again attributed to the solid iron oxide barrier which formed on the iron - nickel alloy leads. olid oxide layer inhibited iron - nickel alloy dissolution by preventing fresh acid from cting the metal surface. The other acid concentrations had a standardized percent weight loss of 20% since the tin - lead solder, tin - lead coated copper leads and iron - nickel alloy leads, were completely solubilized in the first 15 minutes of leaching. The slight variation in percent weight loss for these three acid strengths was caused by the differences in metal content of each board. After one hour of leaching, the percent weight loss for boards immersed in 67%, 44%, 33%, and 22% nitric acid was 35%, 28%, 25% and 27% respectively. The large increase in weight loss for the concentrated nitric acid solution was ascribed to the loss of resin from the fiberglass substrate plus the dissolution of iron - nickel alloy leads. Resin was removed from the core of the substrate by acid penetration of the interior porous fiberglass weaves. Iron - nickel alloy lead dissolution resulted due to the decomposition of the porous oxide layer which allowed the leach reagent to contact the metal surface. Percent weight loss for the other acid concentrations was attributed only to the loss of resin from the fiberglass substrate since all the base metals

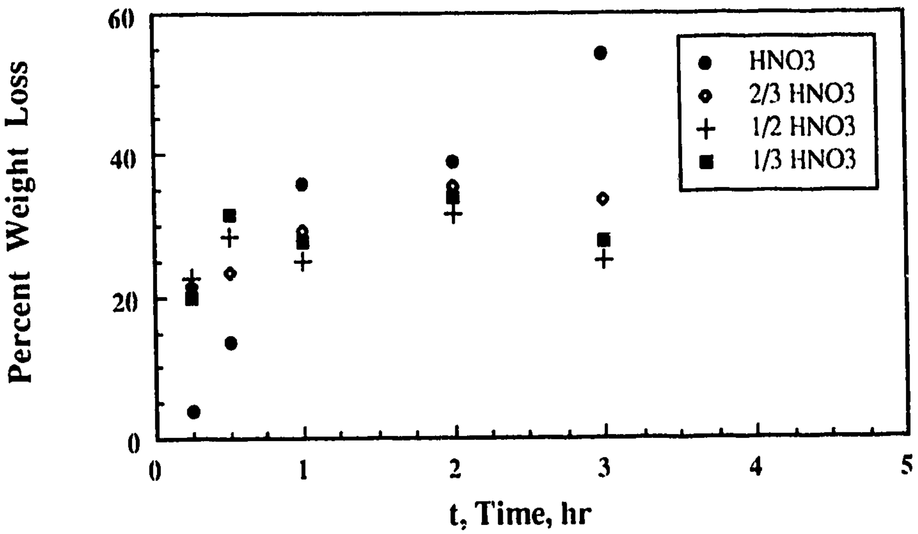

**Figure 4.11:** Epoxy coated computer boards leached in varying concentrations of nitric acid at 90°C.

were solubilized at a previous time. For longer leach times, further weight loss was limited since the metallics were completely solubilized and most of the resin was extracted from the fiberglass substrate.

From these leaching experiments with epoxy coated computer boards in nitric acid - water systems at temperatures of 50°, 70° and 90°C, the following conclusions on the dissolution of metallic strips and leads from computer circuit boards were deduced:

(1) The formation of an iron oxide coat on the component leads prevented the complete dissolution of the iron - nickel alloy leads in a solution containing 67% or 44% nitric acid at a temperature of 50°C.

(2) No iron oxide film formed in 22% nitric acid at a temperature of 50°C allowing for complete solubilization of the metal leads.

(3) At a temperature of 70° and 90°C, the iron oxide film formed but decomposed after one an a half hours and one hour, respectively, in the presence of concentrated nitric acid.

(4) The iron oxide film either broke down in the first few minutes or did not form in the following acid strength - temperature combinations: at a temperature of 50°, 70°, and 90°C for a solution containing 22% nitric acid, and at a temperature of 70° and 90°C for a solution containing 44% nitric acid.

(5) The top resin coat layer was effectively removed from the fiberglass board surface in solutions containing 67%, 44% and 22% nitric acid at elevated temperatures.

(6) The interior resin coat was completely removed from boards immersed in 67% and 44% nitric acid at temperatures above 70°C causing either partial or total separation of the individual fiberglass sheets.

(7) The most effective combination for metal solubilization and resin removal from these experiments occurred in a 22% nitric acid system at 70°C.

The successful dissolution of base metal constituents incorporated in epoxy coated computer boards with 22% nitric acid at elevated temperatures eliminated the other concentrations of nitric acid from further consideration. The high variability of computer board scrap necessitated a check of these dissolution conditions on silicone coated computer boards. The behavior of this board type was assessed in a 22% nitric acid system at temperatures of 50°, 70° and 90°C for a maximum time of three hours.

At 15 minutes of leaching, the percent weight loss for the silicone coated computer boards was 5%, 9%, and 15% at a temperature of 50°, 70° and 90°C, respectively as seen in Figure 4.12. The low percent weight loss for the two lower temperatures was a result of the ineffective acid attack on the resin coat which protected the protruded component leads and the metallic strips. At the highest temperature, the resin coat was severely but unevenly blistered permitting contact between the solution and metallic strips and leads. The random pattern of blistering affected the distribution of metal dissolution throughout the board's surface. For example, in areas where the resin was completely removed from the protruded leads, there was separation of the components from the silicone computer boards

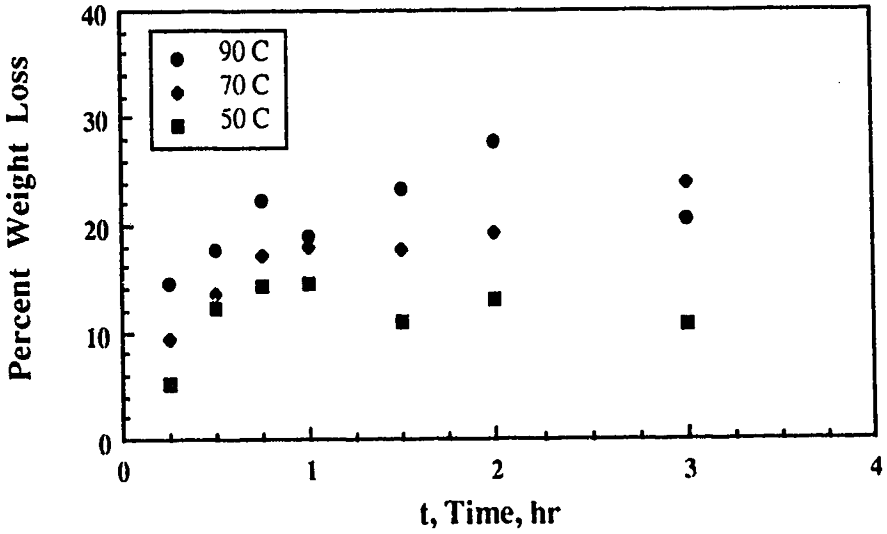

Figure 4.12: Silicone coated computer boards leached in a solution containing one part nitric acid to two parts water at varying temperatures.

while in areas of incomplete resin removal, this separation did not occur. At 30 minutes of leaching, slight blistering of the resin coat occurred in the boards immersed at a temperature of 50° and 70°C. The blistering which was located mostly around the solder joints allowed for contact between the solution and metal causing an increase in the percent weight loss to 12% and 14% for boards immersed at 50° and 70°C, respectively. The boards immersed at 90°C showed an even higher weight loss because of the complete removal of resin over the metallic leads and strips. After one hour of leaching, the boards immersed in a solution at 50°C achieved their maximum weight loss of 14%. This low value can be attributed to the incomplete resin removal over the entire board's surface inhibiting complete metal solubilization and preventing separation of the components from the boards. After this time, no change in the resin coat or metal strips and leads was observed. The boards immersed in a solution at 70°C had a percent weight loss of 18% after one hour since the metallic strips and leads were completely solubilized. Percent weight loss increased over the next two hours due to further loss of resin. At 90°C after one hour, the individual fiberglass sheets of the computer board substrate separated due to the complete removal of resin from the structure. The percent weight loss corresponding to this board breakup was 20%. After this time, no change in the substrate occurred.

From these leaching experiments with silicone coated computer boards in 22% nitric acid at a temperature of 50°, 70° and 90°C, the following conclusions on the dissolution of metallic strips and leads from computer circuit boards were deduced:

(1) Incomplete base metal solubilization occurred at a temperature of 50°C due to the lack of resin removal over the three hour leach period.

(2) Complete dissolution of the base metal occurred in solutions at a temperature of 70° and 90°C.

(3) The rate of metal solubilization is dependent upon solution temperature. A solution at 90°C solubilized the base metal in half the time as solutions at 70°C.

(4) The resin coat is effectively solubilized in solutions above 70°C.

(5) The fiberglass substrate breaks down into a loose conglomeration of fiberglass sheets at a temperature of 90°C after extended periods of leaching.

### 4.2.3.3 Pulp Density

The amount of solution required to completely immerse computer boards is approximately three millilitres per every gram of board. Metal extraction in solutions containing 67%, 44% and 22% nitric acid at a temperature of 90°C is complete within 15 minutes as long as no gold or an iron - nickel alloy is present. If gold is present, the nitric acid must first dissolve the copper substrate by tunneling before gold separation from the computer board can occur. This usually occurs in one hour of leaching. If an iron - nickel alloy is present, time of leach and acid concentration is important since solubilization is dependent upon these two factors. For example, a solution of concentrated nitric acid at 90° C requires a leach time of one hour to break down the oxide layer formed on the iron - nickel alloy, while this oxide film decomposes immediately or does not form at all in a solution of 44% or 22% nitric acid at 90°C. Increasing the amount of acid in comparison to the weight of the boards does not increase the rate of leaching to any extent. Thus, the acid requirement for leaching is approximately three millilitres per every gram of board.

### 4.2.3.4 Retention Time

The rate of metal dissolution in a nitric acid system was determined on as-received computer circuit boards. In most of the nitric acid systems analyzed, complete metal dissolution occurred after one hour of leaching. This is quite impressive considering the various metal constituents, such as copper, lead, iron, nickel, silver and zinc, incorporated in circuit boards. The only metals not solubilized over this time frame are gold, platinum and stainless steel. Any weight loss after this time is attributed to removal of the epoxy resin from the fiberglass boards and decomposition of plastic and ceramic components.

### 4.2.3.5 Agitation

Agitation of the solution was not possible by stirring bars or mechanical stirrers. A stirring bar at the bottom of the beaker failed to mix the solution due to the weight of the circuit boards on top. Mechanical stirrers were also unable to cause agitation. A barrier to this method was that the size of the boards in the beaker prohibited the use of mechanical stirrers. That is, the stirring rod was unable to penetrate the boards. Another problem was the solution level. Insufficient solution level above the boards prohibited complete immersion of the paddle. The final problem was harmful vapours. Nitrous oxide vapours emitted during the reaction caused corrosion of the metal parts in the stirrer. The inability to overcome these problems in both cases resulted in the conclusion that agitation of the solution was not practical.

Solution agitation was only possible through the emission of nitrous oxide vapours. These gases caused bubbling and frothing of the solution. Frothing was completed after approximately 15 minutes due to the solubilization of the majority of the metals. After this point, no agitation occurred.

## 4.2.4 Selection of First Stage Leach Parameters

From the previous analysis of acid concentration, temperature, pulp density, time and agitation, two possible ways of metal extraction exist. The first method is total separation of the individual fiberglass sheets. Total separation ensures the complete removal of all the base metals incorporated on and in the board. A problem with this method is that the individual fiberglass sheets inhibit the easy separation of the computer components. Components do not easily drop to the bottom of the tank. Instead, the wetted fiberglass sheets attach themselves to the components. Upon attachment, bundles begin to form. As a bundle increases in size, the number of electrical components which are tied up increases. The bundles reduce the recovery of the desired electrical components and also provide a site for the coagulated resin to settle on. Coagulated resin causes the bundle to increase its surface tension resulting in a tight conglomeration. Loose gold particles are also lost to this entrapping formation. Thus, this method of extraction is eliminated.

The second way is to minimize the attack of the fiberglass substrate but to maximize the solubilization of the base metals incorporated on computer boards. This way ensures separation of the electronic components from the fiberglass boards. The only problem is a loss of base metals incorporated within the fiberglass substrate. Since these metals are tin, lead and copper, their loss does not hinder the financial success of the operation.

The first stage leach was conducted to optimize metal solubilization but minimize fiberglass substrate decomposition. The parameters selected from the previous tests to employ these conditions were: (1) acid concentration - one part nitric acid to two parts water, (2) temperature - 70°C, (3) pulp density - three millilitres of solution per one gram of solid, and (4) retention time - one hour.

### 4.2.5 First Stage Leach

A generalized flow sheet for the recovery of precious metals from as-received computer circuit boards is presented in Figure 4.13. The division of the computer chips from the fiberglass boards was achieved by leaching in a Pyrex beaker the computer circuit boards with dilute nitric acid. Initially, the beaker was charged with 175 mL of concentrated nitric acid and 350 mL of water to achieve an acid to water ratio of 1:2. After charging, the solution was heated with a hot plate to achieve a stable temperature of 70°C before addition of the computer circuit boards. Upon temperature stabilization, a total of 175 g of computer circuit boards were added to the solution in 25 g increments to minimize the exothermic nature of the reaction. This overall weight was selected since the desired solid-to-liquid ratio was determined from earlier tests to be one gram of solid to three

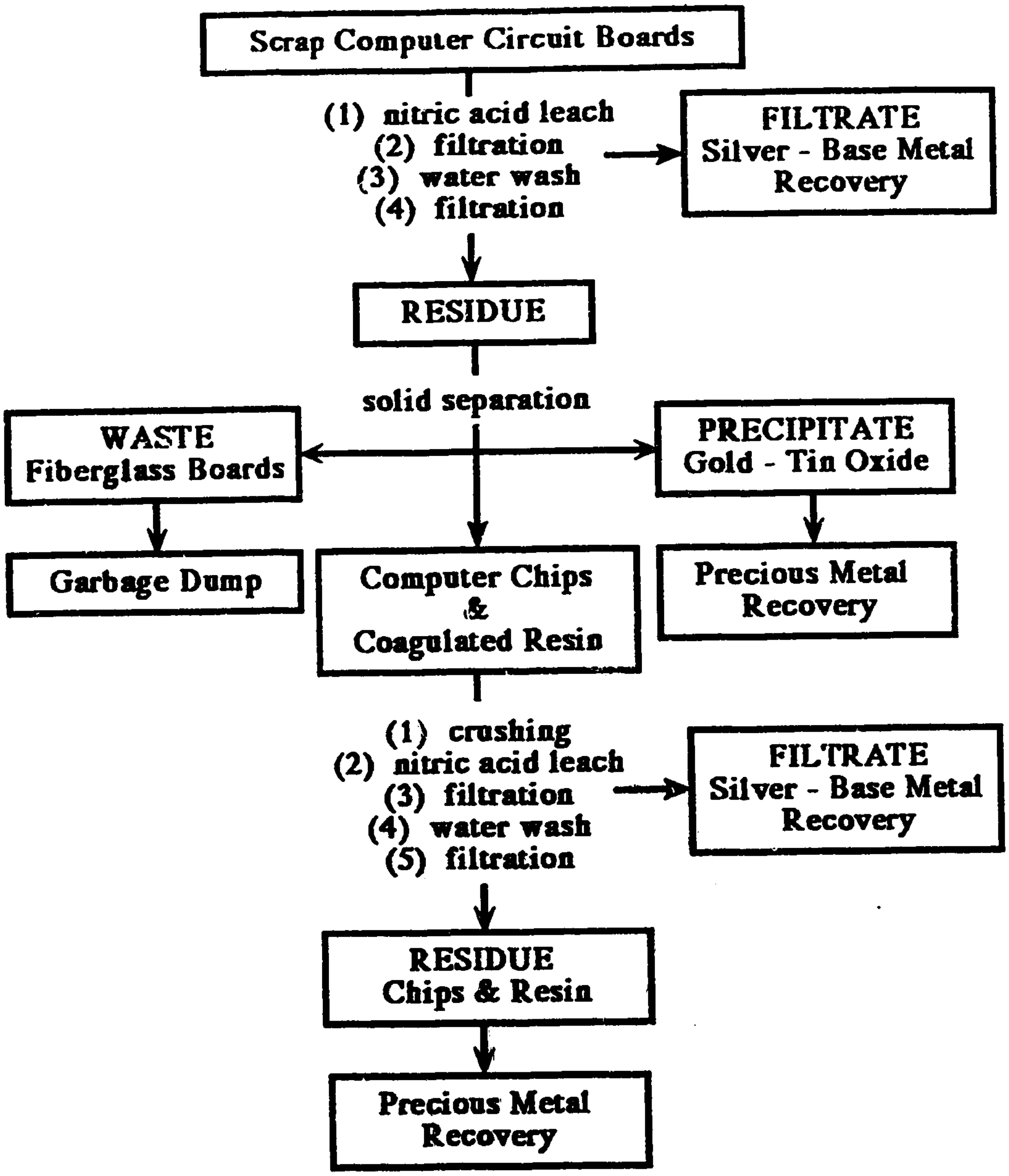

Figure 4.13: Generalized flow sheet for the recovery of base and precious metals from scrap computer circuit boards.

millilitres of solution. During computer board addition, frothing occurred as a result of the release of nitrous oxide fumes from the reaction between nitric acid and the base metals. A small amount of frothing is beneficial to the overall leach process since solution mixing removed the soluble species away from the surface and transported fresh reagent from the solution bulk to the metal's surface. As the reaction proceeded, the nitrous oxide evolution peaked, then subsided within 15 minutes. This reduction coincided with the decomposition of the froth head to a thin film on top of the solution. The thin film comprised principally of coagulated fiberglass resin. After one hour of leaching, the computer chips were completely dissociated from the fiberglass boards, hence, leaching was discontinued.

