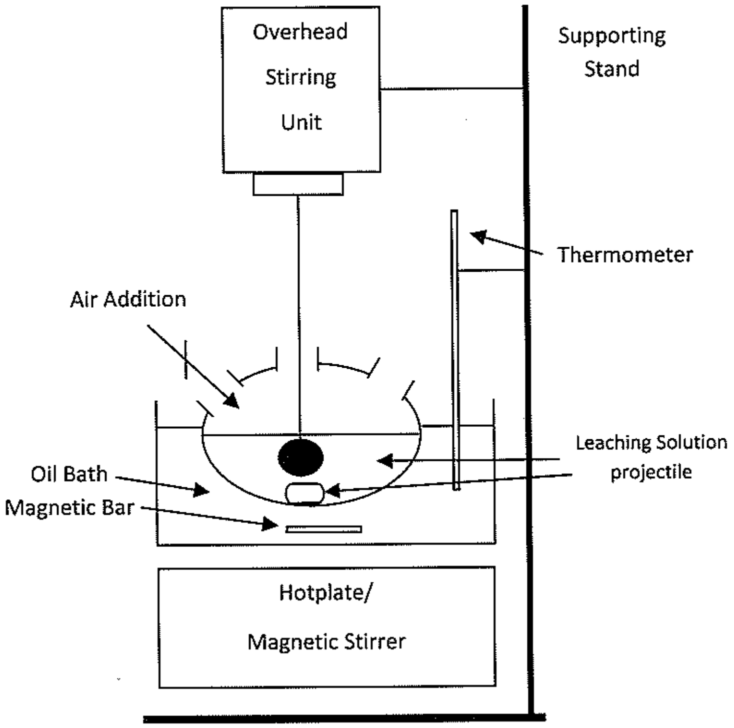

***Figure 3.1**: Experimental Set-up for the leaching of gilding metals from 5.56mmprojectiles*

3.5 Atomic Absorption Spectrometry Analysis

Atomic Absorption Spectroscopy (AAS) analysis was performed using a Shimadzu Model AA-6300. The conditions used for the copper and zinc analyses were;

Conditions	Cu	Zn
Lamp Current (mA)	3.5	5.0
Fuel	acetylene	acetylene
Support Gas	air	air
Wavelength (nm)	324.7	213.9
Slit Width (nm)	0.5	1.0
Concentration range (ppm)	0.6 to 8.0	0.4 to 1.6

Standard calibration plots for Cu and Zn are shown in Appendix (Section 7.2) in ***Figures 7.2 and 7.3*** respectively.

3.6 Sample Analysis

3.6.1 Sample Analysis using Atomic Absorption Spectroscopy (AAS)

At every 20 minutes for the first 2 hours of the experiment, 5mL of the solution was taken out and analysed using atomic absorption spectrophotometer (Shimadzu Model AA-6300) and this was replaced by a fresh 5mL of the leaching solution. Subsequent samplings were carried out at each hour for the 10 hour duration. No further sample preparation was required when the leaching solutions were analysed for their copper and zinc concentrations. However, appropriate dilution had to be made for each solution in order for the absorbance readings to fall within the calibration plot.

3.6.2 Sample Analysis by Weight Measurement.

The weight of the projectiles was measured before and after the leaching process using an analytical balance. The difference in weight before and after, measures the mass of the gilding metals leached by each leaching solution at various conditions.

3.7 pH

Measurement of pH was carried at the start and at specified time intervals of the leaching experiments by using InoLab pH meter, model 720. .

4. Results and Discussions

4.1 Contact time

One of the critical factors in the leaching process of the gilding metal is contact time. Contact time is the time allowable for the projectiles to be in contact with the leaching solution which represents the time it takes for the leaching process to occur. In this work, the leaching process was carried out for a period of 24 hours whilst the concentration of the metals was monitored by taking samples at specified time intervals and analysing the samples using Atomic Absorption Spectrophotometer (AAS). The leaching process for Cu was followed and is represented in ***Figure 4.2*** below.

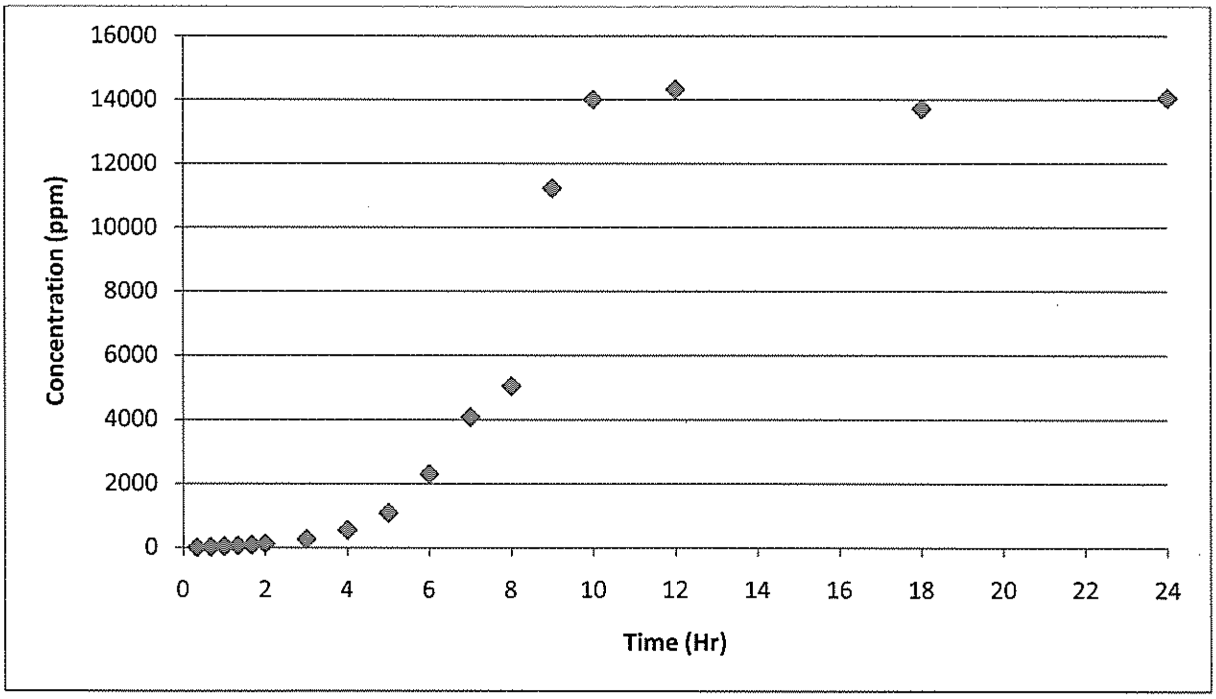

Figure 4.2*:* *Plot showing the amount of Cu leached from the projectiles over a period of 24 hours using Atomic Absorption Spectroscopy. (Conditions: 4M NH_3 to 1M $(NH_4)_2CO_3$ leaching solution; temperature of 40^0C, no oxygen)*

Figure 4.2 shows the absence of Cu in the leaching solution until approximately 4 hours of contact time with the maximum amount observed around the 10 hours period (as shown by the beginning of the plateau region on this plot). As mentioned previously, 5.56mm projectiles are believed to have been coated with acetate material which could explain the 'time-lag' observed from the start of the experiment until around 4 hours, which indicate the time required to remove the acetate material and for the leaching solution to penetrate and to leach the gilding metal. It was also observed that increase in contact time greater than 10 hours shows minimal increased in the leaching of the Cu from the projectiles, indicating that 10 hours could be used to maximally leach the Cu from the projectiles into the leaching solution.

Table 4.1: *The effect of contact time on the efficiency of the gilding metal removed from the projectile using mass measurement method.*

Experiment	***Mass of projectiles before leaching (g)***	***Mass of projectiles after leaching (g)***	***Mass of gilding metal removed (g)***	***Percentage of gilding metal in a projectile (%)***
Theoretical	***16.234***	***11.039***	***5.195***	***32.0***
4M:1M (NH_3/$(NH_4)_2CO_3$)at 40^{0}C, no oxygen for 10hr	16.243	11.169	5.065	31.2
4M:1M (NH_3/$(NH_4)_2CO_3$)at 40^{0}C, no oxygen for 24hr	16.234	10.844	5.362	33.0

Results found in ***Table 4.1*** above are the results obtained when the mass measurements method was used to determine the amount of the gilding metals that had been removed from the projectiles into the leaching solution. Results were obtained at contact times of 10 hours and 24 hours and it was found that for both contact times, almost 100% of the gilding metal was leached. This result is in agreement with the results obtained using AAS measurement above and also results obtained by Andersson and Reinhardt *[4]*, confirming that leaching times longer than 10 hours produced marginal effect in the leaching of the gilding metal. Therefore, contact time of 10 hours was considered sufficient time given for the full leaching process to occur and thus the in subsequent experiments in this study, contact time of 10 hours was used.

4.2 Atomic Absorption Spectroscopy (AAS) versus mass measurement and pH effect

Atomic Absorption Spectroscopy (AAS) is the recommended and most commonly used method of analysis of metals, however the method only allows soluble metal complexes to be detected. In this work, a significant part of the analysis was carried out using AAS to analyse for the gilding metal, more specifically for the Cu, in the leached solution. As mentioned previously, gilding metal is made up of 90% Cu and 10% Zn, thus both metals were initially analysed using AAS to ascertain their presence and also to determine the amount of the metals leached into the aqueous solution. The conditions used in leaching of the gilding metal were; 4M:1M ($NH_3/(NH_4)_2CO_3$) leaching solution, with contact time of 10 hours and temperature of 40^0C. Results can be found in ***Table 4.2***.

Table 4.2: *Amount of gilding metals present in projectiles as measured by AAS and mass measurements.*

Experiment	***Mass of projectiles before leaching (g)***	***Mass of projectiles after leaching (g)***	***Mass of gilding metal removed (g)***	***Percentage of gilding metal in projectiles (%)***
Theoretical	***16.234***	***11.039***	***5.195 (Cu+Zn) 4.676 Cu 0.520 Zn***	***32 (Cu+Zn) 28.8 Cu 3.2 Zn***
4M:1M($NH_3/(NH_4)_2CO_3$) at (40^0C) for 24hr, no oxygen (AAS measurement)	16.234	-	3.112 Cu 0.576 Zn	19.2 Cu 3.5 Zn
4M:1M($NH_3/(NH_4)_2CO_3$)at (40^0C) for 24hr, no oxygen (mass measurement)	16.234	10.844	5.362 (Cu+Zn)	33.0 (Cu+Zn)

Theoretical values found in ***Table 4.2*** made use of the assumption that a projectile comprises of the lead inner core covered with a sheath which made up to approximately

32% of the projectile and the sheath in turn is comprised of gilding metal (90% Cu and 10% Zn), which worked out to be 28.8% Cu and 3.2% Zn in a projectile.

The amounts of Cu and Zn (measured by AAS) shown in ***Table 4.2*** above were generated by measuring the amount of the metal in the leached solution at specified time intervals with the duration of the contact time of 10 hours, for example, in the case of Cu, this is shown in ***Figure 4.3*** below. Similar procedure was utilised for Zn.

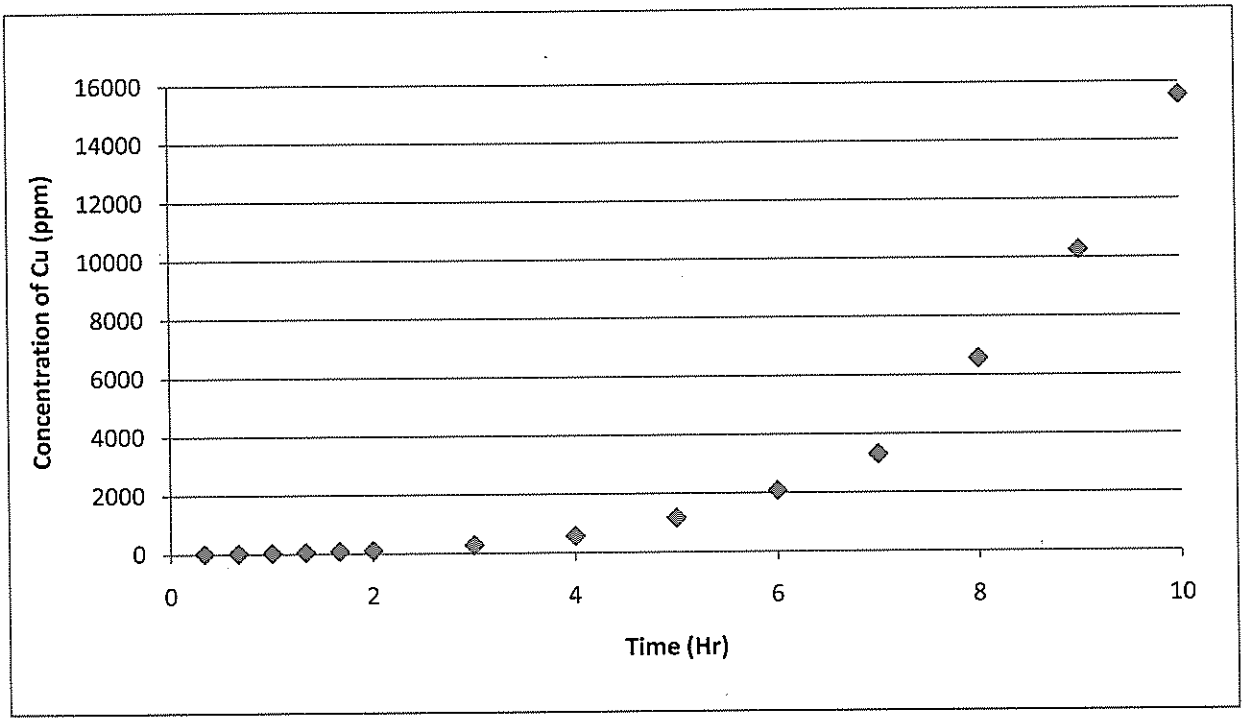

***Figure 4.3**: Plot showing the amount of Cu leached from the projectiles over a period of 10 hours using Atomic Absorption Spectroscopy. (Conditions: 4M NH_3 to 1M $(NH_4)_2CO_3$ leaching solution; temperature of 40^0C, no air)*

In ***Figure 4.3***, at 10 hours of leaching, the amount of Cu found in the leaching solution was 15560ppm which is equivalent to 3.112g of Cu and translated to 19.2% of Cu in each projectile. Similarly for Zn, the amount of Zn found in the leaching solution after 10 hours was 2882ppm which is equivalent to 0.576g of Zn and it is translated to 3.5% of Zn in each projectile. This data can be found in ***Table 4.2*** above. As can be seen from these results, the amount of Cu detected by AAS was only slightly greater than a half of the theoretical value (32%) whereas in the case of Zn, it was comparable to the theoretical value (3.2%). As indicated previously, AAS method only allows soluble metal complexes to be analysed, thus this result indicates that under the specified conditions, all Zn was in the form of soluble Zn complexes and was therefore able to be fully detected, whereas only about half of the Cu was in the form of the soluble Cu complexes in the leached solution. It was also observed during the experiments that precipitation occurred and because the amount of Cu detected by AAS was only about half of the theoretical value, it can thus be speculated that this precipitate could be due to the insoluble Cu complexes found in the leached solution. Similar results were obtained throughout the work carried out in this study for all the Cu measurement when AAS method was used. Some of these results can be seen in Appendix (Section 7.3). It can be said from these results that AAS offered unsatisfactory method of measurement and it can be concluded that quantitative measurements by AAS were unreliable. Consequently, alternative method was sought and this method was by measurement of mass which measured the mass of projectiles before and after the leaching process. The difference in the mass measures the total amount of the gilding metal, namely Cu and Zn, in a projectile. ***Table 4.2*** above compares the results obtained by AAS and mass measurement methods. It can be seen that a more reliable result was obtained when mass measurement method was used, as the result was close to that of the theoretical value. Consequently, the results obtained using the mass measurement method will only be used throughout the discussion of this work.

Further work was carried out in order to rationalise the discrepancy in the results obtained by the two methods. As discussed above, it was believed that the formation of insoluble Cu complexes during the leaching process resulted in the AAS method being unable to detect all the Cu in the leached solution. It was thought that this was due to the variation in the pH of the solution during the leaching process. An experiment was therefore conducted in order to observe any changes in pH which resulted in the formation of precipitates during the leaching process. The variation of pH in the leaching solutions before and during the leaching process can be seen in ***Figure 4.4*** and ***Figure 4.5*** respectively.

Figure 4.4 shows the pH of all the leaching solutions at the start of the leaching process for the various compositions ($[NH_3]$: $[(NH_4)_2CO_3]$) of the leaching solutions. It can be expected that the pH is higher the higher is the composition of ammonia in the leaching solutions. pH of the leaching solutions varies from 9 to about 11.5, depending on their compositions.