Filtration separated the nitrate solution from the solid constituents consisting of a tin oxide precipitate mixed into the solid gold flakes, fiberglass boards, coagulated epoxy resin and computer chips. The nitrate solution was sent for base metal recovery, as discussed in Chapter 5, while the solid residue was divided into the following fractions: a tin oxide - gold mixture, a fiberglass board product, and a computer chip - coagulated epoxy resin product. A material breakdown, as shown in Table 4.1, identified that the majority of the weight was associated with the computer chips and fiberglass boards. The overall weight, however, was 25 g lower than the original computer board weight selected for first stage

**Table 4.1: Weight analysis of the computer board solid constituents developed from first stage nitric acid leaching.**

| Solid Constituent | Weight (grams) | Weight (%) |
|---|---|---|
| Fiberglass Board | 55 | 36.7 |
| Computer Chips | 75 | 50 |
| Epoxy Resin | 10 | 6.7 |
| Tin Oxide Precipitate | 10 | 6.7 |
| Total | 150 | 100.1 |

leaching. The discrepancy between the two figures is a result of metal dissolution during nitric acid leaching. The tin oxide precipitate, shown in Figure 4.14, was identified only by EDX analysis. The x-ray diffraction pattern was inconsequential since this compound was amorphous.

The computer chips and coagulated epoxy resin contain a considerable amount of precious metals within the protective plastic and ceramic encasements and undergo further processing for precious metal recovery. The tin oxide - gold mixture requires further processing to separate the gold flakes from the tin oxide particles, hence this material also undergoes precious metal recovery. The only fraction designated as waste from the first stage leach is the fiberglass boards. This product is discarded to a garbage dump.

### 4.2.6 Selection of Second Stage Leach Parameters

The second stage leach is conducted to separate gold and the platinum group metals from silver and the base metals. Without this selective leach, base metal impurities would contaminate the precipitates formed at later stages of the process. Separation of the precious metals from the base metals is achieved with a nitric acid leach. The following parameters selected for this leach stage are identical to the parameters determined in the first stage leach experimentation:

(1) Acid Concentration - 1 part nitric acid to 2 parts water
(2) Temperature - 70°C
(3) Pulp Density - 3 mL of solution per 1 g of solid
(4) Retention Time - 1 hour

### 4.2.7 Second Stage Leach

The processing [illegible]ed for computer chips and coagulated epoxy resin involves an initial mechanical crushing stage followed by a leaching stage. Mechanical crushing changes the structure of the computer chip - coagulated epoxy resin mixture from that of a

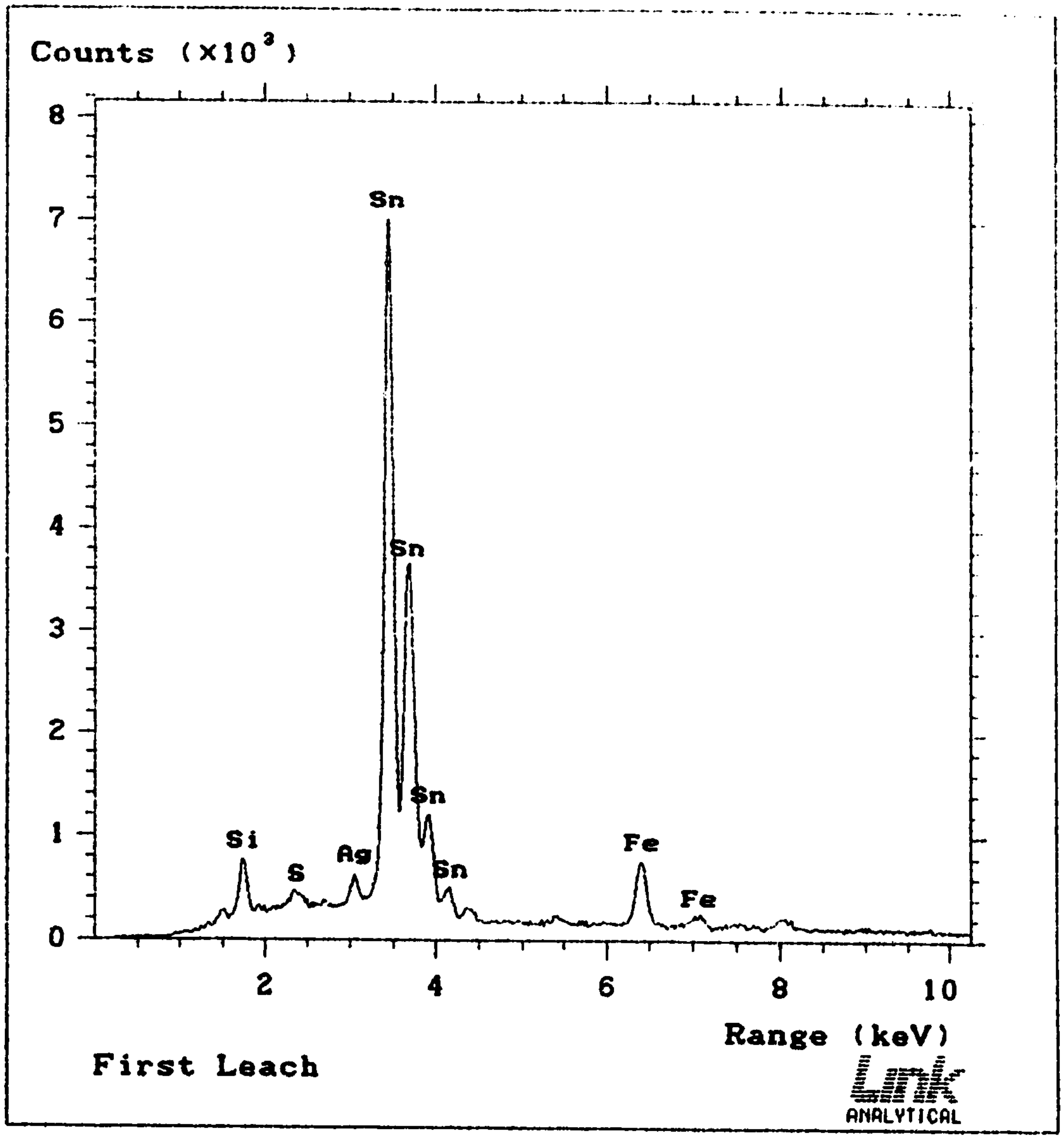

Figure 4.14: EDX analysis of the elements incorporated in the tin oxide precipitate developed from first stage nitric acid leaching.

plastic or ceramic case to a fine particulate product. This reduction in particle size of the computer chip and coagulated resin aids in the separation of the precious metals from the gangue materials. Reduction is undertaken by the employment of a jaw crusher and a cone crusher. The jaw crusher breaks the protective plastic or ceramic encasement and reduces the chips and resin to a size suitable for feeding to the cone crusher. The cone crusher further reduces the size of the chips and resin to such an extent that the precious metals and gangue materials exist as separate particles. In this liberated state, the computer chips and coagulated resin are now ready for the second stage leach.

The crushed particulate matter was leached with dilute nitric acid to separate gold from silver and the base metals. Without this selective leach, base metal impurities would contaminate the precipitates formed at later stages of the process. Leaching was again conducted in a beaker exposed to the atmosphere with a charge of 175 mL of concentrated nitric acid and 350 mL of water. After charging, the temperature was allowed to stabilize at 70°C. Once achieved, 175 g of crushed computer chips and resin were added to the solution in small increments to inhibit excessive frothing caused by the evolution of nitrous oxide vapors from the dissolution of base metals. As the reaction proceeded, this froth layer brokedown and a thin film of extraneous matter, such as: plastic, resin and ceramics, developed on the solution's surface. At the conclusion of leaching, the charge was filtered to segregate the metal nitrate solution from the solid gold flakes intermixed with ceramics, plastics and a tin oxide precipitate. These solid constituents saturated with metal nitrates were washed with water. After water washing, the slurry was filtered to create a clean solid product for precious metal recovery, as discussed in Chapter 6, and a wash product which is united with the previous nitrate filtrate to obtain a solution for base metal recovery, as discussed in Chapter 5.

## 4.3 Crushed Computer Circuit Boards

### 4.3.1 Complexity and Heterogeneity Problem Solving

High levels of precious metal recovery are limited by the problems of complexity and heterogeneity. These problems are dismissed by changing the overall structure of the computer circuit board. Alteration is achieved through comminution, the reduction of the particle size to the point where the valuable metal species are adequately liberated so that they may be effectively separated from the gangue materials.[12] This liberation of valuable metals is undertaken by crushing which is accomplished by compression of the ore against a rigid surface or by impact against surfaces in a rigidly constrained motion path. The resultant product of comminution is a distribution of particles ranging in size from coarse to fine. This crushed product is no longer complex or heterogeneous, but instead, it is homogeneous.

### 4.3.2 Comminution

Liberation of the valuable metals from as-received computer boards is achieved by comminution in a hammermill. Hammermills reduce the particle size of the ore by impact rather than by compression.[12] Impact is achieved by applying sharp blows to the computer boards at high speeds. These blows are caused by moving parts called beaters. Contact between the beaters and computer boards cause a transfer of kinetic energy between the two bodies. This impact causes immediate fracture of the computer circuit boards. Shattering is increased by forcing the computer circuit boards to impact upon a breaker plate.

As-received computer circuit boards are reduced to a size amenable for metal separation by employing two hammermills in series. The first hammermill acts as a primary crusher. It reduces the as-received rectangular computer boards to a size suitable for feeding into the secondary crusher. The second hammermill further reduces the particle size of the computer boards to such an extent that the metal and gangue exist as separate particles. In this liberated state, the computer boards are now ready for further processing.

### 4.3.3 Exploratory Test on Crushed Computer Boards

As previously outlined, a number of preliminary or exploratory experiments was conducted on as-received computer circuit boards to identify the acid required for effective metal dissolution. From these experiments, nitric acid at elevated temperatures was determined to be very successful in dissolving not only the plastic coating on the boards but also the base metal strips. Crushed computer circuit boards being derived from as-received computer boards should also be susceptible to nitric acid leaching.

An exploratory nitric acid leaching test was carried out on crushed computer circuit boards. Acid strength was selected at one part nitric acid to two parts water, a diluted solution being used to minimize the amount of nitric acid. The temperature required to dissolve base metals rapidly was 70°C. A temperature below the boiling point of water was necessary to ensure minimal solution evaporation. The amount of solution needed to cover crushed computer boards was approximately four millilitres per gram of board. At these preselected conditions, a leach time of one hour was required to ensure complete base metal dissolution.

The nitric acid - water mixture was preheated to 70°C before addition of crushed computer circuit boards. Addition of one gram of board to three millilitres of solution resulted in the complete absorption of the solution by the crushed product. The lack of solution for effective leaching necessitated the addition of one extra part of acid mixture. Thus, the required solution amount was roughly four millilitres per gram of board. After solution makeup, severe frothing occurred. The developed froth head was approximately five times greater than the original solution volume. For example, a solution of 200 mL produced a froth of one litre. The froth head developed as a result of the high reaction rate between nitric acid and copper.[32,33] This reaction produced large amounts of nitrous oxide fumes to be emitted; these gases caused the formation of the froth head.

Froth reduction was undertaken by agitation provided by a magnetic stirring bar at the bottom of the tank. No reduction in froth was observed at low or high speeds. Only at violent speeds was any reduction noticed. At this rate, the froth head was reduced by about one quarter. In other words, the froth was only four times greater than the original solution volume. This amount of reduction is minuscule considering the method employed.

Production of the froth head decreased as the reaction proceeded. After approximately 15 minutes, the froth head decreased in size to a thin film on top of the solution. This reduction coincided with the elimination of gas emissions. The lack of new gas bubbles being added to the froth resulted in froth head breakdown. The thin layer on top of the solution consisted of fiberglass, plastics, ceramics and undissolved metals. This layer must be mixed into the nitric acid - water solution to cause metal dissolution. Mixing was undertaken by the magnetic stirring bar at low rates.

Filtration after leaching easily separated the solid residue from the solution. The solid residue consisted of fiberglass, plastics, ceramics and undissolved precious metals. Separation of these metals from the fiberglass waste requires a second leach. A problem of another leach is the presence of fiberglass waste carried into the cycle. Without fiberglass removal in this next stage, excessive amounts of lixiviants amenable to precious metals must be used to minimize solution absorption by the fiberglass.

### 4.3.4 Avoidance of Fiberglass Fines

Initially, direct leaching of crushed circuit boards appeared quite attractive until problems of fiberglass fines were exposed in the exploratory test. A possible solution is the reduction of fines before the leaching step. Reduction is undertaken by gravity separation techniques which employ density to separate heavy and light particles of roughly the same size. Particle size control is required to ensure that separation is purely a result of density.[12] An initial screening of the crushed product divides the particles into large, medium, small and tiny fractions. These fractions are then tabled to remove the fiberglass fines from the metal chips.

### 4.3.4.1 Screening

Crushed particles are not of uniform size, but a wide variation in particle sizes is produced. This mixture of sizes is undesirable for gravity separation processes since separation is not based solely on density. Screening of the crushed computer circuit boards separated the mixed material into a large, medium, small and tiny fractions. A breakdown of the percent material retained in the above fractions is listed below.