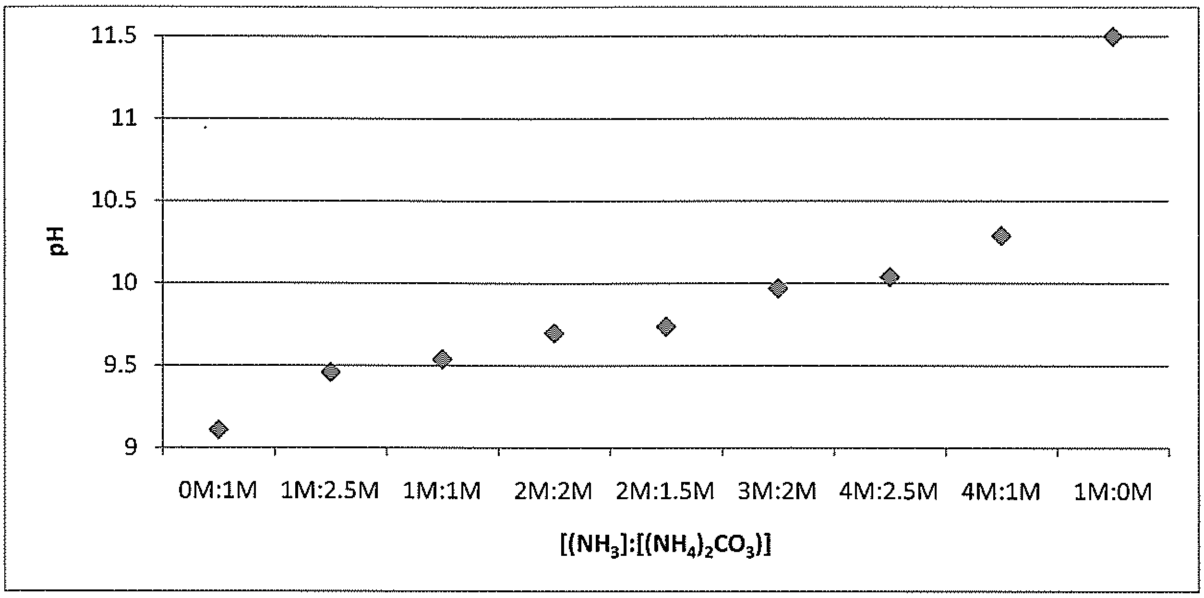

Figure 4.4: *pH of the leaching solutions of various concentration ratios of* NH_3 *to* $(NH_4)_2CO_3$ *at the start of the leaching process.*

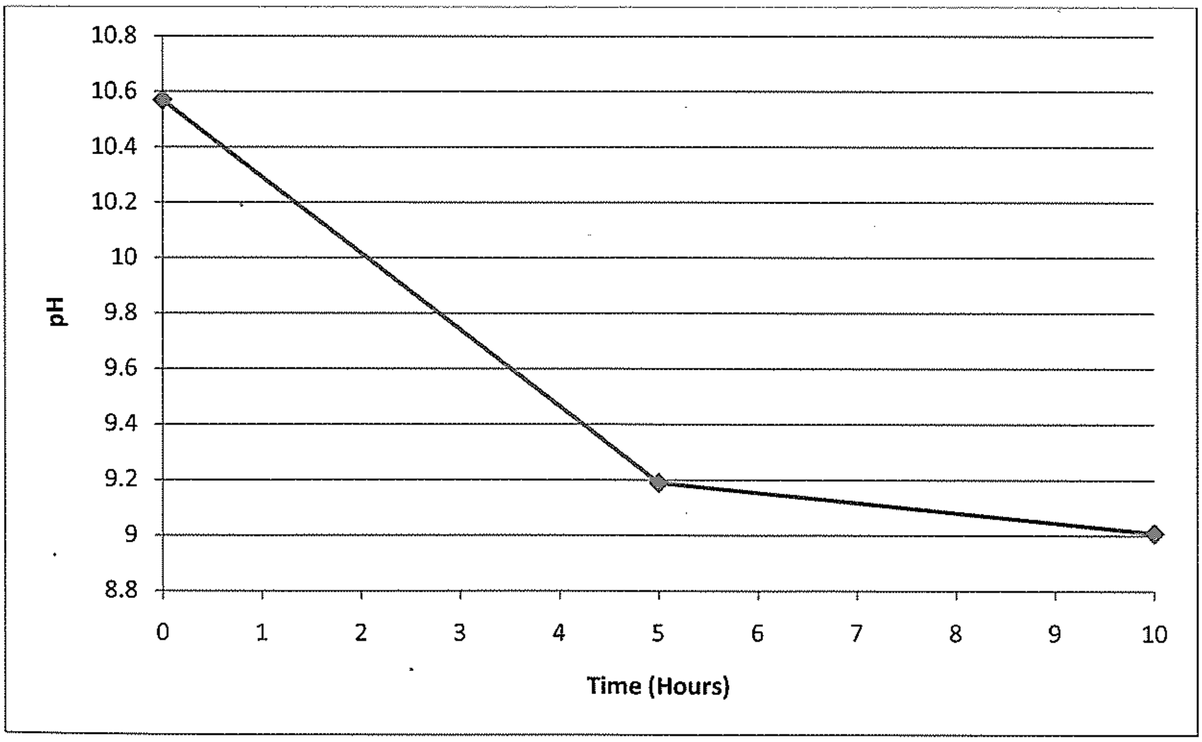

Figure 4.5: *pH measured during the leaching process up to 10 hours when 4M:1M* $(NH_3/(NH_4)_2CO_3$ *was used as the leaching solution.*

In order to see if the pH of the leaching solutions changed during the course of the leaching process, pH of the leaching solutions was monitored for a period of 10 hours. ***Figure 4.5*** above are the results obtained showing the variation of pH during the leaching process, using a leaching solution composition of 4M:1M ($NH_3/(NH_4)_2CO_3$). In here, three pH measurements were carried out; one at the beginning of the experiment; second was at 5 hours of contact time and the third was at the 10 hours of contact time. The results indicate that there is a significant decline in pH from the pH 10.6 to 9.2 from the start of the leaching process up to 5 hours of the reaction. However, there was a smaller change in pH between 5 to 10 hours of the leaching process with the pH change from 9.2 to 9.0. It was also observed that during the course of the leaching process, precipitates were formed. The greater decline of pH resulted in the greater amount of precipitate formed in the solution. Similar results were observed for all the leaching solutions used in this work. It is believed that insoluble precipitates formed at lower pH and thus it is crucial that high pH should be maintained in order to avoid the formation of these precipitates. However, in this study the pH in which precipitates started to form could not be determined, thus a further study is necessary. The identity and the nature of this precipitate are currently unknown and are also the subject for further investigation.

From the above results, it can be concluded that pH of the leaching solution plays a crucial part in maintaining the formation of soluble copper complexes and failing to maintain this pH resulted in the formation of insoluble precipitate of the copper complexes. Zinc at this pH was found to form soluble zinc complexes and was therefore able to be quantitatively determined using AAS. From these results, it can be concluded that the loss in weight during the leaching process, measured by the mass measurement method, was indicative of the true value of the amount of gilding metal removed from the projectiles. Consequently, mass measurement method was used in the subsequent discussion of the results.

4.3 Effects of varying the ratios of concentrations of NH_3 and $(NH_4)_2CO_3$ used as the leaching solution.

Table 4.3 shows the results from the 'control experiments'. The 'control experiments' were carried out by using ammonia solution in the absence of ammonium carbonate as leaching solution and vice versa. It can be seen that when NH_3 only was used, 2% of the gilding metal was leached into the solution, however, when $(NH_4)_2CO_3$ only was used, 87% was obtained. As shown in ***Table 4.1*** above, 100% gilding metal recovery was obtained when the two components of the leaching solution was used. It is therefore concluded that the two components of the leaching solution, namely NH_3 and $(NH_4)_2CO_3$, complement each other in the recovery of the gilding metal and NH_3 alone is incapable of leaching the metals, which is indicative of the synergistic effect of the two components in the leaching solution.

***Table 4.3**: "Control Experiment" representing % gilding metal removed from projectiles at 40^0C for 10 hours contact time in the presence of oxygen.*

Experiment	***Mass of projectiles before leaching (g)***	***Mass of projectiles after leaching (g)***	***Mass of gilding metal removed (g)***	***Percentage of gilding metal removed (%)***
Theoretical	***16.234***	***11.039***	***5.195***	***100***
1M NH_3 at (40^0C) for 10hr + oxygen	16.224	16.106	0.118	2
1M $(NH_4)_2CO_3$) at (40^0C) for 10hr + oxygen	16.194	11.689	4.505	87

The effect of the leaching efficiency of the various compositions of the leaching solutions on the removal of the gilding metal from the projectiles was studied and the results are shown in ***Table 4.4*** below.

Table 4.4: *% gilding metal removed from projectiles using various ratios of the concentrations of* $NH_3 : (NH_4)_2CO_3$ *at* 40^0C *for 10 hours contact time with absence of oxygen.*

Experiment	***Mass of projectiles before leaching (g)***	***Mass of projectiles after leaching (g)***	***Mass of gilding metal removed (g)***	***Percentage of gilding metal removed (%)***
Theoretical	***16.234***	***11.039***	***5.195***	***100***
1M:2.5M($NH_3/(NH_4)_2CO_3$ ***)*** ***at*** 40^0C***, no oxygen for 10hr***	16.263	15.336	0.9267	18
2M:1.5M($NH_3/(NH_4)_2CO_3$ ***)*** ***at*** 40^0C***, no oxygen for 10hr***	16.261	11.681	4.580	88
1M:1M ($NH_3/(NH_4)_2CO_3$ ***)*** ***at*** 40^0C***, no oxygen for 10hr***	16.246	14.127	2.119	41
2M:2M ($NH_3/(NH_4)_2CO_3$ ***)*** ***at*** 40^0C***, no oxygen for 10hr***	16.234	14.777	1.457	28
3M:2M ($NH_3/(NH_4)_2CO_3$ ***)*** ***at*** 40^0C***, no oxygen for 10hr***	16.229	13.643	2.586	49
4M:2.5M ($NH_3/(NH_4)_2CO_3$ ***)*** ***at*** 40^0C***, no oxygen for 10hr***	16.293	12.944	3.349	65
4M:1M ($NH_3/(NH_4)_2CO_3$ ***)*** ***at*** 40^0C***, no oxygen for 10hr***	16.243	11.169	5.074	98