**Table 4.2: Size Analysis of Crushed Computer Circuit Boards**

| Fraction | Size (μm) | Weight Retained | Percent Retained |
|---|---|---|---|
| +35 | +425 | 7232.9 g | 48.8% |
| -35 +80 | -425 +200 | 4093.1 g | 27.6% |
| -80 +150 | -200 +106 | 1216.6 g | 8.2% |
| -150 | -106 | 2287.4 g | 15.4% |
| Total | | 14830.0 g | 100.0% |

The precious metal content of each crushed computer circuit board fraction was determined by sampling a representative quantity of material with the Rapid method, which is described in Appendix A.[104] The large (+35 mesh), medium (-35 +80 mesh), small (-80 mesh) and tiny (-150 mesh) fractions identified a satisfactory amount of gold and a deficiency of platinum in each fraction. As noted in Table 4.3, all four samples contained greater than three ounces of gold per ton but less than seven ounces per ton, while the platinum quantity was less than one third of an ounce per ton in each sample. On a fraction basis, the quantity of gold ranged from a low of 0.142 g in the small fraction to a high of

1.680 g in the large fraction, as shown in Table 4.4. The lack of gold in the small fraction was attributed only to the low fraction weight since this fraction's gold content per ton of sample was similar to the medium fraction gold content.

**Table 4.3: Analysis of gold and platinum incorporated in the individual size fractions.**

| Fraction | Wt % of Au | Au (oz/ton) | Wt % of Pt | Pt (oz/ton) |
|---|---|---|---|---|
| +35 | 0.0232 | 6.77 | 0.000650 | 0.189 |
| -35 +80 | 0.0123 | 3.57 | 0.000700 | 0.204 |
| -80 +150 | 0.0117 | 3.41 | 0.000813 | 0.237 |
| -150 | 0.0175 | 5.09 | 0.000963 | 0.281 |

**Table 4.4: Distribution of gold in the screened fractions.**

| Fraction | Fraction Weight (grams) | Gold in Fraction (grams) | Gold Distribution (percent) |
|---|---|---|---|
| +35 | 7232.9 | 1.680 | 61.7 |
| -35 +80 | 4093.1 | 0.501 | 18.4 |
| -80 +150 | 1216.6 | 0.142 | 5.20 |
| -150 | 2287.4 | 0.399 | 14.7 |
| Total | 14830.0 | 2.722 | 100.0 |

The gold content in each fraction is sufficient to treat the entire ore weight for gold recovery without any upgrading. However, as identified by the exploratory test on crushed computer circuit boards, leaching problems exist due to the presence of fiberglass fines. Reduction of this species was attempted by gravity separation techniques.

### 4.3.4.2 Gravity Separation

Each fraction of the crushed boards contains an amount of undesirable fiberglass fines. These fines are extraneous material which only increase the overall weight and volume of the ore. Reduction of these fines is desirable to ensure the profitable recovery of precious metals. One technique available for gangue material removal is gravity separation. Gravity concentration methods separate materials of different specific gravity by their relative movement in response to gravity and resistance to motion imparted by water.[12] Particles in water are dependent on density and size. Large particles are affected more than smaller ones. The efficiency of gravity processes therefore increases with particle size. Discrepancy of sizes hinders the overall efficiency of separation by increasing the dependence on size while minimizing the effect of specific gravity.

#### 4.3.4.2.1 Tabling

The shaking table separates liberated materials by exploiting differences in specific gravity among the materials.[12] The shaking table consists of a slightly inclined deck which is oscillated back and forth lengthwise at the same time as water is being forced to flow at right angles to the direction of the shaking. The vibration of the table is not a constant back and forth oscillation. Instead, the motion is a slow forward stroke followed by a rapid return. This type of oscillation forces the particles to crawl along the table parallel to the motion direction. The water flow at right angles to the table motion also affects the particle motion. For example, if the water feed rate and shaking motion force equalled one another, the particles would move diagonally across the deck from the feed end. However, the overall water effect on particle motion is dependent upon the size and density of the particles. The overall particle difference produces a fan distribution on the table. The fan shape is produced because the smaller, denser particles ride at the top of the table and move toward the concentrate end while the larger, lighter particles move toward the tailings end.

The shaking table action is also influenced by the velocity gradient in the water stream. The water velocity varies from zero at the surface of the table to a maximum value some distance away from the table. If particles are introduced into the flowing water, small particles will not travel as rapidly as large particles since they are immersed in the slower moving portion of the stream. Particles of high specific gravity will travel slower than light particles because they have greater weight which restricts movement. Thus, a lateral distribution of the material will be produced. This lateral distribution in effect separates coarse, light particles from small, dense particles.

The table riffles help separate fine sized and higher density particles from the other particles. The tapered riffles allow the coarse and light particles to be in contact with the flowing water while the finest and heaviest particles remain at the bottom, so that vertical stratification of the particles takes place. Through vertical stratification the lightest and coarsest particles are removed from the riffles.

Particle size plays an important role in table separation. When the minimum and maximum particle sizes vary greatly from the average particle size, the efficiency of separation decreases immensely. Thus, improper particle separation results in the feed. Better separation would be achieved in the feed material if the original sample was sized into various fractions. The improved separation is the result of the shaking table action of separating light particles from heavy.

Separation of the feed material is influenced also by the length of the stroke. A fine material requires a higher speed and shorter stroke than a coarse material. This setup causes particles to slide forward more and experience the effect of the riffles.

The table elevation along the line of motion from the feed end to the concentrate end helps particle separation. A moderate table slope allows the high density particles to climb more readily than the low density particles. Hence, a sharp split between the concentrate, middlings and tailings is achieved. The slope of the table is dependent upon the feed size. A very coarse, heavy gravity feed requires a very large table slope while a fine feed requires very little table slope. However, the slope of the table should always be greater than the taper of the riffles; otherwise the water flows around the riffles rather than over them.

A few problems were highlighted during the tabling of crushed computer circuit boards. Tabling was ineffective in producing a clean separation between the gold and the gangue material in the large fraction even though a large density difference existed between the two species. The lack of separation resulted from the incomplete liberation of gold from the ceramic and plastic components. These components reported to the middlings or tailings instead of to the concentrate. Therefore, tabling was not effective on the large fraction.

Tabling initially was a complete failure for the medium, small and tiny fractions. In these cases, the fiberglass and metal particles both reported to the tailings. This lack of separation was attributed to particle flotation, since both particle types floated on the water surface. Actually, most of the metallics floated on top of the fiberglass. Hydrophobicity is eliminated by wetting the surface of the fiberglass and metal fines.

Wetting agents employed were acetone, gasoline and dish soap. Acetone wets each individual particle by being absorbed. Absorption of acetone hinders its application due to economic reasons; acetone is quite expensive and hence would make concentration a costly process.

Gasoline is inexpensive relative to acetone but as a wetting agent it is less effective. Washing fiberglass and metal fines with gasoline causes agglomeration of the particles. Agglomeration is undesirable since clumps of particles cannot be separated by any gravity separation technique.

Dish soap effectively wets the fiberglass and metal surfaces. Wetting also causes the soap to absorb into the fiberglass, but this is not of concern since soap is inexpensive. After wetting, the crushed product is now amenable to tabling.

Upon tabling of the fine fractions, a concentrate consisted of mainly of base and precious metals with some fiberglass contamination. The middlings contained high amounts of fiberglass with some base and precious metals while the tailings consisted mainly of fiberglass fines. These separations were possible only with tabling the fractions a couple of times. This type of treatment resulted in a high loss of fiberglass and metallics from each fraction. For example, approximately 20% of the overall weight of the medium fraction was lost by water overflowing the containment pails which thereby caused fiberglass and the metallics to be carried along with the water. Hence, tabling was not practical for the medium, small and tiny fractions.

#### 4.3.4.2.2 Sink and Float

Sink and float is the simplest of all gravity processes.[12] The method employs heavy liquids of suitable density to separate metals and minerals of different specific gravity. Those metals lighter than the liquid will float while those denser than it will sink. Favourable circumstances for separation include liberation of the desired metals, coarse particle size and wide density difference. Without liberation, the desired metals are tied to the gangue minerals; therefore, separation is not possible. As the particle size decreases, the separation efficiency also decreases since smaller particles settle at a slower rate. Particles should be larger than about three millilitres in diameter, in which case separation is effective on a specific gravity difference of one-tenth of a point or less. Without a density difference, sink and float is inappropriate in separating metals from gangue minerals. However, materials of similar density are separated sharply with a high degree of efficiency with the proper particle size and amount of liberation.

Crushed computer circuit boards are not amenable to sink and float separation even though the material has a high degree of liberation and large density difference. The very small particles ranging in size from 75 μm (200 mesh) to 38 μm (400 mesh) settle at a rate too slow for effective separation. Another problem with sink and float separation is the use of heavy liquids. Most of these liquids are toxic or give off harmful vapours. For this reason, liquids on a commercial scale are not feasible.

### 4.3.4.2.3 Sedimentation

Sedimentation utilizes particle settling rate in a fluid medium to separate similar sized particles of differing densities.[12] For example, powder particles in a beaker are gently stirred to distribute the particles throughout the entire volume of water. In the case of crushed computer circuit boards, a wetting agent such as dish soap or dishwasher detergent is required to ensure sinkage and complete dispersion of the fiberglass particles. After complete dispersion, agitation is stopped and the pulp is allowed to stand for a designated time. The amount of time needed is calculated by Stokes' Law for the various sizes and densities of the powder particles. For silica particle sizes of 38 µm, 75 µm and 200 µm, settling times of 198.5, 51.0 and 7.17 seconds, respectively, are required for a distance of 25 cm. For a gold particle size of the same dimensions, settling times of 17.6, 4.5 and 0.6 seconds are required, respectively. As seen from these values, silica and gold particles will be separated for a short period of time depending upon the ore's particle size. In reality, a fraction of the silica exists below this specified distance since most of the material commenced settling from various positions below the water level. In order to remove these particles, several repetitions must be made. After the designated time, the water and silica particles above the specified distance are poured off. Pouring is conceptually wrong since settled sediment is also removed. A better method of water removal is achieved by the immersion of a syphon tube into the water to a depth h corresponding to about 90% of the liquid depth L. The lack of a syphon tube connected to a pump to achieve rapid filtration prevented application of this method.

### 4.3.5 No Preconcentration

The exploratory test on crushed computer circuit boards highlighted the problem of fiberglass fines absorbing the leach reagent. This problem is prevented by initially employing a wet gravity process to minimize the ore's fiberglass content before the leaching stage. Preconcentration, however, is not very effective since the only fraction containing minimal gold is the tailings. The other fractions, the concentrate and the middlings, represent approximately 75% of the ore and 99% of the gold. Further fiberglass reduction is possible by only considering the concentrate fraction, but this would cause a relatively high loss of gold from the middling fraction.

Upgrading of the crushed computer circuit boards is not required since sufficient amounts of gold relative to the fiberglass is present for straight leaching. Fiberglass, however, inhibits the success of leaching by absorbing the leach reagent, and this can be prevented by initially saturating the fines with water. As stated earlier, water does not wet the surface. Hence, a wetting agent is necessary. Dish soap is able to wet the surface of the fiberglass particles assuring absorption of water. Upon leaching, the absorbed soap caused the formation of foam which is undesirable. Thus, dish soap is inappropriate as a suitable wetting agent. Another soap agent, dishwasher soap, is a better wetting agent since it does not cause foaming. After surface wetting, the ore is ready for straight leaching.

For low grade ores, direct leaching with aqua regia is inappropriate. First, large quantities of reagent are required to dissolve the base and precious metals. This chemical treatment is quite expensive and thereby decreases the financial success of the operation. Second, the filtrate is contaminated with several base metals. Therefore, pretreatment is required to reduce the base metal impurities before gold is precipitated. Third, the precipitated gold purity is quite low and hence upgrading is required. These problems make it quite impractical for aqua regia to be used as a reagent for crushed computer circuit boards.

The best lixiviant for the recovery of gold from low grade ores is cyanide but its application to crushed computer circuit boards is hindered by the fact it is a poison and an environmental hazard. These problems are solved by elaborate containment procedures to limit the emission of cyanide into the water table and by expensive chemical treatment with chlorine or hydrogen peroxide to destroy the cyanide in solution. An advantage of cyanide is its inability in co-extracting base metals during leaching. The lack of base metal impurities in solution allows a high grade gold product to be precipitated. Since the disadvantages out weigh the advantages, this method will not be considered as a practical process for crushed computer circuit boards.

The lack of a suitable lixiviant for this ore type inhibited further work in this area.

## 4.4 Summary

Nitric acid leaching of as-received computer circuit boards containing either epoxy or silicone resin was conducted to optimize base metal dissolution, but, minimize fiberglass substrate decomposition. The conditions most favorable were: (1) acid concentration of 23% (one part nitric acid to two parts water), (2) temperature of 70°C, (3) pulp density - three millilitres of solution per gram of solid, and (4) retention time of one hour. These parameters ensured the complete dissolution of base metals, such as: copper, lead, nickel, tin and zinc, and the total separation of the computer chips from the fiberglass boards.

Previous processes developed for computer circuit boards employed concentrations of nitric acid between 30% and 67% at temperatures ranging from ambient to boiling for a time of one to sixteen hours, but, it was determined that at elevated temperatures, these acid strengths caused decomposition of the fiberglass substrate, which hindered separation of the chips from the developed fiberglass - resin clump. At temperatures below the favorable condition of 70°C, incomplete base metal dissolution occurred due to the formation of a porous iron oxide layer on the iron - nickel computer leads. This prevented complete computer chip separation from the fiberglass boards. Leach times above one hour hindered the operation since the fiberglass boards were inclined to decompose into a fiberglass - resin clump. Thus, these previous processes may have been suitable for their intended application, but, it has been determined that the listed process leach conditions are not favorable for epoxy or silicone coated computer circuit boards.

# Chapter 5

# Silver - Base Metal Separation

## 5.1 First Stage and Second Stage Solutions

The analysis of the first and second stage metal nitrate solutions, noted in Table 5.1, identified four major base metal constituents, a host of minor base metal impurities and a deficiency of precious metals. The four major base metals in both solutions were copper, iron, lead and nickel. The quantities of these elements in the first stage leach were approximately 15.4 g/L of copper, 1.7 g/L of iron, 2.3 g/L of lead and 2.2 g/L of nickel while the second stage leach contained 4.3 g/L of copper, 2.3 g/L of iron, 0.5 g/L of lead and 1.6 g/L of nickel. In both solutions, the base metal impurities: aluminum, chromium, magnesium, manganese, titanium and zinc, ranged from approximately 10 to 1000 mg/L depending upon the element and solution while the precious metals, gold, palladium and platinum, all varied between 1 and 5 mg/L.

The first leach % and second leach % columns in this table represent the percentage of a particular element incorporated in the 175 g computer circuit board sample and the 175 g crushed computer chip sample, respectively. For example, the percentage of copper in the first and second leaches was 8.7% and 2.4%, respectively. These values were attained by dividing the first or second leach copper concentration by their solution volume which in both cases was one litre. This value represents the amount of copper incorporated in the sample weight. The percentage was obtained by dividing the copper weight by the overall sample weight.

The high copper concentration justifies developing an extraction process for this element while the other three elements, iron, lead and nickel, are borderline for recovery based upon solution concentration. On a financial basis, the relatively high price per pound of nickel requires that this element be recovered either as an impure metallic sponge or compound while on an environmental standpoint, lead definitely requires recovery as well

**Table 5.1: Analysis of the base and precious metals incorporated in the first and second stage filtrate solutions.**

| Base Metals | | First Leach (mg/L) | First Leach (%) | Second Leach (mg/L) | Second Leach (%) |
|---|---|---|---|---|---|
| Aluminum | Al | 360 | 0.206 | 1110 | 0.634 |
| Chromium | Cr | 3 | 0.00171 | 4 | 0.00229 |
| Copper | Cu | 15350 | 8.771 | 4250 | 2.429 |
| Iron | Fe | 1700 | 0.971 | 2360 | 1.349 |
| Lead | Pb | 2300 | 1.314 | 500 | 0.286 |
| Magnesium | Mg | 110 | 0.0629 | 140 | 0.0800 |
| Manganese | Mn | 35 | 0.0200 | 165 | 0.0943 |
| Nickel | Ni | 2150 | 1.229 | 1570 | 0.897 |
| Tin | Sn | 0 | 0.000 | 0 | 0.000 |
| Titanium | Ti | 12 | 0.00686 | 15 | 0.0855 |
| Zinc | Zn | 535 | 0.306 | 300 | 0.171 |
| **Precious Metals** | | **First Leach (mg/L)** | **First Leach (%)** | **Second Leach (mg/L)** | **Second Leach (%)** |
| Gold | Au | 4.6 | 0.00263 | 1.8 | 0.00103 |
| Palladium | Pd | < 1.0 | < 0.00057 | < 1.0 | < 0.00057 |
| Platinum | Pt | < 2.5 | < 0.00143 | < 2.5 | < 0.00143 |
| Silver | Ag | 12.0 | 0.00686 | 23.0 | 0.0131 |

as all the other elements incorporated in computer circuit boards. The lack of gold, palladium and platinum in solution was desired since the first two leach stages were conducted to eliminate base metal impurities before precious metal recovery. The low amount of silver in solution was unforeseen since this metal is soluble in nitric acid. The only conclusion possible was an overall general lack of silver in the computer circuit boards selected for metal recovery. However, a recovery method will be proposed for this element since Reddy and Mishra[3] determined that computer scrap generally contains approximately 40 to 100 troy ounces of silver per ton of waste.

## 5.2 Silver Recovery

Silver extraction from a nitrate solution containing aluminum, copper, iron, lead, nickel, silver and zinc is easily performed by selective precipitation with either sodium chloride or sulfuric acid, or by selective cementation with copper powder, as shown in Figure 5.1. Selective precipitation with sodium chloride produces silver chloride which can be converted into metallic silver by one of four routes: (1) calcination process, (2) peroxygen process, (3) sulfide process or (4) zinc reduction process. Cement silver produced by metallic copper addition is an impure metallic silver product which can be further upgraded to a high purity silver product. Selective precipitation with sulfuric acid precipitates silver sulfate from solution which can be converted into metallic silver through hydrogen reduction.

### 5.2.1 Sodium Chloride Addition

At room temperature, silver removal from a nitrate solution is almost complete with the addition of a slight excess of chloride ions above the stoichiometric quantity. This anion amount is easily determined since the moles of silver ion in solution equals the moles of silver nitrate dissolved. The reaction between silver nitrate and sodium chloride:[36]

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$$

shows that the moles of silver chloride formed is limited by the moles of silver ion in solution and is therefore equal to the number of moles of silver nitrate. For example, a solution containing one gram of silver per litre would require 0.542 g of sodium chloride per litre of solution to carry out this precipitation. Since complete precipitation requires a slight excess of above 10% sodium chloride, 0.6 g of sodium chloride per litre is needed to maximize the amount of precipitate.[105]

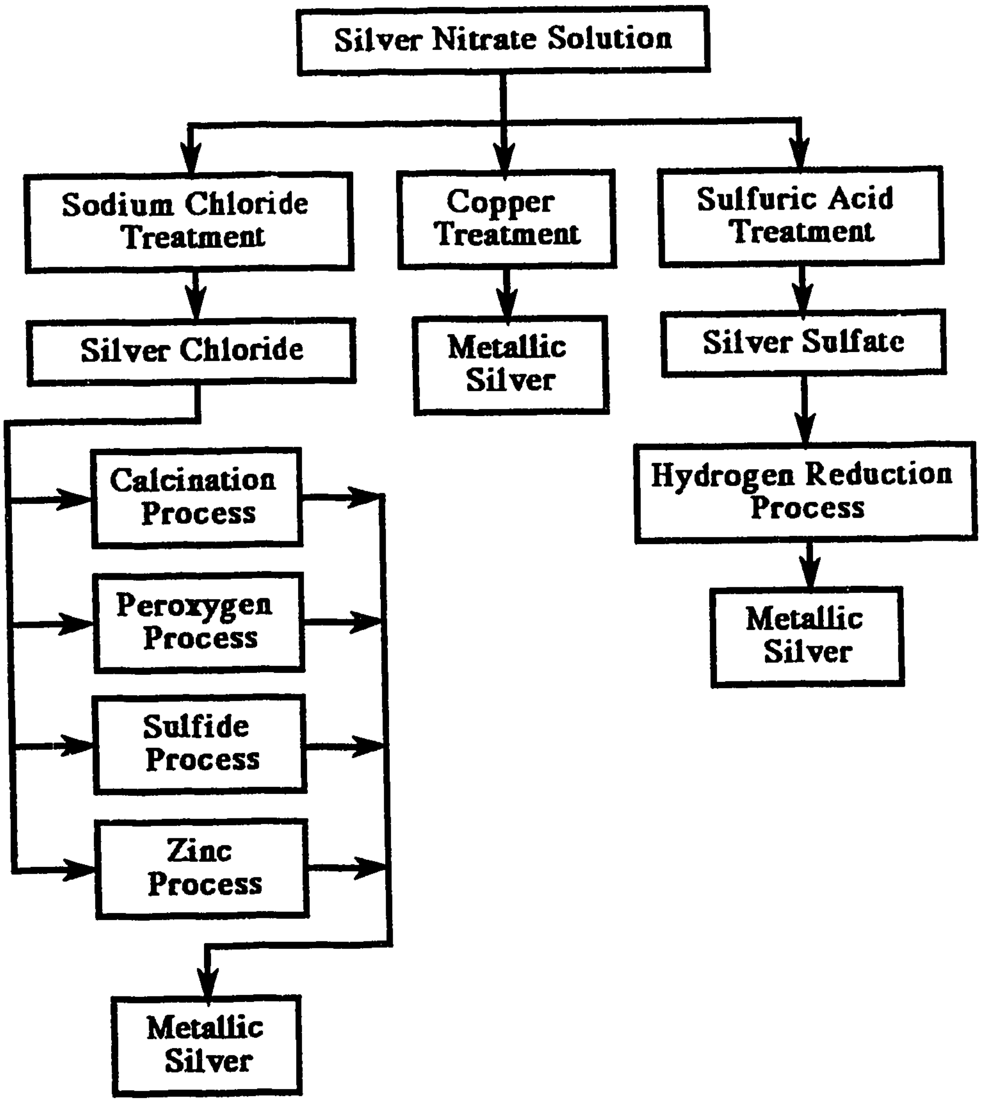

Figure 5.1: Process options for the recovery of metallic silver from a silver - base metal nitrate solution.

Upon sodium chloride addition, silver chloride is formed immediately as a white curdy precipitate suspended in solution.[106] During precipitation, agitation is necessary to ensure contact between the silver and chloride ions and to break up the formed silver chloride lumps into individual particles to reduce the amount of base metal impurities which can become entrapped in the silver chloride residue. After precipitation, the solution is checked for silver content before undergoing filtration. In silver checking, a small quantity of solution is removed from the overall bulk and placed into a test tube which is held in strong, direct sunlight while a few drops of hydrochloric acid is added. The presence of a white cloud of silver chloride at this stage implies that silver ions still exist in solution which means insufficient chloride species was employed for silver precipitation. This situation is remedied by adding extra sodium chloride to the bulk solution. After chloride addition, the solution is retested. The absence of silver chloride in the sample indicates the complete removal of silver from the bulk solution therefore the bulk solution can undergo solid - liquid separation. After filtration, the silver chloride cake is washed with water to remove the base metal impurities while the filtrate is transferred to base metal recovery. Entrapped impurities are removed by washing the silver chloride at least once with dilute or concentrated nitric acid to redissolve the base metals but not silver chloride since it is insoluble in this reagent. After acid washing, silver chloride is water washed to ensure complete removal of the base metal solution.

The cleaned silver chloride is checked for the presence of lead chloride.[106] In checking, a pinch of silver chloride is placed in a test tube and enough ammonium hydroxide is added to cover the solid's surface. In this medium, silver chloride solubilizes while lead chloride remains as a residue. If the solution is crystal clear, the silver chloride is of high fineness while if the solution is murky, the silver chloride must undergo cleaning with ammonium hydroxide. After cleaning, the filtered ammonium solution is doped with small increments of nitric acid to alter the solution pH to acidic. Once acidic, silver chloride is reprecipitated as a high fineness product.

#### 5.2.1.1 Calcination Process

Silver chloride is easily converted into metallic silver by calcination with sodium carbonate at a temperature in the range from 500°C to 650°C.[107] The stoichiometric requirement of sodium carbonate is one mole per every two moles of silver chloride, in accordance with the following reaction:

$$4\,AgCl + 2\,Na_2CO_3 \rightarrow 4\,Ag + 4\,NaCl + 2\,CO_2 + O_2.$$

On a weight basis, 370 g of sodium carbonate is required to convert 1000 g of silver chloride into metallic silver, but for complete reduction, at least a 100% stoichiometric excess of sodium carbonate is needed. This works out to be approximately three quarters of a gram of sodium carbonate per every gram of silver chloride. Before calcination, the silver chloride - sodium carbonate mixture is ground and mixed to ensure that the salts are in intimate contact. This is executed to increase the effectiveness of the sodium carbonate and to promote the reduction of silver. The solid state reaction is usually completed after one hour at these temperatures and the reaction products formed are elemental silver and sodium chloride. The silver product is generally obtained as a uncontaminated fine powder, however a hard sinter cake is possible at high temperatures and incomplete conversion at low temperatures. For this reason, the mixture is preferably heated at a temperature over 575°C to ensure completeness of reaction and below 625°C to lessen the likelihood of sintering. Silver chloride and any unreacted sodium carbonate are easily removed from the mixture by an ammonium hydroxide leach and a high temperature water wash at approximately 60°C, respectively. The other reaction products are carbon dioxide and oxygen which are of course harmless gases and thereby vented to the atmosphere.

After calcination at a temperature in the preferred range of 575° to 625°C, the silver - sodium chloride mixture is washed with water at 60°C to solubilize the sodium chloride. The filtered metallic silver residue is then resolubilized with nitric acid, and the formed silver nitrate is neutralized with ammonia according to the following reaction:[103]

$$AgNO_3 + NH_3 \rightarrow Ag(NH_3)NO_3.$$

The silver ammine nitrate is converted into a high purity metallic silver product by hydrogen reduction at a pressure of 1.47 MPa and a temperature of 150°C according to the following reaction:[103]

$$2\,Ag(NH_3)NO_3 + H_2 \rightarrow 2\,Ag + 2\,NH_4NO_3.$$

After filtration, the metallic silver is water washed and dried while the ammonium nitrate solution is evaporated to produce fertilizer. This process scheme for the conversion of silver chloride into a high purity metallic silver product is shown in Figure 5.2.

#### 5.2.1.2 Peroxygen Process

Silver chloride can be converted into silver metal by a two step process consisting of silver oxide formation and decomposition, as shown in Figure 5.3. Silver oxide is produced by immersing the silver chloride salt in a potassium hydroxide solution which is represented by the following reaction:[36]

$$2\,AgCl + 2\,KOH \rightarrow Ag_2O + 2\,KCl + H_2O.$$

Conversion of silver oxide to metallic silver is then achieved by using peroxygens, particularly hydrogen peroxide. This peroxygen is a very strong and rapid oxidant, and for this reason, elevated temperatures are generally not required to increase the effectiveness of the reaction.[108] The high rate of reactivity produces a large degree of selectivity; rapid-reacting oxidants do not oxidize high oxidation state metals to any degree. The complexes formed from the metal - peroxygen reaction change the relative solubility of the metal itself. This effect causes the metal either to become more soluble or to precipitate. In the case of silver oxide, hydrogen peroxide causes silver metal to precipitate by the following reaction:[36]

$$2\,AgCl + H_2O_2 + 2\,KOH \rightarrow 2\,Ag + 2\,KCl + 2\,H_2O + O_2.$$

After precipitation, the metallic silver is separated from the potassium chloride solution by filtration, water washed, dried and then analyzed for percent conversion.

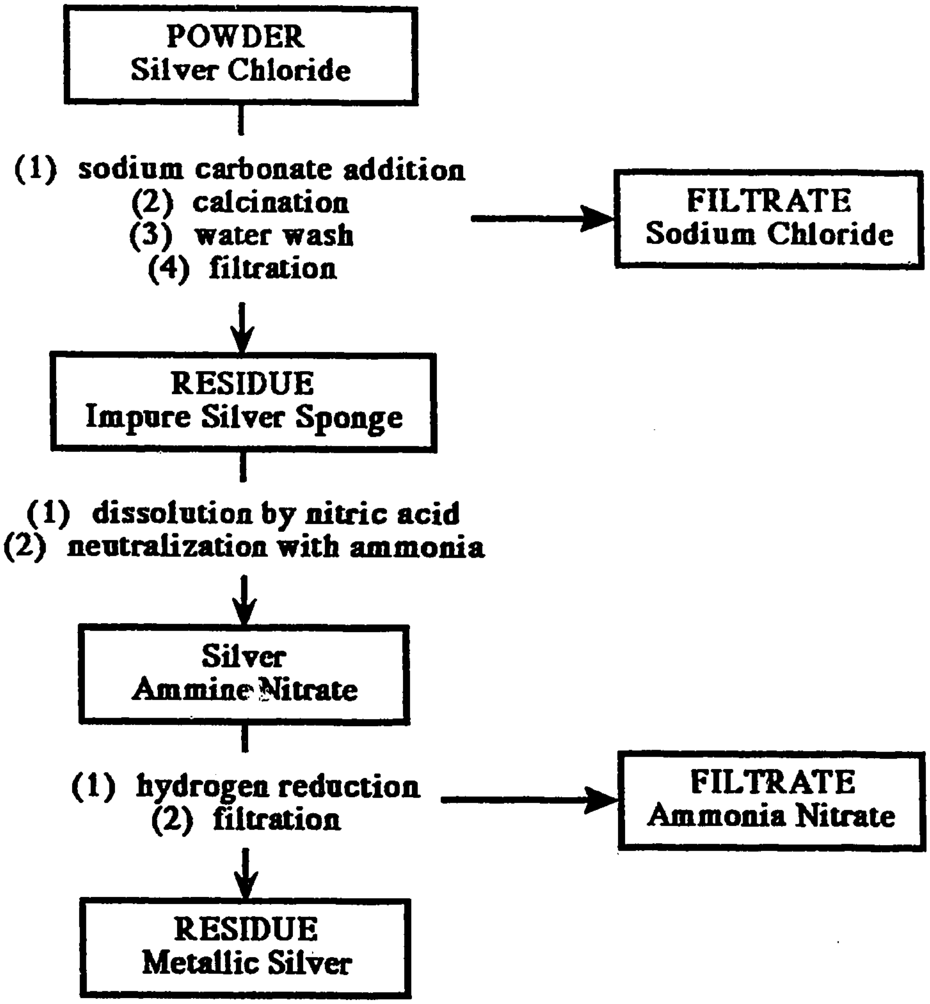

Figure 5.2: Conversion of silver chloride to metallic silver by the Calcination process.