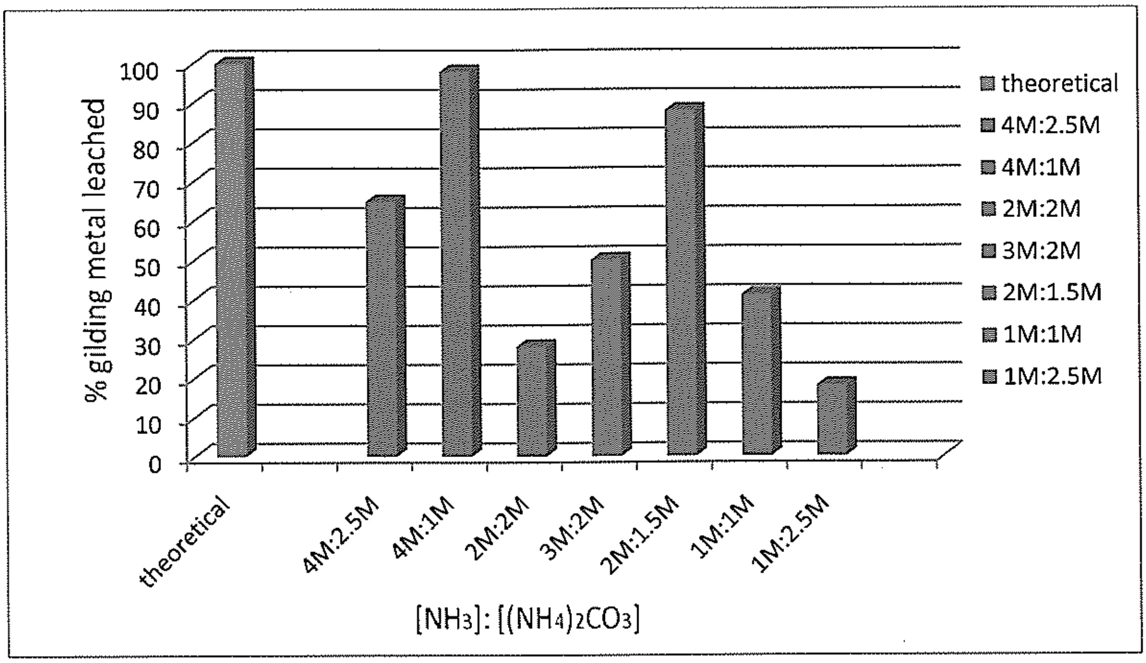

***Figure 4.6**: The percentage of gilding metal removed from projectiles using various compositions of the $NH_3/(NH_4)_2CO_3$ leaching solutions. Experimental conditions: temperature, 40^0C; contact time, 10 hours; absence of oxygen*

Data in ***Table 4.4*** is represented in ***Figure 4.6*** for comparison purposes. The leaching solutions used in which greater than 50% of the gilding metal leached were 4M NH_3 to 1M $(NH_4)_2CO_3$, showing 98% leaching, followed by 2M NH_3 to 1.5M $(NH_4)_2CO_3$ with 85% leaching and 65% leaching when 4M NH_3 to 2.5M $(NH_4)_2CO_3$ was used. The results indicate that at the specified experimental conditions and in the absence of oxygen, the optimum ratio of the concentration of NH_3 and $(NH_4)_2CO_3$ that gives the most efficient leaching of the gilding metal was 4M NH_3 to 1M $(NH_4)_2CO_3$.

4.4 Effects of temperature

In the work carried out by Andersson and Reinhardt *[4]*, two methods had been used in the leaching of copper and zinc from flue dust. These were; the H-MAR (Sulfuric acid – Metal and Acid Recovery) and the Am-MAR (Ammoniacal-Metals and Acids Recovery) processes. In the H-MAR process, copper and zinc were successfully leached in a pH-controlled leaching at 60^0C and in the Am-MAR process they found that increased leaching temperatures over 20^0C showed marginal effects on the efficiency for the leaching of copper only. Thus, it was anticipated that temperature of 40^0C should initially be carried out in this work, which would see both copper and zinc being leached when Am-MAR process was applied. It was envisaged that this temperature should optimally leached both copper and zinc of the gilding metal from the projectile. In this work, the effect of temperature was carried out at temperatures of 40^0C and 60^0C on the leaching efficiency of the gilding metal from the projectiles, with the view that ambient temperature would also be investigated.

Comparison of the results was made using the leaching solutions that were found to give the higher leaching efficiency from the results shown in ***Table 4.4*** and ***Figure 4.6***, which were conducted at temperature of 40^0C. They were 4M NH_3 to 1M $(NH_4)_2CO_3$, 2M NH_3 to 1.5M $(NH_4)_2CO_3$ and 4M NH_3 to 2.5M $(NH_4)_2CO_3$ which produced 98%, 88% and 65% gilding metal leached, respectively. The same leaching solutions were used to study the effect of temperature and this time it was run at 60^0C. It was rather unfortunate that due to time constraint, the effect of leaching efficiency at ambient temperature was unable to be investigated.

The results comparing the % removal of the gilding metal from projectiles for both temperatures can be found in ***Table 4.5 and Figure 4.7***. Results obtained for the two temperatures indicate minimal change on the leaching efficiency as the temperature was increased from 40^0C to 60^0C, when 4M : 2.5M and 4M : 1M ($[NH_3]$: $[(NH_4)_2CO_3]$) leaching solutions were used with changes of -2% and 4% respectively were observed. However, a change of about 14% was found when 2M : 1.5M ($[NH_3]$: $[(NH_4)_2CO_3]$) solution was used.

It was also observed that at temperature of 60^0C, in both solutions of 2M : 1.5M and 4M : 1M ($[NH_3]$: $[(NH_4)_2CO_3]$), 102% of the gilding metal were leached from the projectiles into the leaching solutions. The greater than the expected value found in these systems at this temperature could probably be due to the leaching of some of the lead inner core. However, due to time constraint, the presence of lead in the leaching solutions could not be confirmed.

Table 4.5*: Comparison of % gilding metal removed from projectiles using various ratios of the concentrations of NH_3 : $(NH_4)_2CO_3$ at 40^0C and 60^0C for 10 hours contact time, in absence of oxygen.*

Experiment	*Mass of projectiles before leaching (g)*	*Mass of projectiles after leaching (g)*	*Mass of gilding metal removed (g)*	*Percentage of gilding metal removed (%)*
Theoretical	***16.234***	***11.039***	***5.195***	***100***
4M:2.5M (NH_3/$(NH_4)_2CO_3$) at 40^0C, no oxygen for 10hr	16.293	12.944	3.349	65
4M:2.5M(NH_3/$(NH_4)_2CO_3$) at 60^0C, no oxygen for 10hr	16.243	12.958	3.285	63
4M:1M (NH_3/$(NH_4)_2CO_3$) at 40^0C, no oxygen for 10hr	16.243	11.169	5.074	98
4M:1M (NH_3/$(NH_4)_2CO_3$) at 60^0C, no oxygen for 10hr	16.240	10.917	5.324	102
2M:1.5M(NH_3/$(NH_4)_2CO_3$) at 40^0C, no oxygen for 10hr	16.261	11.681	4.580	88
2M:1.5M(NH_3/$(NH_4)_2CO_3$) at 60^0C, no oxygen for 10hr	16.180	10.894	5.286	102

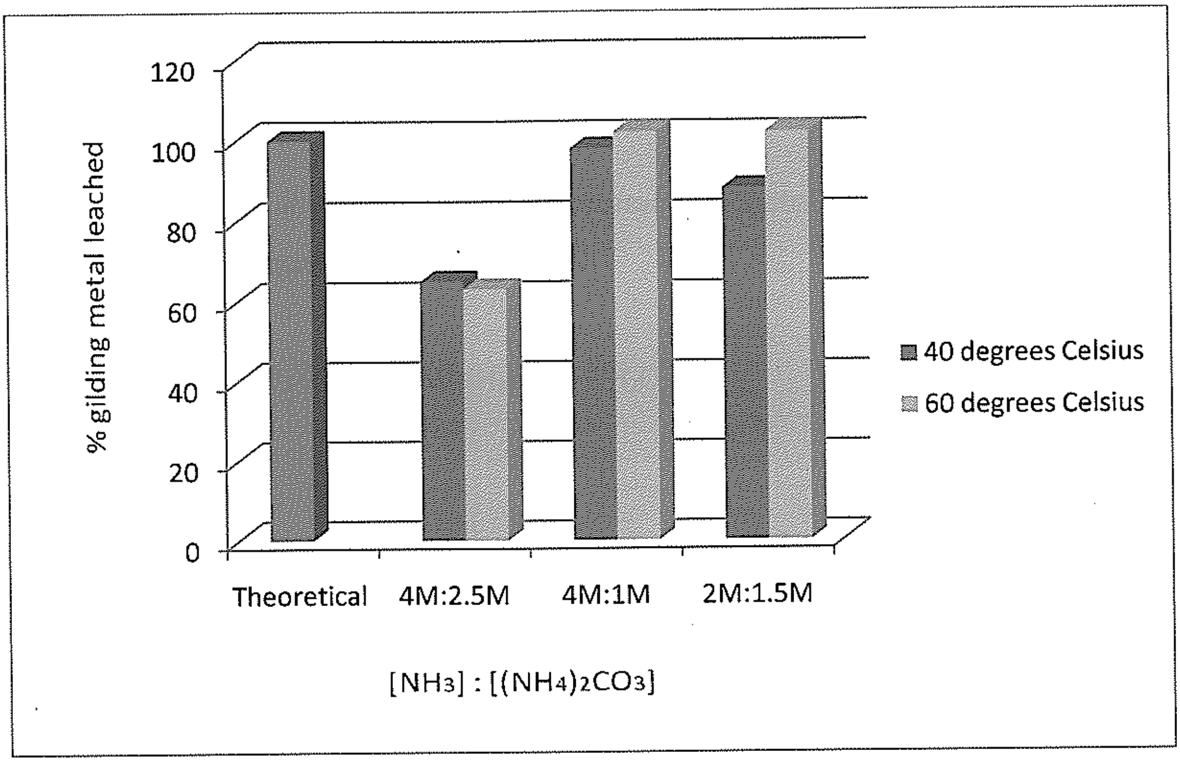

***Figure 4.7**: Comparison of the gilding metal leaching efficiency for the various ratios of the concentrations of NH_3: $(NH_4)_2CO_3$ at temperatures of 40^0C and 60^0C, in verifying the effect of temperature; for 10 hours contact time, in absence of oxygen*

From this result, it can be said that the lower temperature of 40^0C can be used if 4M : 1M ($[NH_3]$: $[(NH_4)_2CO_3]$) leaching solution was to be utilised and in fact it is anticipated from this finding that lowering the temperature further, say to the ambient temperature, will not compromise the leaching efficiency of the gilding metal but if 2M : 1.5M ($[NH_3]$: $[(NH_4)_2CO_3]$) was to be selected, then temperature of 60^0C is recommended. However, in industrial application, the lower temperature is normally preferred.

As mentioned previously, due to time constraint, the temperature effect was only studied at the temperatures of 40^0C and 60^0C. A study at other temperatures and in particular at the ambient temperature should have been carried out in order to comprehensively understand the effect of temperatures on the leaching of the gilding metal from projectiles.

4.5 The influence of oxygen in the leaching process.

Leaching of copper and zinc by the ammoniacal carbonate leaching solution follows the proposed reaction equation shown below; *[4]*

$M + 2NH_3 + (NH_4)_2CO_3 + \frac{1}{2}O_2 \rightarrow M(NH_3)_4CO_3 + H_2O$ ....(4)

where M = Cu or Zn.

This equation indicates the role of oxygen in the formation of the extractable species of the gilding metals. In this study, comparison of the leaching efficiency of gilding metal was made in the leaching process in the absence and the presence of oxygen and at temperatures of 40^0C and 60^0C. Oxygen was introduced into the reaction mixture in the form of air which contains 72% nitrogen, 27% oxygen and traces of other gases. The amount of oxygen introduced into the reaction mixture in 10 hours was determined by measuring the flow rate of the air delivered into the reaction mixture. The average rate of volume of the oxygen delivered was calculated to be 187 ± 2mL per second.

Two leaching solutions were selected in this study and they were 4M : 1M and 2M : 1.5M ($[NH_3] : [(NH_4)_2CO_3]$). These solutions at 40^0C and in the absence of oxygen gave 98% and 88%, respectively and at 60^0C both produced 102%. ***Table 4.6*** and ***Figure 4.8*** show the results of the effect of oxygen added into the reaction mixture measured at 40^0C and ***Table 4.7*** and ***Figure 4.9*** show the data obtained at 60^0C.

Table 4.6: *Comparison of the % gilding metal removed from projectiles using various ratios of the concentrations of NH_3 : $(NH_4)_2CO_3$ at 40^0C for 10 hours contact time in the absence and the presence of oxygen.*

Experiment	***Mass of projectiles before leaching (g)***	***Mass of projectiles after leaching (g)***	***Mass of gilding metal removed (g)***	***Percentage of gilding metal removed (%)***
Theoretical	***16.234***	***11.039***	***5.195***	***100***
4M:1M ($NH_3/(NH_4)_2CO_3$) at 40^0C for 10hr, no oxygen	16.243	11.169	5.074	98
4M:1M ($NH_3/(NH_4)_2CO_3$) at 40^0C for 10hr with oxygen	16.206	10.904	5.302	102
2M:1.5M($NH_3/(NH_4)_2CO_3$) at 40^0C for 10hr, no oxygen	16.261	11.681	4.580	88
2M:1.5M($NH_3/(NH_4)_2CO_3$) at 40^0C for 10hr with oxygen	16.257	10.911	5.346	103

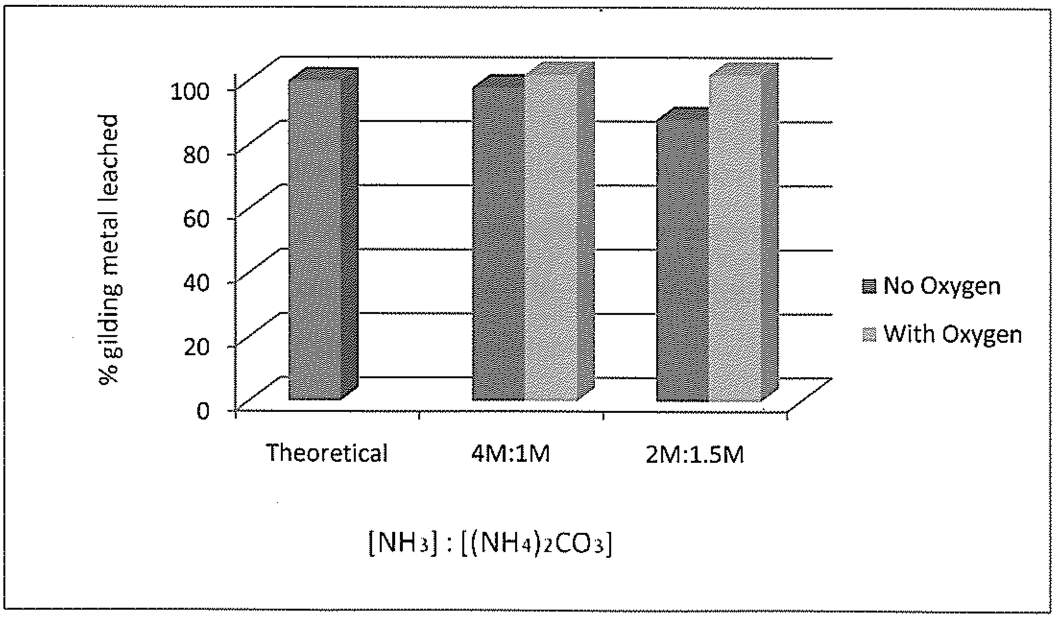

Figure 4.8: *Comparison of the gilding metal leaching efficiency for the various ratios of the concentrations of NH_3: $(NH_4)_2CO_3$ at temperatures of 40^0C in absence and presence of oxygen.*

Table 4.6 and ***Figure 4.8*** above show the results of the effect of the addition of oxygen into the reaction mixture measured at 40^{0}C. A significant increase is observed for the leaching solution of the composition of 2M : 1.5M ([NH_3] : [$(NH_4)_2CO_3$]) in the presence of oxygen at this temperature, showing a 103% leaching but in its absence, a 15% decrease was observed. These results indicate that oxygen to some extent played a role in the formation of the extractable complex species as depicted in equation (4) above.

A small change in the percentage of the gilding metal leached from the projectile, was however observed when leaching solution composition of 4M : 1M ([NH_3]:[$(NH_4)_2CO_3$]) was used. In the absence of oxygen, 98% of the gilding metal was leached but in its presence only about 4% increase was observed, indicative of the lesser involvement of oxygen in the formation of the extractable complex species of the gilding metal.

Results in ***Table 4.7 and Figure 4.9*** shown below were obtained using similar conditions as above except that the temperature used was at 60^{0}C. In all cases, there was no significant change in the percentage of leaching of the gilding metal from the projectiles neither in absence nor in the presence of oxygen in both leaching solutions used. In all cases, the percentage removal of the gilding metal from the projectile was all comparable to the theoretical value.

In summary, due to the limited empirical findings and without further studies on the effect of oxygen on the leaching process, it is difficult to ascertain and to extrapolate the involvement and also the role of oxygen in the leaching process of the gilding metal from the projectiles. Thus further studies are necessary.