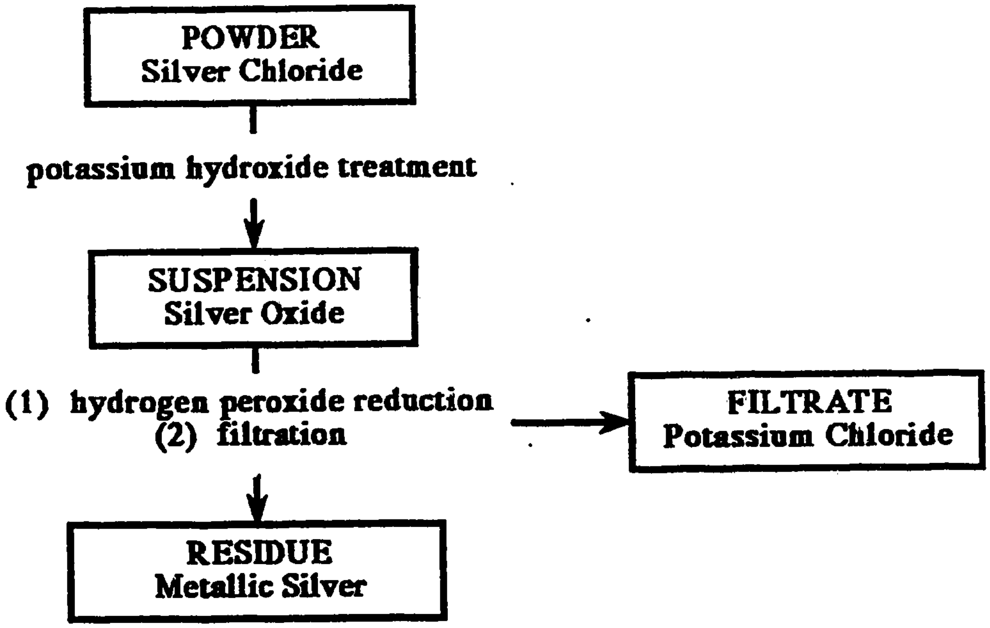

Figure 5.3: Conversion of silver chloride to metallic silver by the Peroxygen process.

The conversion of silver chloride to metallic silver was undertaken in two stages. In the first stage, the optimum conditions for silver oxide formation was identified by initially charging a 250 mL Pyrex beaker with 100 mL of water and a calculated quantity of potassium hydroxide per gram of silver chloride which varied between the stoichiometric quantity, 0.391 g, to a level fifty times above the stoichiometric requirement, 19.55 g. After charging, the solution was stirred with a magnetic spin bar to dissolve the pellets of potassium hydroxide and to ensure solution uniformity. Upon complete solubilization, one gram of silver chloride powder at a particle size below 425 µm was added to the solution. Very small particle sizes were difficult to achieve with this compound since the material clumps together on crushing. This mixture was then stirred for 15 minutes to convert the silver chloride to silver oxide. After this time, the precipitate was separated from the potassium chloride by filtration, dried and then analyzed for percent conversion.

The most favourable conditions for silver oxide formation were then employed in metallic silver precipitation. In this second stage, the potassium chloride solution containing the silver oxide precipitate was again stirred with a magnetic spin bar to ensure solution uniformity during the slow injection of hydrogen peroxide. The amount of hydrogen peroxide used for the precipitation of metallic silver was 1, 2.5, 5, and 10 mL. During the conversion reaction between silver oxide and hydrogen peroxide, excessive frothing occurred as a result of the release of oxygen while the temperature of the solution rose approximately 15°C due to the exothermic nature of this reaction. As the reaction proceeded, oxygen evolution peaked and then subsided once the specified amount of hydrogen peroxide was completely injected. This reduction coincided with the total decomposition of the froth head. On completion of the test, the charge was cooled, filtered and washed with distilled water. The silver product was then analyzed for percent conversion to metallic silver.

The conversion of silver chloride to silver oxide by a potassium hydroxide solution was dependent upon the molar ratio of potassium hydroxide to silver chloride and the particle size of silver chloride. At the stoichiometric quantity, 0.391 g of potassium hydroxide per gram of silver chloride, no conversion of silver chloride to silver oxide occurred since the solution was deficient in hydroxide ions to undertake the conversion reaction. This insufficient quantity of hydroxide ions remained until a potassium hydroxide to silver chloride molar ratio of fifteen to one, as shown in Figure 5.4. Above this molar ratio, silver chloride converted to some degree to silver oxide since an adequate amount of hydroxide ions existed in solution for oxide formation. At a potassium hydroxide to silver chloride molar ratio of twenty to one, only 15% of the overall quantity of silver chloride converted to silver oxide. This low percentage conversion represented a change in the outer shell of the silver chloride particle to silver oxide but not the internal core. The percent conversion increased dramatically above this molar ratio since the hydroxide ions absorbed into the internal silver chloride core causing further oxide formation. At a potassium hydroxide to silver chloride molar ratio of twenty five to one, 60% of silver chloride converted to silver oxide. Above a potassium hydroxide to silver chloride ratio of thirty to one, further percent conversion was limited since over 85% of the original compound was changed to silver oxide. Molar ratios above forty to one converted over 98% of silver chloride to silver oxide but excessive amounts of potassium hydroxide were required to carry out this action.

The particle size of silver chloride is a contributing factor in the percent conversion of silver chloride to silver oxide. Large particles inhibit conversion because the converted shell prevents absorption of the hydroxide ions into the central core of the particle as the oxide layer increases in thickness. This problem was minimizing the largest particle diameter to 425 µm. At this diameter, sufficient oxide formation occurred at the potassium hydroxide to silver oxide molar ratio of twenty five to one. Smaller particle sizes were difficult to achieve with this compound since the material clumps together on crushing and grinding. Better control of the particle size can be attained by avoiding the drying stage after silver chloride formation from a silver nitrate solution by sodium chloride. In this case, the fine silver chloride particles remain intact as a wet slurry.

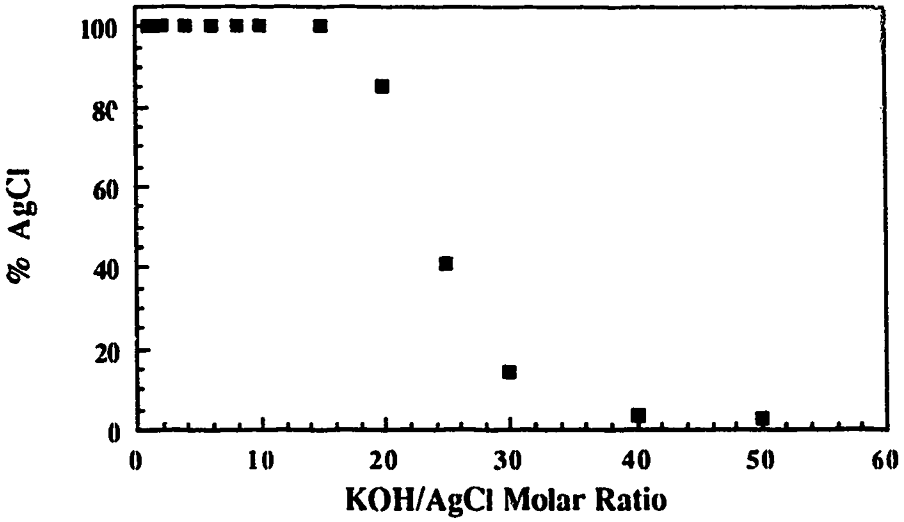

**Figure 5.4: Effect of potassium hydroxide quantity on the conversion of silver chloride to silver oxide.**

The only molar ratio that provided enough hydroxide ions in solution without an oversupply of potassium hydroxide in relation to the chloride silver salt was twenty five to one. On a weight basis, 9.775 g of potassium hydroxide is required to convert approximately half of the one gram sample weight of silver chloride to silver oxide. This molar ratio was therefore selected to carry out the second step, oxide decomposition, in the silver chloride to metallic silver conversion process.

The conversion of silver oxide to metallic silver was dependent upon the amount of hydrogen peroxide. At an addition of one millilitre of hydrogen peroxide, 89% of the suspended silver oxide shell - silver chloride inner core particulate matter converted to metallic silver, as shown in Figure 5.5. This exceeds the amount of silver oxide present in the suspension since from previous tests at a potassium hydroxide to silver chloride molar ratio of twenty five to one only 60% of the original amount of silver chloride converted to silver oxide. The discrepancy between the two figures resulted since as the outer core converted to metallic silver it flaked off the particle thereby allowing the inner silver chloride core to be further converted by the hydroxide solution to silver oxide. As the reduction process continued, any converted silver chloride to silver oxide was consequently altered to metallic silver. After the hydrogen peroxide was spent, further conversion of silver oxide to metallic silver was prohibited. At a hydrogen peroxide addition of two and a half millilitres, metallic silver formation was increased to 96% since the decomposition reaction lasted for a longer period of time. Presence of a plateau after this hydrogen peroxide quantity indicated that complete metallic silver formation from this silver compound was not achievable without excessive volumes of hydrogen peroxide. The maximum conversion obtained, 98%, was obtained at a hydrogen peroxide addition of ten millilitres.

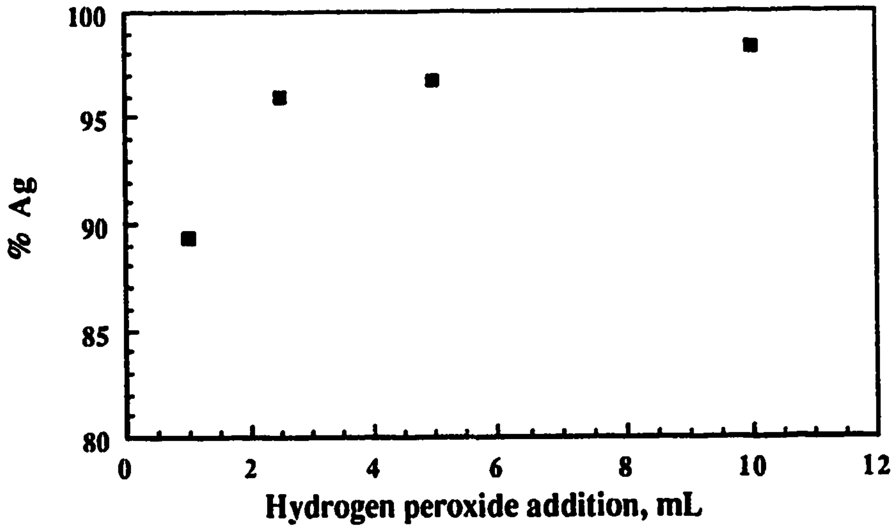

**Figure 5.5: Effect of hydrogen peroxide quantity on the conversion of silver oxide to metallic silver.**

#### 5.2.1.3 Sulfide Process

Silver chloride is easily converted into silver sulfide by reaction with ammonium sulfide at room temperature in an alkaline solution.[103] This conversion is almost complete in the presence of strong agitation which breaks up the lumps of silver chloride and with stoichiometric amounts of sulfide ions in solution. The following reaction shows that two

$$2\,AgCl + (NH_4)_2S \rightarrow Ag_2S + 2\,NH_4Cl.$$

moles of silver chloride react with one mole of ammonium sulfide. On a weight basis, 1000 g of silver chloride requires 250 g of ammonium sulfide. During conversion, the temperature of the solution rose approximately 40°C due to the exothermic nature of the reaction while an alkaline solution is essential to prevent the evolution of hydrogen sulfide gas.

The production of elemental silver from this silver compound can be undertaken by either the Kunda process or the Calcination process. The Kunda process achieves conversion through a sequence of steps which comprise of : (1) oxidation of silver sulfide to silver sulfate, (2) dissolution of silver sulfate in ammonia, (3) reduction of silver ammine sulfate solution with hydrogen, and (4) casting of silver bullion; where as, the Calcination process transforms the compound to elemental form by a solid state reaction at high temperature with sodium carbonate.[103,109]

### 5.2.1.3.1 Kunda Process

Before metallic silver can be produced by the Kunda process, as shown in Figure 5.6, silver sulfide must be converted into an amenable compound such as silver ammine sulfate. The formation of this compound is undertaken by first converting the silver sulfide to silver sulfate by oxidation in an autoclave. The autoclave charge consisted of silver sulfide, water, nitric acid and sulfuric acid. The two acids provided only the leach medium, with oxidation occurring by the following reaction:[103]

$$Ag_2S + 2\,O_2 \rightarrow Ag_2SO_4.$$

Since silver sulfate is partially soluble in nitric acid, the small amount of silver nitrate formed is reverted back to silver sulfate with additional sulfuric acid. The conversion rate

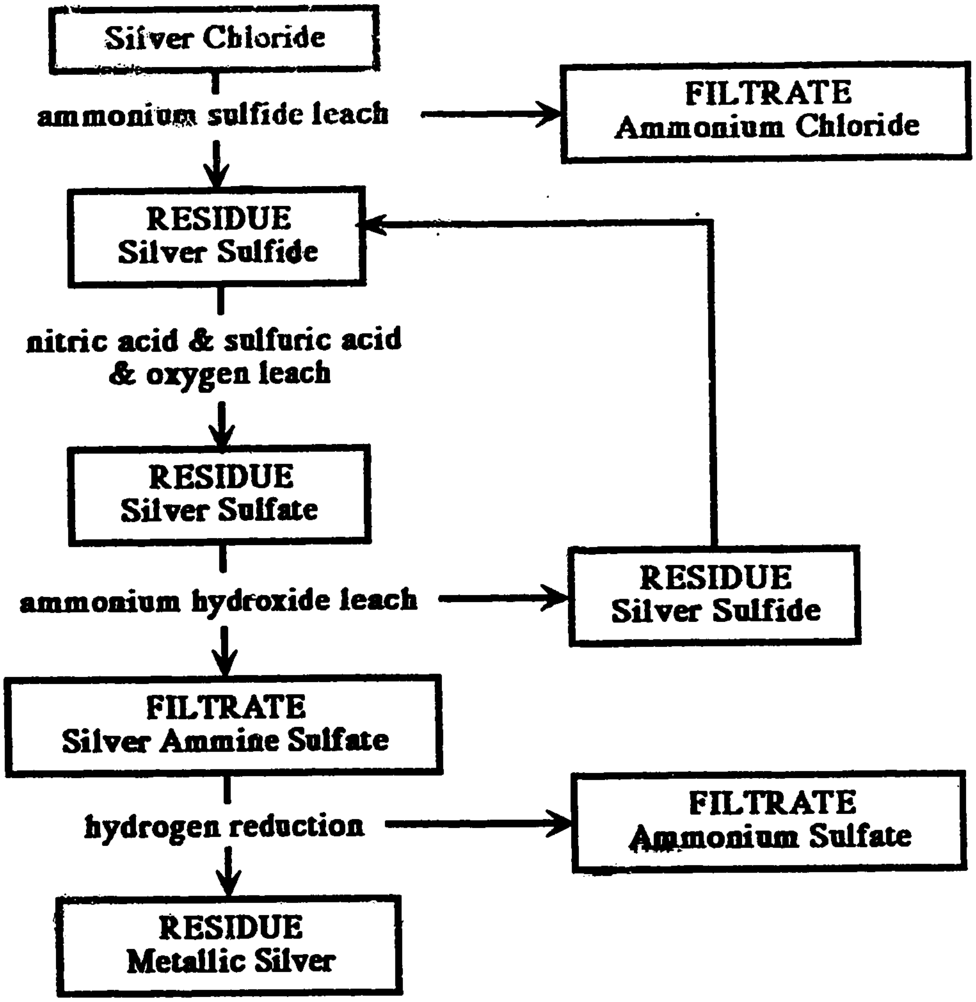

Figure 5.6: Conversion of silver chloride to metallic silver by the Kunda process.

for this method is approximately 90%. The unconverted silver sulfide is then included in the ammonia leaching step below.

The silver sulfate - silver sulfide precipitate next underwent ammonium hydroxide leaching at room temperature to separate the soluble silver sulfate from the insoluble silver sulfide, and to convert silver sulfate into a species amenable for hydrogen reduction.[103] During leaching, rigid control of the quantity of ammonia in solution is required to ensure the neutralization of entrapped acids in the residue, dissolution of silver sulfate, and avoidance in the reduction of silver ammine sulfate solubility. At an ammonia to silver molar ratio of one to two the silver concentration in solution is 250 g/L while at an ammonia to silver molar ratio of two to one the silver concentration is only 165 g/L.[103] After solid - liquid separation, the residue is recycled to the silver sulfide conversion stage while the filtrate is hydrogen reduced.

Metallic silver is produced from silver ammine sulfate by reducing the silver ammine complex in an autoclave at a hydrogen pressure of 1.47 MPa and a temperature of 125°C.[103] This reduction is represented by the following reaction:

$$[Ag(NH_3)]_2SO_4 + H_2 \rightarrow 2\,Ag + (NH_4)_2SO_4.$$

however, incomplete reduction is only achieved since a small portion of the sulfate complex precipitated out of solution as silver sulfate. After filtration, the metallic silver is water washed and dried while the ammonium sulfate solution is evaporated to produce fertilizer.

### 5.2.1.3.2 Calcination Process

The conversion of silver sulfide to metallic silver by the Sulfide Kunda process produces high purity silver by a cumbersome, time consuming process. An easier method of conversion is by calcination of the silver sulfide with sodium carbonate. This conversion to metallic silver probably proceeds by a two step process consisting of an oxidation roast and decomposition.[110] Before roasting, the silver sulfide - sodium carbonate mixture is ground and mixed to ensure that the salts are in intimate contact which increases the effectiveness of the sodium carbonate and promotes the reduction of silver.[109] The solid state reaction converted silver sulfide to silver sulfate rather than silver oxide, as shown by the following reaction:[110]

$$Ag_2S + O_2 \rightarrow Ag_2SO_4.$$

During roasting, the temperature of reaction is presumed to be high enough everywhere in the silver sulfide ore to allow the above desired chemical reaction to occur at a fairly early stage in the process. Each silver sulfide particle is oxidized from the outside so that initially an inner unchanged sulfide core and an outer sulfate shell exist. As the roast reaction continues, further conversion of the inner sulfide core is made possible by the diffusion of oxygen from the atmosphere to the reaction interface. After conversion, the formed silver sulfate is then decomposed to metallic silver, as shown by the following reaction mechanism:[110]

$$2\,Ag_2SO_4 + 2\,Na_2CO_3 \rightarrow 4\,Ag + 2\,Na_2SO_4 + 2\,CO_2 + O_2.$$

The stoichiometric requirement of sodium carbonate is one mole per every mole of silver sulfide. On a weight basis, 428 grams of sodium carbonate is required to convert 1000 grams of silver sulfide into metallic silver. After calcination, the silver - sodium sulfate mixture is washed with warm water to solubilize the sodium sulfate. This process scheme for the conversion of silver sulfide into metallic silver is shown in Figure 5.7.

The silver sulfide salt was prepared by two methods: (a) precipitation of silver sulfide from a spent photographic fixer solution by addition of sodium hydrosulfide, and (b) purchase of three nine purity silver sulfide from Johnson Matthey. The first silver sulfide salt listed was used for the majority of tests in this study while the second salt was used as a check of the results obtained from the first method.

Silver recovery from the spent fixer solution used to develop various types of photographic films, including black and white, color and x-ray films was conducted to exploit the availability of a cheap source of silver. The fixer solution based upon sodium thiosulfate is used in industry to dissolve the residual silver halides (AgCl, AgBr, and AgI)

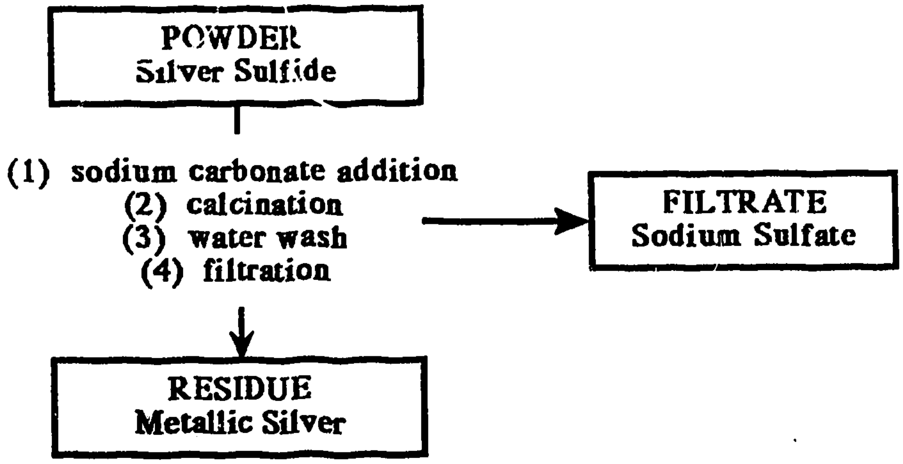

Figure 5.7: Conversion of silver sulfide to metallic silver by the Calcination process.

from the photographic film. The reaction between these two compounds produced a complex silver-sodium thiosulfate ($AgNaS_2O_3$) solution.

Silver is removed from this complex at ambient temperature and pressure by using sodium hydrosulfide which is available as a concentrate solution or a hydrate salt.[111] The 47.5% concentrate solution and the hydrated salt in the form of NaHS - 0.89 $H_2O$ are both readily diluted in water to the desired solution concentration of two molar. Upon reaction between the thiosulfate complex solution and hydrosulfide, silver sulfide is produced. In this particular solution, the silver sulfide is not soluble; hence it immediately precipitated out of solution. The suggested chemical reaction representing this phenomenon is listed as follows:

$$2\,AgNaS_2O_3 + NaHS \rightarrow Ag_2S + Na_2S_2O_3 + NaHS_2O_3.$$

Sodium hydrosulfide preferentially reacts only with the thiosulfate complex and not in any appreciable manner with the other components of the fixer solution, such as sodium sulfite, acetic acid, potassium aluminum sulfate and boric acid.[111] However, sodium hydrosulfide also reacts with sodium thiosulfate to produce elemental sulfur which is undesirable. This reaction is minimized by controlling the quantity of hydrosulfide used in precipitating silver so that the desired reaction is only completed. Minimal degradation of thiosulfate occurred by using approximately one-half to one mole of sodium hydrosulfide per one mole of silver in the fixer solution. An excess of over one mole of hydrosulfide produced prevalent degradation of thiosulfate.

Other parameters, which influence the effectiveness of the process, were the rate of introduction of sodium hydrosulfide to the fixer solution, the degree of agitation of the solution, and the acidity of the spent fixer solution prior to treatment.[111] The introduction rate of sodium hydrosulfide was at a relatively slow rate to prevent the evolution of hydrogen sulfide gas into the environment. Slow addition hindered the reaction between sodium hydrosulfide and sodium thiosulfate thereby avoiding the formation of elemental sulfur. Agitation also minimized the degradation of the thiosulfate by creating sufficient solution mixing which eliminated any pockets of high concentration of sodium hydrosulfide and ensured that the preferential reaction with the silver complex proceeded. The solution acidity was above a pH of five to prevent the formation of hydrogen sulfide gas which affects the precipitation of silver from solution.

In the calcination process, a porcelain boat was initially charged with a calculated quantity of silver sulfide and sodium carbonate. The quantity of sodium carbonate selected was between the stoichiometric quantity to a level above or below two times the stoichiometric requirement. Before charging, these components were crushed and mixed together to ensure intimate contact between the two species. This was conducted to increase the effectiveness of the sodium carbonate and to promote the reduction of silver. The particle size of silver sulfide and sodium carbonate employed in these trials was less than 208 μm (65 mesh) and 425 μm (35 mesh), respectively. Upon charging with two grams of silver sulfide and a predetermined amount of sodium carbonate, the porcelain boat was placed in a preheated muffle furnace at a specified temperature in the range of 450° to 650°C. On completion of the test, the treated charge was cooled, pulverized and washed two or three times with water at 60°C to remove the formed sodium sulfate salt and the unreacted sodium carbonate. The silver product was then dried and analyzed for percent conversion.

A series of experiments with two grams of silver sulfide and a varying quantity of sodium carbonate between a level above or below two times the stoichiometric quantity was conducted at 650°C for a reaction time of four hours to determine the dependency of sulfide conversion to elemental form on the carbonate amount. As seen in Figure 5.8, almost 100% of the silver sulfide converted to metallic silver at all sodium carbonate to silver sulfide molar ratios tested. Even though complete conversion resulted, an undesirable form of metallic silver, hard sinter cake, co-existed with the desired fine particulate metallic powder at molar ratios below 2.05:1. This cake form of silver diminished the overall purity of the silver product since it contained a relatively high sodium sulfate impurity level.

Above this molar ratio, no hard sinter cake existed in the silver powder. Another detriment to the conversion process was the insufficient removal of sulfur dioxide. This resulted at molar ratios below 0.94:1 since insufficient sodium carbonate existed in the starting mixture to scavenge all the sulfur dioxide produced during the decomposition of silver sulfide.

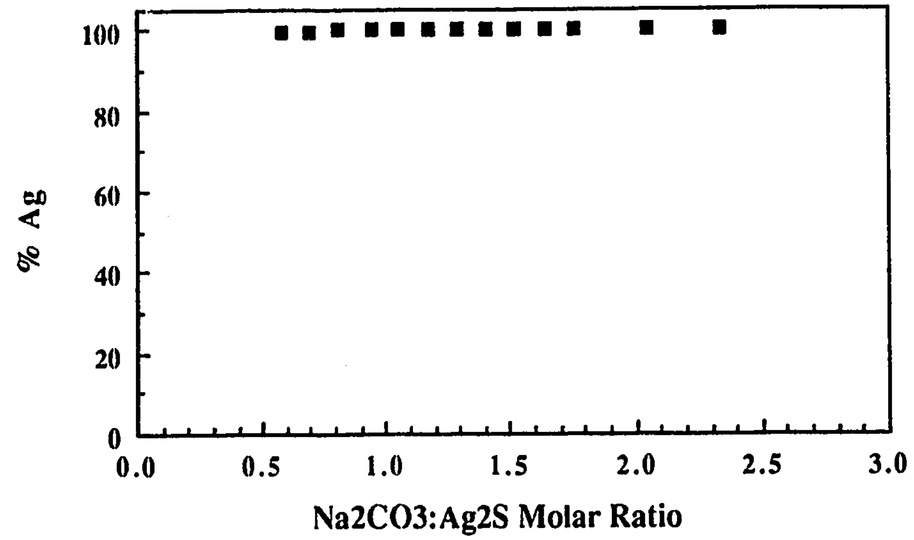

**Figure 5.8:** **The effect of sodium carbonate to silver sulfide molar ratio on the conversion of silver sulfide to metallic silver for a temperature of 650ºC and a reaction time of 4 hours.**

The reaction temperature necessary for at least 99% conversion of silver sulfide to metallic silver in four hours was determined by varying the temperature between 450° and 650°C for the following sodium carbonate to silver sulfide molar ratios: 0.94:1, 1.40:1, 1.75:1, and 2.34:1. At 450°C, the solid state reaction between silver sulfide and sodium carbonate occurred at too slow a rate to entice complete formation of elemental silver. Instead, conversion ranged from a low of 60% at a molar ratio of 0.94:1 to a high of 70% at a molar ratio of 1.75:1, as seen in Figure 5.9. At this temperature, incomplete scavenging of the formed sulfur dioxide resulted since a strong, pungent odor was prevalent throughout the first hour of reaction. The minimum temperature required for complete silver conversion was 500°C for all the molar ratios except for 2.34:1. At this ratio, only 98.5% of the silver sulfide converted to metallic silver. The preferred temperature range was between 550° and 600°C since at all molar ratios tested, complete conversion resulted. At 650°C, complete conversion also occurred but the silver product was contaminated with a hard silver sinter cake containing a high impurity level of sodium sulfate. From the above analysis, it was concluded that the desulfurization of silver sulfide was very temperature dependent.

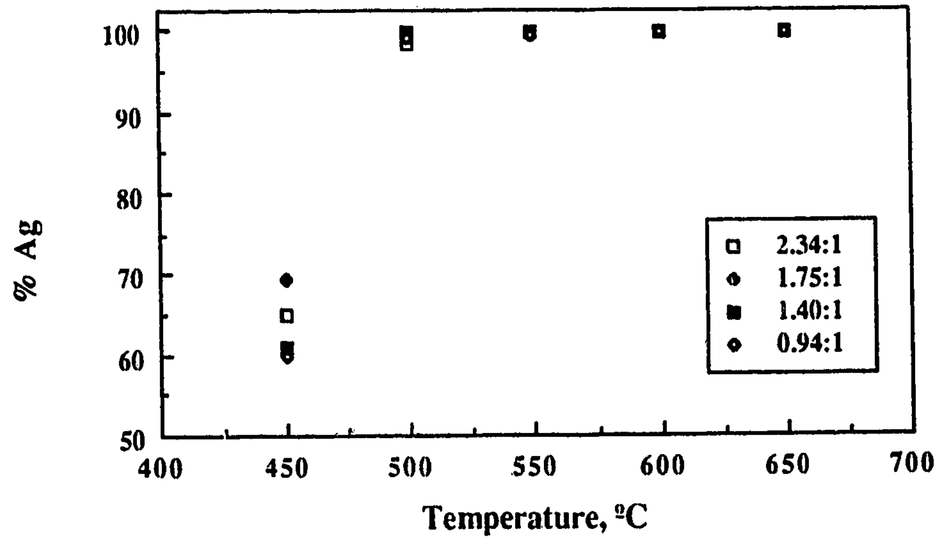

**Figure 5.9:** **The effect of temperature on the conversion of silver sulfide to metallic silver for the following sodium carbonate to silver sulfide molar ratios: 0.94:1, 1.40:1, 1.75:1, and 2.34:1.**

A series of experiments were undertaken on a sodium carbonate to silver sulfide molar ratio of 1.40:1 at 600°C to determine the reaction time required to convert 99% of the silver sulfide to metallic silver. As seen from Figure 5.10, at least three hours were required for complete conversion to metallic silver. Below this time, a mixture of silver sulfide and metallic silver was existent in the reaction product.

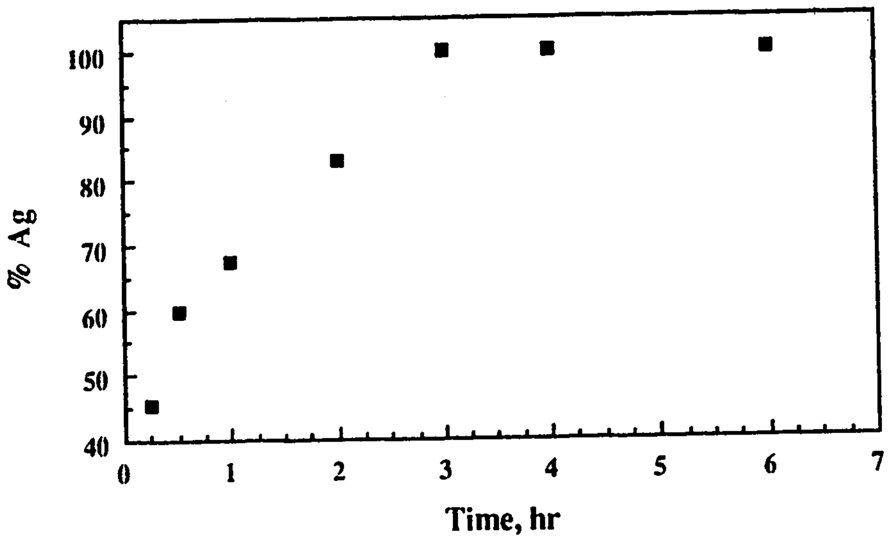

**Figure 5.10:** The effect of time on the conversion of silver sulfide to metallic silver for a sodium carbonate to silver sulfide molar ratio of 1.40:1 reacted at 600ºC.