Table 4.7: *Comparison of the % gilding metal removed from projectiles using various ratios of the concentrations of NH_3 : $(NH_4)_2CO_3$ at 60^{0}C for 10 hours contact time in the absence and the presence of oxygen.*

Experiment	***Mass of projectiles before leaching (g)***	***Mass of projectiles after leaching (g)***	***Mass of gilding metal removed (g)***	***Percentage of gilding metal removed (%)***
Theoretical	***16.234***	***11.039***	***5.195***	***100***
4M:1M (NH_3/$(NH_4)_2CO_3$) at 60^{0}C for 10hr, no oxygen	16.240	10.917	5.324	103
4M:1M (NH_3/$(NH_4)_2CO_3$) at 60^{0}C for 10hr with oxygen	16.236	10.922	5.314	102
2M:1.5M(NH_3/$(NH_4)_2CO_3$) at 60^{0}C for 10hr, no oxygen	16.180	10.894	5.286	102
2M:1.5M(NH_3/$(NH_4)_2CO_3$) at 60^{0}C for 10hr with oxygen	16.261	10.959	5.302	102

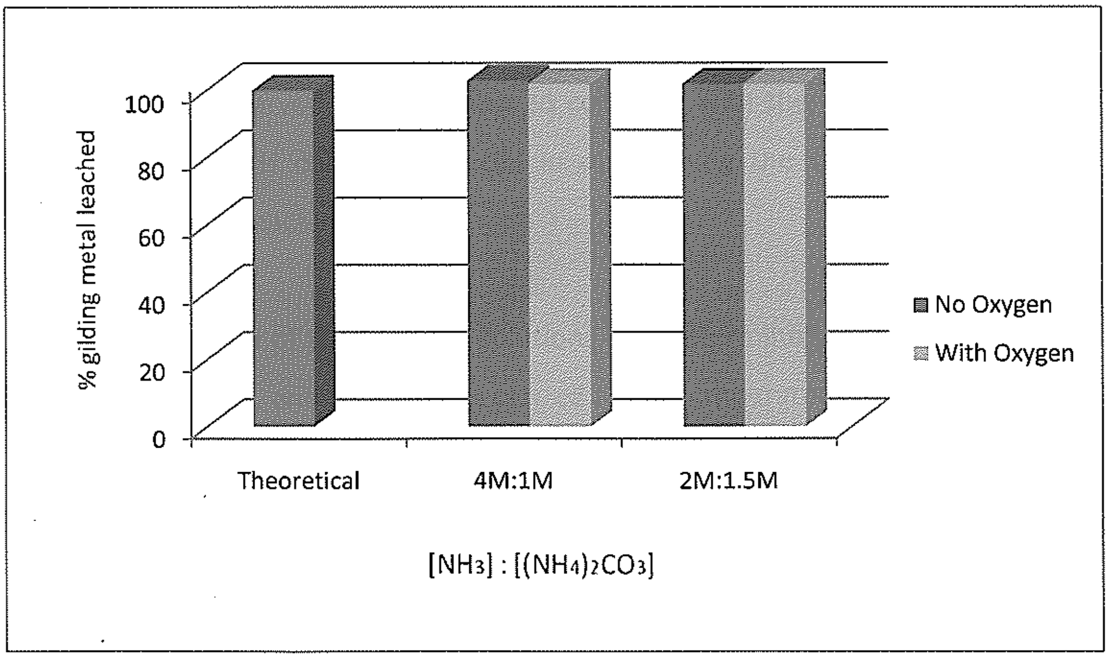

Figure 4.9: *Comparison of the gilding metal leaching efficiency for the various ratios of the concentrations of NH_3: $(NH_4)_2CO_3$ at temperatures of 60^{0}C in absence and presence of oxygen.*

5. Conclusion

The work carried out in this study involved investigating the factors that can affect the leaching efficiency and determining the optimum leaching conditions in leaching the gilding metal from 5.56mm projectiles. Factors that were found to influence the leaching efficiency were: contact time, composition of the leaching solution, pH of the leaching solution, temperature and addition of oxygen.

In analysing the amount of the gilding metal that had been leached, two methods were used and they were Atomic Absorption Spectroscopic (AAS) method and the Mass Measurement method. AAS only measured the soluble component of the metal complexes whereas the mass measurement measured the difference in the mass of the projectiles before and after the leaching process. Thus Mass Measurement measures the total mass of the gilding metal which had been removed from the projectiles, whereas AAS measures only the soluble components of the gilding metal in the aqueous solution. Thus Mass Measurement was the more reliable method and was used throughout the study.

pH was found to vary during the leaching process which influenced the solubility of the metal complexes in the leaching solution. Formation of precipitate during the course of the leaching process was observed, which seems to correlate with the decrease of pH of the leaching solution. Thus pH control is crucial in maintaining the solubility of the metal complexes formed in the leaching solution.

The optimum composition of the leaching solutions was determined to be 4M ammonia to 1M ammonium carbonate, and when it was carried out at temperature of 40°C, efficiency of leaching seems to be maintained even in the absence of oxygen. Oxygen was however needed if the reaction made use of the leaching composition of 2M ammonia to 1.5M ammonium carbonate at temperature of 40^0C but if it was carried at higher temperature of 60^0C, it seems that oxygen plays an insignificant role in the process. This work, however needs to be further qualified.

The optimum contact time was determine to be 10 hours and further increase in the contact time showed marginal effect in the leaching efficiency of the gilding metal. Similarly, for the effect of temperature, an increase in the temperature from 40^0C to 60^0C seems to produce marginal effect in the leaching efficiency, however, in ascertaining the optimum temperature condition, the effect of other temperatures, in particular at ambient temperature, should have been investigated. This will be the subject for further studies.

6. References

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7. Appendix

7.1 Weight of each 5.56mm projectile

Figure 7.1 shows the mass of each projectile used in this study. The weight ranges between 4.031 g to 4.087 g. A total of sixty-eight 5.56mm projectiles were weighed and the average weight was determined to be 4.059 ± 0.002g.

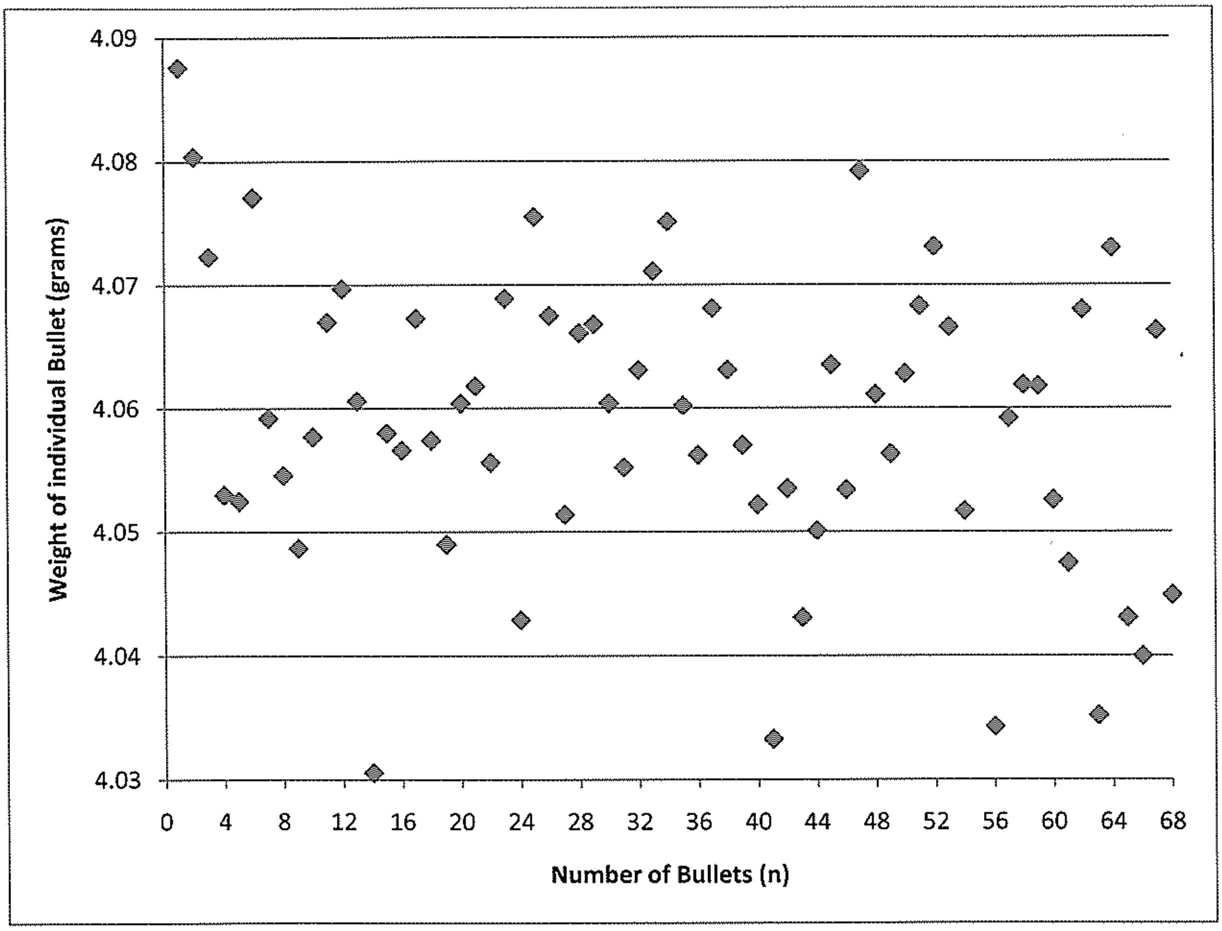

Figure 7.1: *Individual weight distribution of each 5.56mm projectile*

7.2 Calibration plots of Cu and Zn measured by Atomic Absorption Spectrophotometer

Figures 7.2 and 7.3 are the calibration plots measured by AAS for Cu and Zn respectively. These plots were utilised to measure the amount of the metals in the leaching solutions.