From these trials, it was determined that elemental silver in the form of fine powder can be produced by mixing silver sulfide with sodium carbonate, and heating the mixture in the range of 550° to 600°C to effect a solid state reaction. Sodium sulfate was also produced during this reaction. These two species formed by the following oxidation reactions:

$$Ag_2S + O_2 \rightarrow 2\,Ag + SO_2.$$

$$2\,SO_2 + 2\,Na_2CO_3 + O_2 \rightarrow 2\,Na_2SO_4 + CO_2.$$

The other reaction products formed were carbon dioxide and oxygen which are of course harmless gases. Stoichiometrically, it would have been expected that one mole of sodium carbonate would have been sufficient for one mole of silver sulfide. However, it was found that a sodium carbonate to silver sulfide molar ratio required to ensure completeness of reaction was between 1.40:1 and 1.75:1. Below a temperature of 550°C, the possibility of incompleteness for the conversion reaction is increased while above a temperature of 600°C, the likelihood of sintering is increased. Finally, the reaction was found to be substantially complete under these conditions in about three hours.

### 5.2.1.4 Zinc Reduction Process

The reduction of silver chloride to metallic silver with zinc is a relatively simple operation which minimizes the loss of silver.[106] Silver chloride is placed in a shallow Pyrex pan along with a mixture containing one part sulfuric acid and twenty parts water. This pan is consequently immersed in a heated sand bath to ensure a uniform temperature of 40°C throughout the sample. Upon temperature stabilization, zinc in the form of powder, shot or foil is added to these constituents. As zinc dissolves, giving off hydrogen bubbles, the silver chloride in contact with the dissolving species is reduced to metallic silver. At this point, heating is discontinued. Complete reduction to metallic silver is assured through solution agitation since every particle of silver chloride is contacted by the dissolving zinc. This reduction requires 0.25 to 0.5 g of zinc and 0.5 g of concentrated sulfuric acid to reduce one gram of silver chloride. After reduction, the solid residue is submitted to cleaning while the filtrate is discarded. Metallic silver is cleaned of undissolved zinc by washing the residue in one part hydrochloric acid and twenty parts water. After filtration, the metallic silver is water washed, dried, melted with flux (soda ash, borax, and lead - free glass in equal volumes), and cast into a silver ingot.

### 5.2.2 Copper Addition

The recovery of silver from a pregnant leach solution is easily undertaken by cementation, the transfer of electrons between a dissolving agent and the precipitating silver. The advantage of copper addition over sodium chloride addition is the precipitation of palladium and avoidance of lead salt precipitation.[91] When copper is immersed in an aqueous nitrate solution containing silver ions, the copper tends to enter solution while the metallic silver tends to precipitate. Silver cementation is described by the following reaction:

$$Cu + 2\,Ag^{+} \rightarrow Cu^{2+} + 2\,Ag$$

This reaction states that one mole of copper should precipitate two moles of silver, which is equivalent to 0.29 g of copper per gram of silver. The cement silver product is of low purity due to contamination by copper and palladium. The copper impurity is removed by a two step process consisting of cement silver dissolution with nitric acid followed by silver precipitation with sodium chloride.[91] After precipitation, the silver product is separated from the metal nitrate solution by filtration and then water washed. Entrapped impurities are removed by washing the silver chloride at least once with dilute or concentrated nitric acid to redissolve the base metals but not silver chloride since it is insoluble in this reagent. After acid washing, silver chloride is water washed to ensure removal of the base metal solution. This process is continued until the purity of the silver product is at a silver fineness of 99. At this point, silver chloride is converted to metallic silver by one of the processes described earlier while the remaining liquor is treated further for base metal recovery.

### 5.2.3 Sulfuric Acid Addition

Scrap computer circuit boards were treated with nitric acid and the resulting suspension containing dissolved metal nitrates and solid particles of gold and tin oxide underwent solid - liquid separation. The resulting filtrate was consequently acidified with sulfuric acid to convert the metal nitrates in solution into metal sulfates. According to Loebel and Meissner[80], conversion is complete at a solution to sulfuric acid ratio of 2.5:1. Upon addition of this desired amount of sulfuric acid, the solution temperature increased from room to 65°C due to the exothermic reaction produced between the two chemicals. Once the nitrate solution is converted to a sulfate solution, lead sulfate is immediately precipitated. According to Hilliard *et al.* [68] silver is precipitated also out of solution but only incompletely. Other sulfates, such as copper, nickel and iron, only precipitate out of solution when the solubility product of these sulfates is surpassed. This is usually accomplished upon reduction of the solution volume through heating or addition of sufficient quantities of sulfuric acid to produce a solid cake. Separation of lead and silver sulfate from the other sulfates is possible through a water leach since lead and silver sulfate are insoluble in this medium while the other sulfates are not.

Silver sulfate is converted to metallic silver by a two step process comprising of an ammonium hydroxide leach followed by hydrogen reduction. In leaching, silver sulfate is solubilized by ammonium hydroxide thereby forming silver ammine sulfate. This silver species is reduced to metallic silver in an autoclave at a hydrogen pressure of 1.47 MPa and a temperature of 125°C.[103] After filtration, the metallic silver is water washed to remove any soluble impurities while the ammonium sulfate solution is evaporated to produce fertilizer.

## 5.3 Base Metal Recovery

The silver free metal nitrate solution contains four major elements: copper, iron, lead and nickel, and a multitude of impurities: aluminum, magnesium, manganese, titanium and zinc. Of these elements, copper, lead and nickel will be recovered as an impure metal or compound while the other constituents will be neutralized from the leach solution as a solid residue. The order of base metal extraction from the nitrate solution is dependent upon the process mechanism selected for individual metal segregation. Nemes *et al.* [85] recovered copper from a complex nitrate solution initially by treating the solution with iron scrap to cement an impure copper product. After copper extraction, the solution acidity was adjusted first to 4-5 then to 9.5-10.5 with calcium hydroxide to selectively precipitate iron hydroxide and nickel hydroxide, respectively. Loebel's and Meissner's[82] approach to the complex nitrate solution was to precipitate lead first as lead sulfate by addition of sulfuric acid at a solution to acid ratio of 2.5:1 before copper was recovered by electrolytic refining. Hill and Lear[40] also recovered lead as the initial precipitate from a metal nitrate solution but in this case, a chloride species was added to the solution to precipitate lead chloride. From these metal extraction schemes, it is obvious that either lead or copper will be recovered first while nickel will be recovered last. After extraction of these desired metals, the solution will be doped with a hydroxide species to precipitate all the impurities remaining in solution as a stable hydroxide solid residue mixture.

## 5.3.1 Copper Recovery

### 5.3.1.1 Background Information

The recovery of copper from a pregnant leach solution is easily undertaken by cementation with the electrons of the dissolving agent being transferred to the precipitating copper. Cementation agents commonly used are aluminum, iron and zinc; iron being the economically practical choice. When iron is immersed in an aqueous solution containing copper ions, the iron tends to enter solution while metallic copper tends to precipitate. The major steps incorporating this reaction are: (1) diffusion of copper ions to the iron surface, (2) adsorption of copper ions on the surface, (3) chemical reaction at the surface, (4) desorption of iron ions from the surface, and (5) diffusion of iron ions away from the surface.[112] The overall reaction rate is dependent upon the slowest step amongst these; hence, the reaction can be either diffusion or chemically controlled. Copper cementation is described by the following reaction:[113]

$$Fe + Cu^{2+} \rightarrow Cu + Fe^{2+}$$

This reaction states that one mole of iron (55.85 g) should theoretically precipitate one mole of copper (63.54 g), which is equivalent to 0.88 g of iron per gram of copper. In actual practice, the amount of iron required for copper precipitation is usually two to three times the stoichiometric quantity due to side reactions such as:[112,113]

$$Fe + 2\,Fe^{3+} \rightarrow 3\,Fe^{2+}$$

$$Fe + 2\,H^{+} \rightarrow Fe^{2+} + H_2$$

which consume a portion of the available iron. These undesirable reactions can be inhibited by reducing the concentrations of ferric iron and free acid. The cement copper produced varies in copper percentage from 50% to 90%. Impurities in the cement are iron oxide and gangue associated with the iron source material.

Cementation of copper on iron from acidic copper nitrate solutions is a poorly documented topic. Background information on this subject is amassed from the more common procedure of recovering copper from sulfate solutions. In this reaction, parameters which influence cementation are stirring rate, copper concentration, acid concentration and temperature.

The predominant rate controlling step in the copper cementation reaction according to Biswas and Reid[114] is either the chemical reaction rate at the metal - solution interface or the rate of transport of copper and iron ions to and from the interface. At negligible speeds (200 to 800 r.p.m.), the cementation reaction is diffusion controlled since the removal of copper from solution is dependent upon the transport of ions to and from the interface. Under this condition, the removal of copper from solution is relatively slow and follows first order reaction kinetics, $dC_B = - C_B (R_oA/V) dt$, where $C_B$ = concentration of diffusing species ($Cu^{2+}$) in the bulk of the solution ($g\ cm^{-3}$), V = volume of the solution ($cm^3$), t = duration of cementation reaction (s), and $R_o$ = specific rate constant (cm/s).[112,114] This reaction states that the rate of cementation of copper varies directly with the copper ion concentration in the solution and the effective depositing surface area of iron. As in the case of all diffusion controlled processes, the rate of reaction improves significantly with the degree of agitation. At very fast speeds (above 1000 r.p.m.), the reaction is virtually chemically controlled since no improvement in the overall cementation rate is noted at various amounts of solution turbulence.[114] Under this condition, the reaction rate between the deposited copper and iron precipitant is relatively fast. High flow rates are also beneficial since the amount of low acid stagnant areas that encourage salt precipitation are minimized, the contact between iron and solution is increased and the amount of excess iron consumed by acid dissolution is minimized.

The range of copper concentration in solution that can be effectively treated by the iron precipitant is between 0.5 and 20 g/L.[112] At copper contents below this range, the reaction rate is relatively slow which yields a precipitate of low copper purity. At copper contents above this range, the contact time between the dissolving iron and cementing copper is minimized from the extremely rapid rate of copper precipitation which prevents further reaction by forming an impenetrable dense copper coat on the iron surface.

The acidity of the sulfate solution affects the cementation of copper on iron reaction.[112] At pH's below 1.5, the deposited copper and iron precipitant both react with the concentrated free acid which results in the incomplete removal of copper from solution and excessive use of iron. At pH's between 1.5 to 2.5, ideal cementation conditions exist even though the free acid tends to dissolve iron. At higher pH's, ferric iron and alumina salts precipitate as hydroxides, phosphates, and other complex salts which causes contamination of the copper cement. Since purification of the solution before copper cementation is not economically feasible, the solution pH must be kept in the desired range to hold the contaminants in solution.

The cementation of copper from a copper sulfate solution with iron is dependent upon temperature. Higher temperatures are more beneficial than lower temperatures since the cementation reaction takes place at a faster rate. For example, the cementation rate at 60°C is at least nine times greater than at 10°C.[114] The detriment at operating at elevated temperatures is increased iron consumption.

As a separation scheme, copper cemented out of solution with iron has a few drawbacks.[112] First, excessive amounts of iron are consumed under the conditions of high acidity and temperature. Second, contaminants such as ferric iron and alumina salts precipitate as hydroxides at solution pH's greater then three. Third, the copper cements are of insufficient purity to be classified as high grade copper without intermediate refining. Fourth, solutions containing in excess of 20 g of copper per litre tend to experience copper plating of the iron surface which prevents further reduction. Fifth, low copper content solutions yield low grade cements. Sixth, the method is not applicable for a closed circuit with an acid leach since the solvent is not regenerated.

These shortcomings are outweighed by the numerous advantages of the method.[113] First, the operation is impeccably simple. Second, the method is very cost effective if a cheap source of iron is available for precipitating copper. Third, the process is effective on all concentrations of copper in solution, and particularly on dilute concentrations from which copper cannot be recovered economically by electrolytic precipitation. Fourth, impurities in solution which are usually detrimental to electrolytic precipitation do not affect this method. For these reasons, this method was selected for copper removal from the complex metal nitrate solution.

### 5.3.1.2 Experimental

In order to achieve complete cementation of copper from the complex nitrate solution, experiments were undertaken on the first stage filtrate containing approximately fifteen grams of copper per litre of solution using iron as the precipitating agent. These tests all employed 50 mL of nitrate solution at an initial pH in the range of -1.0 to 0.5, a temperature of either 22°, 35°, 50° or 70°C and various weights (1, 2, 3, 3.5, 4, 4.5, and 5 g) of particulate iron. Acidity adjustment of the standard -0.25 pH solution in the negative and positive directions was executed with concentrated nitric acid and 10 M sodium hydroxide, respectively. Elevated temperatures was achieved with a hot plate. Testing was accomplished by charging a 200 mL Pyrex beaker with the previously noted nitrate solution quantity. A variable speed stirrer with plastic impeller was also introduced into the solution to ensure solution uniformity and contact between the dissolving iron and depositing copper. Upon temperature stabilization, one of the preselected iron weights was slowly added to the stirred solution. This addition rate was required to minimize the exothermic reaction between the dissolving iron and the nitrate solution, limit the emission of nitrous oxide vapours into the atmosphere, and prevent excessive frothing. The cement reaction was completed within ten minutes. At this time, the acidity and temperature of the solution was remeasured to determine whether a change in these conditions resulted. After conversion, the charge was filtered with no washing of the solids. The filtered solution was then analyzed for copper content using atomic absorption spectrophotometry.

The effect of starting temperature on the cementation of copper was studied by immersing particulate iron in a -0.25 pH nitrate solution at either 22°, 35°, 50°, or 70°C. Starting temperature implies that the solution temperature stabilized at a predetermined value before iron addition. It does not represent that the mean temperature was held throughout the entire experiment within a few degrees of this value. For example, upon addition of three grams of iron to a solution preset at 35°C, the temperature rose immediately to 65°C as a result of the exothermic reaction of the dissolving iron. As the reaction proceeded, the temperature drifted slowly downwards due to the lack of external heating. At the completion of the test, the solution temperature was 27°C.

The lack of copper cementation at the temperatures of 50° and 70°C, as shown in Figure 5.11, was possibly due to either passivation of the iron surface or dissolution of the cemented copper. At an iron addition of 10 g/L of solution, virtually all the iron was consumed by the free acid existent in the solution while at higher iron additions, particulate iron was present in excessive quantities. This indicated that passivation of the iron occurred over the cementation process. However, the superabundance of frothing during the reaction period implied that nitrous oxide gases were emitted during the dissolution of iron and possibly copper. Cement copper solubilization was a reality since copper coloured particles in the developed froth layer dissolved leaving grey specks behind. This indicated that the reaction at these temperatures involved the following stages: dissolution of iron, cementation of copper, dissolution of copper, and passivation of iron.

At a starting temperature of 22° and 35°C, copper cementation was 97% and 97.5%, respectively as shown in Figure 5.11, with two and a quarter times the iron stoichiometric requirement. Successful cementation under this condition was achieved since passivation of iron and dissolution of cemented copper was minimized. Further recovery of copper required excessive quantities of iron in relation to the amount of copper remaining to be extracted. For example, at four times the stoichiometric requirement approximately 99.5% of the copper in both cases was recovered which was equivalent to 30 grams of iron needed to extract a further 0.3 grams of copper. Excessive amounts of iron was uncalled for since the recovery was uneconomical and the cement product was contaminated with undesirable materials such as metallic iron and iron hydroxide. The iron compound was precipitated from the nitrate solution since the condition required for precipitation, a solution acidity of 2.5 to 5, existed due to the eradication of free acid by the iron.