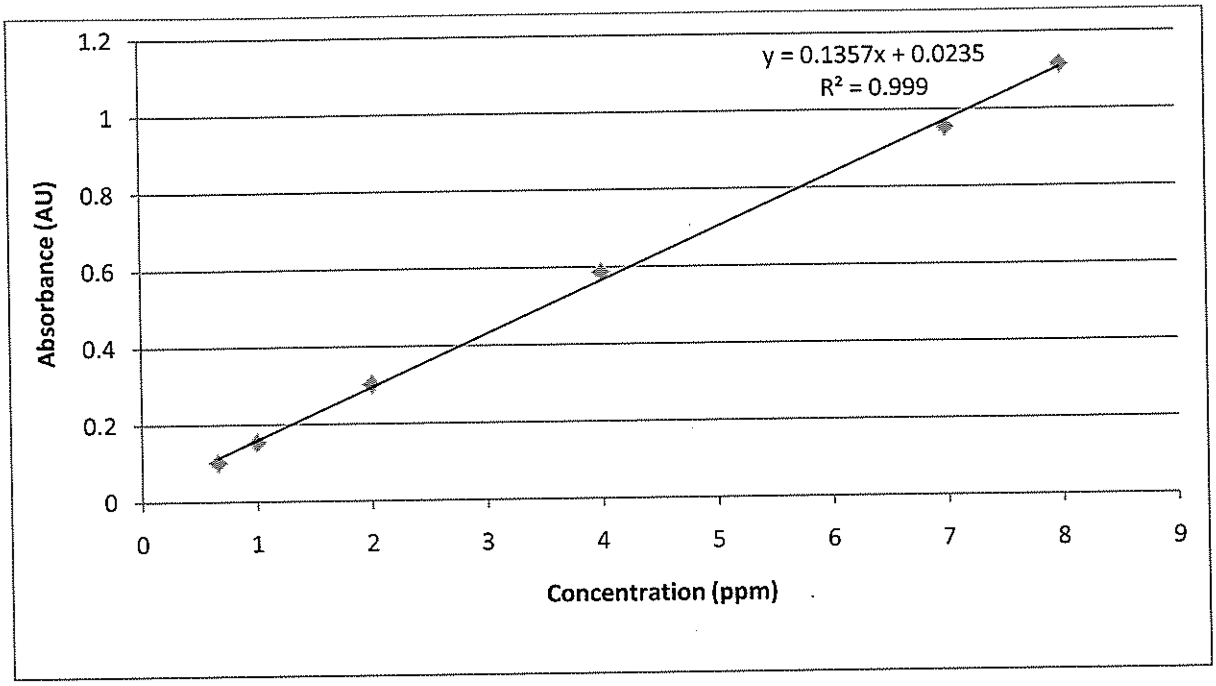

Figure 7.2*: Calibration plot for copper using Atomic Absorption Spectrophotometer*

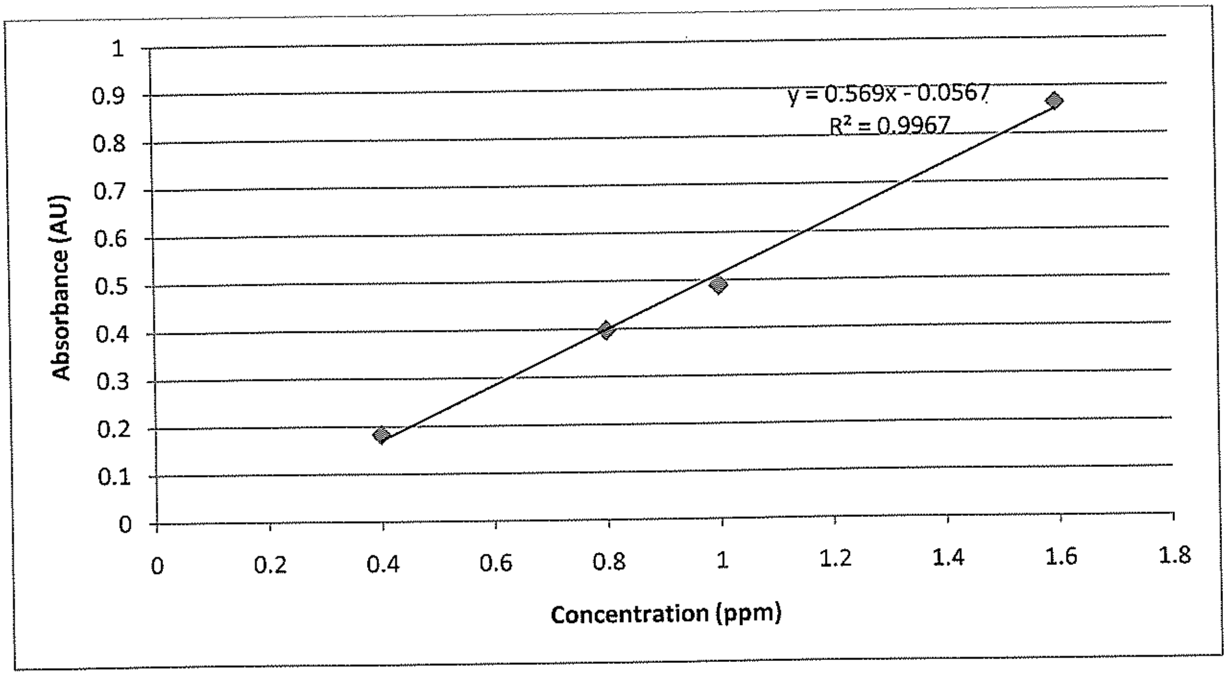

Figure 7.3*: Calibration plot for Zinc using Atomic Absorption Spectrophotometer*

7.3 Results obtained using Atomic Absorption Spectroscopic Method in analysing Cu in the gilding metals.

Figures 7.4, 7.5, 7.6, and 7.7 below are the results obtained by using AAS method of measuring the Cu in the leaching solutions. All results indicate that the concentration of Cu analysed by AAS was only about a half of what was the theoretical value.

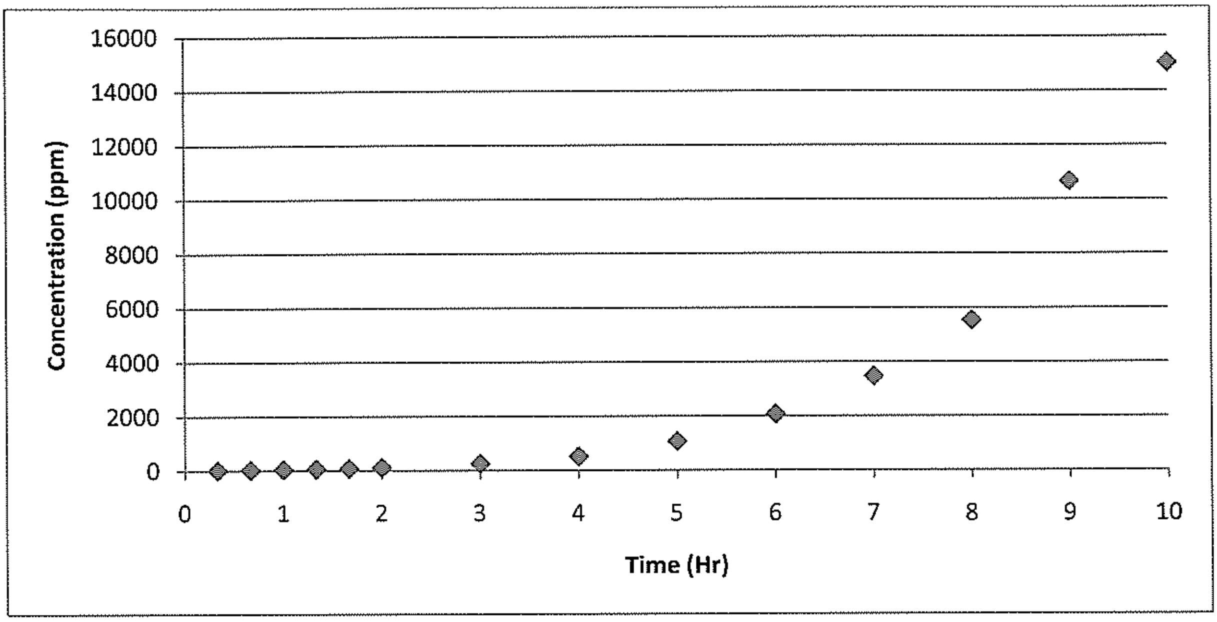

Figure 7.4: *Concentration of Cu leached into leaching solution of composition* 2M : 1.5M ([NH_3]:[$(NH_4)_2CO_3$]); contact time of *10hours at 40^0C and no oxygen.*

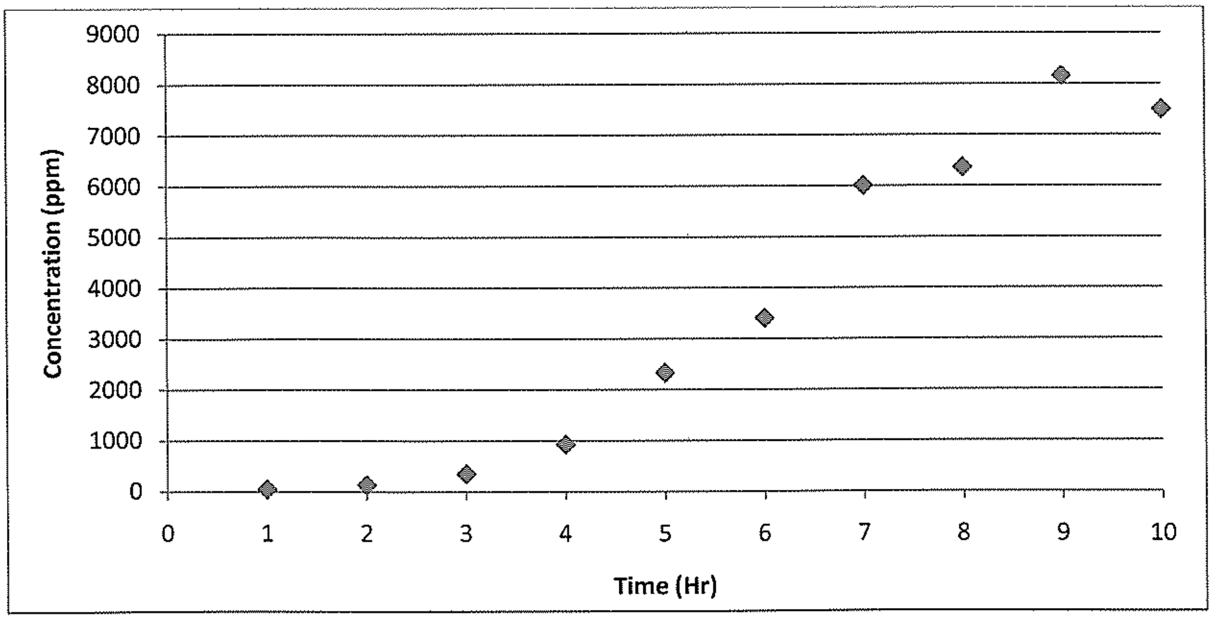

Figure 7.5: *Concentration of Cu leached into leaching solution of composition* 2M : 1.5M ([NH_3]:[$(NH_4)_2CO_3$]); contact time of *10hours at 40^0C and with added oxygen.*

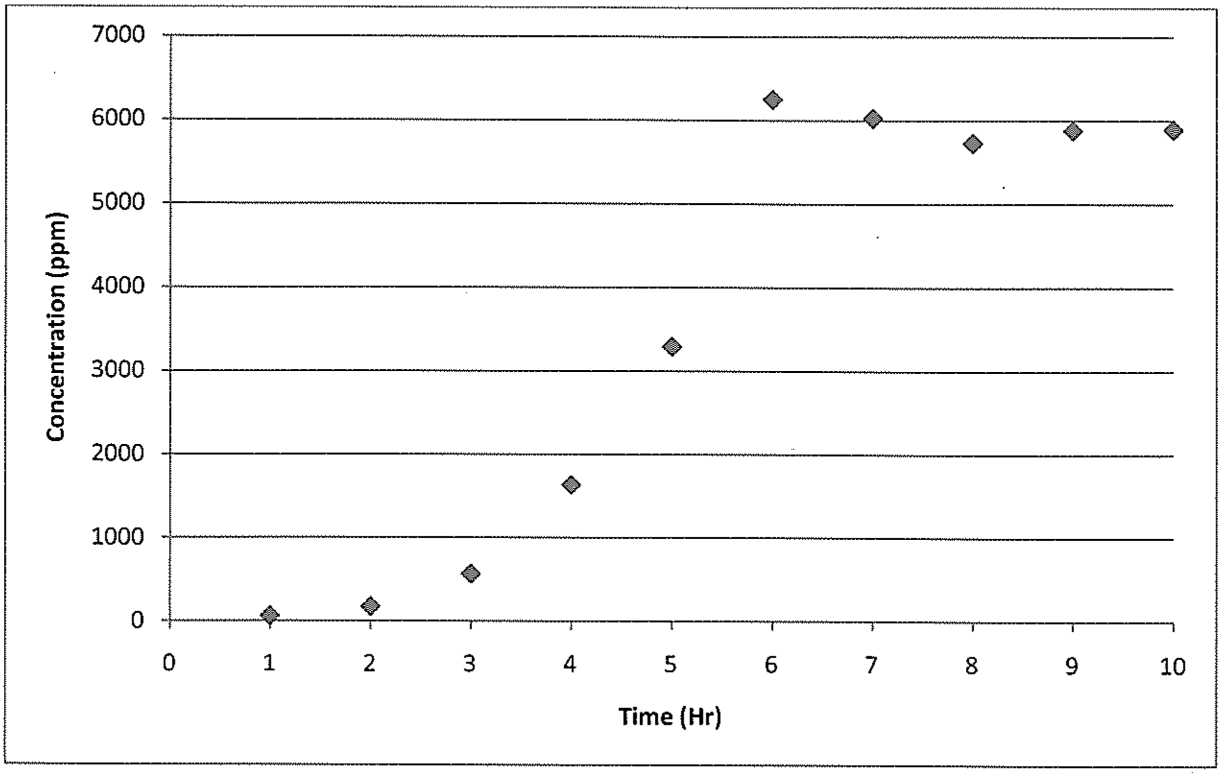

Figure 7.6: *Concentration of Cu leached into leaching solution of composition* 2M : 1.5M ([NH_3]:[$(NH_4)_2CO_3$]); contact time of *10hours at 60^{0}C and no oxygen.*

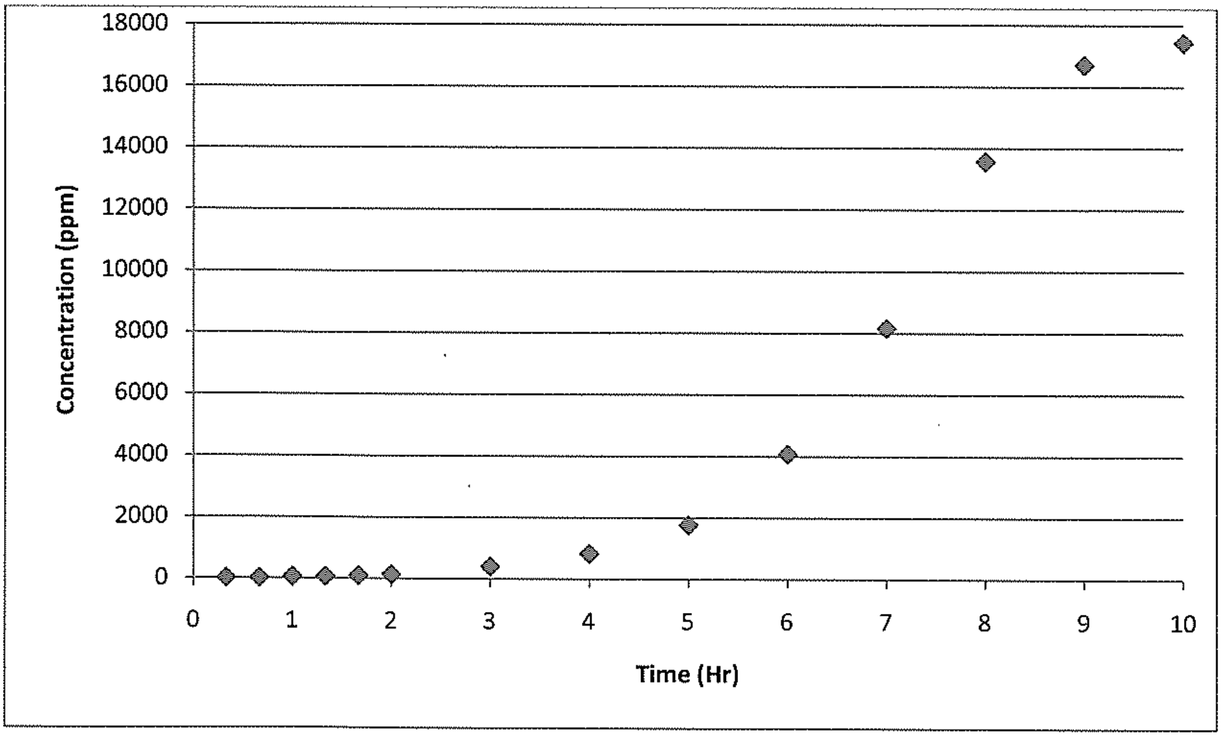

Figure 7.7: *Concentration of Cu leached into leaching solution of composition* 2M : 1.5M ([NH_3]:[$(NH_4)_2CO_3$]); contact time of *10hours at 60^{0}C and with added oxygen.*