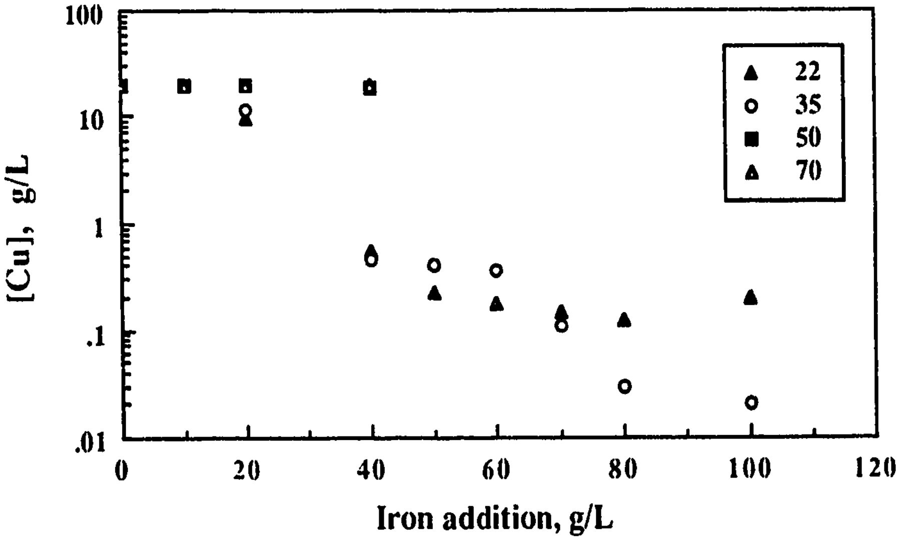

**Figure 5.11:** The effect of starting temperature on the cementation of copper from a nitrate solution using particulate iron.

The effect of starting pH on the cementation of copper was studied by immersing particulate iron in a nitrate solution at room temperature. At a highly acidic condition, -1.0 pH, no metallic copper was cemented permanently out of solution, as seen in Figure 5.12. Instead, copper cemented than redissolved. The iron precipitant also reacted with the concentrated acid under this condition. Cement copper, however, endured the acidic conditions of a solution at -0.5 pH; but, three times the iron stoichiometric amount was required to decrease the copper concentration in the nitrate solution to just under one gram per litre. The original solution, -0.25 pH, required only two and a quarter times the stoichiometric requirement to achieve 97% copper recovery. At higher stoichiometric requirements, three a half times stoichiometry, copper remaining in solution was reduced to 0.2 g/L. The acidity of this solution was 0.35 pH due to the consumption of free acid during the cementation reaction. Iron additions above four times stoichiometry resulted in no further gain in copper recovery. Instead, cement copper became contaminated with iron hydroxide since the condition of precipitation, a solution acidity of 2.5 to 5, existed. At a starting solution pH of 0 or 0.5, copper cementation was almost 100% complete at two and a quarter times stoichiometry. However, the cement product was severally contaminated with iron hydroxide.

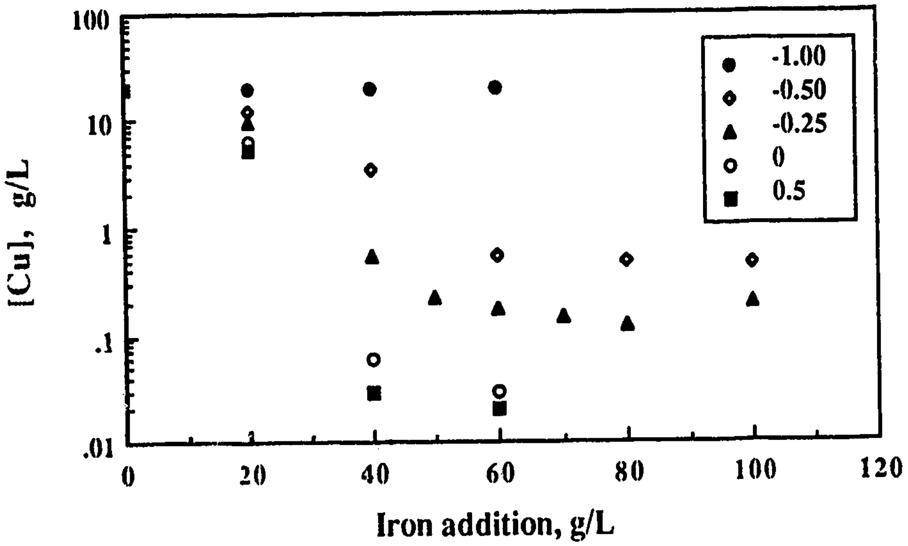

**Figure 5.12:** The effect of starting pH on the cementation of copper from a nitrate solution using particulate iron.

Cementation of copper from nitrate solutions by particulate iron indicated a dependency on starting temperature and acidity. However, the fluctuation of these conditions, especially temperature, prevented proper comprehension of the cementation reaction. For this reason, a series of experiments were conducted using three grams of iron to recover copper from 50 mL of nitrate solution held at a mean temperature of 25°, 40°, 55° and 75°C to determine the influence of temperature on copper cementation. Mean temperatures, in this case, represent that the stated values were not exceeded or reduced by more than five degrees Celcius. Figure 5.13 shows that a solution with an initial pH value of -0.25, no copper cementation resulted at 55° or 75°C while 92.5% and 99.8% of the copper in solution was recovered at temperatures of 40° and 25°C, respectively. This indicated that temperature has an adverse effect on copper cementation. That is, lower temperatures are more beneficial to copper cementation from nitrate solutions. At an initial pH of 0.5, temperature again influenced cementation but only at the high value of 75°C.

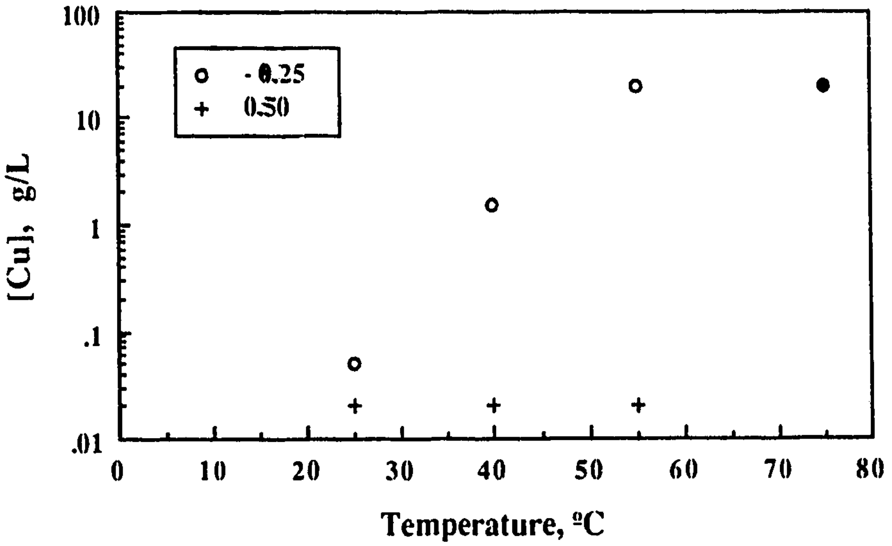

**Figure 5.13: The effect of temperature on the cementation of copper from a nitrate solution using particulate iron.**

The lack of cementation at this temperature resulted from the complete dissolution of cement copper and partial solubilization of particulate iron. Temperatures below 75°C resulted in almost complete copper cementation but the cement product had a high contamination of iron hydroxide. This compound precipitated since the solution pH had rose to its precipitation range of 2.5 to 4.5 due to the consumption of free acid during the cementation reaction.

The success of iron addition in almost completely recovering copper from a complex nitrate solution at a solution acidity of -0.25 and a temperature of 25°C ratified this procedure as a viable method for copper removal.

The next experiment undertaken was the recovery of copper from a lead free sulfate solution by using iron as the precipitating agent. The lead free solution was procured by adding sulfuric acid to the complex nitrate solution at an acid to solution ratio of one to two which caused solidification of the mixture. After water washing, lead sulfate remained behind as a precipitate while copper sulfate solubilized. The tests employed with this solution were identical to the previous copper cementation trials. At the theoretical requirement, 0.88 g of iron per gram of copper, no copper cementation occurred because free nitric acid, observed by the emission of brown nitrous oxide fumes over the 15 minute reaction period, dissolved the iron precipitant and cemented copper. This condition was prevalent until the free nitric acid was spent which resulted at approximately ten times the stoichiometric requirement of iron. After this point, copper metal cemented onto the iron particles. The excessive quantity of iron required to achieve cementation eliminated this procedure of extracting copper after lead removal as a viable recovery method.

### 5.3.2 Lead Recovery

As for silver, lead removal from a nitrate solution is realized in the presence of a chloride species such as, hydrochloric acid or sodium chloride. Upon addition of a slight excess of chloride ions above the stoichiometric quantity, lead chloride is precipitated by one of the following reaction mechanisms:[36]

$$Pb(NO_3)_2 + 2\,HCl \rightarrow PbCl_2 + 2\,HNO_3$$

$$Pb(NO_3)_2 + 2\,NaCl \rightarrow PbCl_2 + 2\,NaNO_3.$$

This anion amount is easily determined since the moles of lead ion in solution equals the moles of lead nitrate dissolved. For the reaction between lead nitrate and sodium chloride, the moles of lead chloride formed is limited by the moles of lead ion in solution and is therefore equal to the number of moles of lead nitrate. For example, a solution containing one gram of lead per litre would require 0.564 grams of sodium chloride per litre to carry out this precipitation.

Lead chloride precipitation tests were undertaken on a complex metal nitrate solution containing approximately three grams per litre of lead using hydrochloric acid as the precipitating agent. These experiments all used 25 mL of nitrate solution and varying amounts (1, 2.5, 5, 7.5, 10, 12.5, 15, 20 and 25 mL) of concentrated hydrochloric acid. For example, a 100 mL Pyrex beaker was initially charged with 25 mL of the complex metal nitrate solution at room temperature. After charging, one of the predetermined volumes of hydrochloric acid was slowly added to the magnetically stirred solution which ensured solution uniformity during chloride addition and breakage of the lead chloride lumps into individual particles. This mixture was allowed fifteen minutes for lead chloride to precipitate from the complex metal nitrate solution. After conversion, the charge was filtered with no washing of the solids. The filtered solution was then analyzed for lead content.

The metal nitrate solution containing approximately three grams per litre of lead was only partially extracted of lead with the use of hydrochloric acid as the precipitating agent. At a hydrochloric acid addition of 40 mL per litre of nitrate solution, traces of lead chloride were only precipitated from the solution, as seen in Figure 5.14. This minute amount corresponded to a reduction of approximately 9% of the overall quantity of lead in solution. As the volume of hydrochloric acid was increased to 200 mL, the lead concentration in solution decreased by about half of its original value. Hydrochloric acid additions above 200 mL created a detrimental effect on lead recovery from nitrate solutions since the excess chloride ions in solution caused the precipitated lead chloride to resolubilize into a lead chloride soluble complex. At a hydrochloric acid addition of 600 mL, all the precipitated lead chloride was resolubilized thereby decreasing the amount of lead extracted from solution to zero.

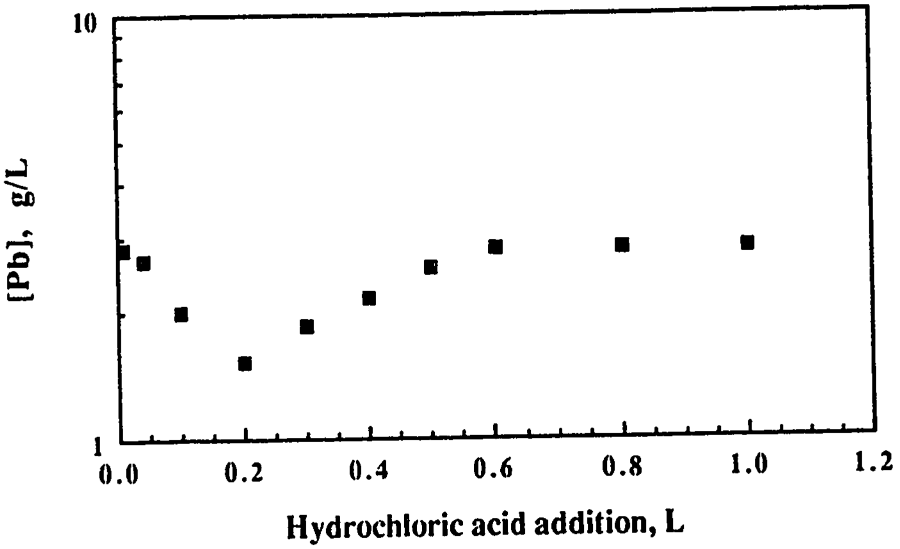

**Figure 5.14: Precipitation of lead from a complex nitrate solution using hydrochloric acid.**

The failure of hydrochloric acid, a chloride species, in recovering lead as a compound from a nitrate solution probably indicates that other chloride species may have identical results. This hypothesis was investigated by employing sodium chloride as the precipitating agent. These experiments again all used 25 mL of nitrate solution and varying amounts (0.1, 0.15, 0.2, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2, 2.5, 3.0, 4.0, and 5.0 g) of sodium chloride. For example, a 100 mL Pyrex beaker was initially charged with 25 mL of the complex metal nitrate solution at room temperature. After charging, one of the predetermined volumes of sodium chloride was slowly added to the magnetically stirred solution. This mixture was allowed fifteen minutes for lead chloride to precipitate from the complex metal nitrate solution. After conversion, the charge was filtered with no washing of the solids. The filtered solution was then analyzed for lead content.

The extraction of lead from a nitrate solution with sodium chloride was insignificant to employ this species as a precipitation agent. At a sodium chloride addition of 10 g per litre of nitrate solution, no lead chloride was precipitated from the solution. Particles of lead chloride suspended in solution were observed with the addition of 20 g of sodium chloride. This amount corresponded to a reduction of approximately one third of the overall quantity of lead in solution, as shown in Figure 5.15. As the weight of sodium chloride was increased to 40 g, the lead in solution was decreased to approximately two-fifths of its original value. Further sodium chloride addition did not decrease the lead concentration in the nitrate solution. Instead, the lead in solution at first levelled to a minimum between the sodium chloride weights of 50 g and 80 g, then the lead in solution increased with chloride salt additions above 80 g. The reverse effect on lead concentration in solution with excess amounts of sodium chloride is a result of an overindulgence of chloride ions in solution which causes the precipitated lead chloride to resolubilize into a lead chloride soluble complex. At a sodium chloride addition of 200 g, approximately 20%

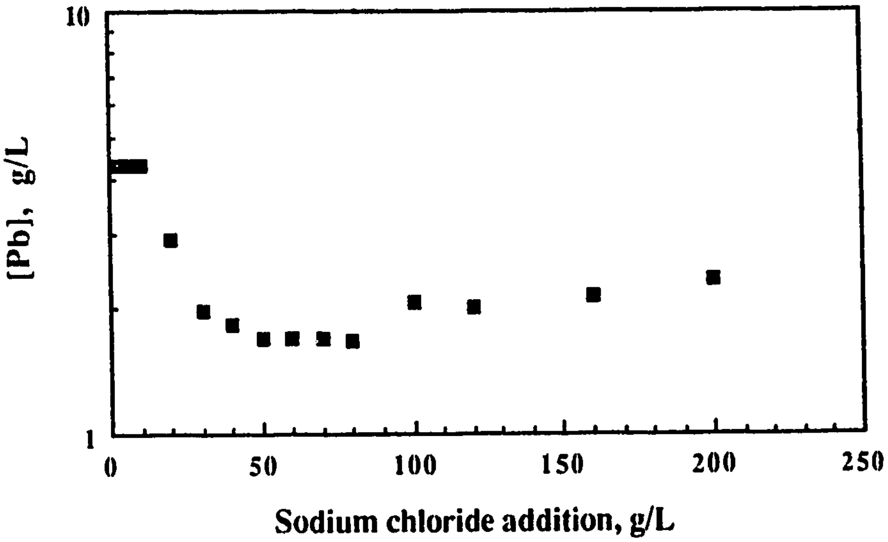

Figure 5.15: Precipitation of lead from a complex nitrate solution using sodium chloride.

of the precipitated lead chloride was resolubilized thereby decreasing the amount of lead extracted from solution to half of its original value.

The inability of hydrochloric acid or sodium chloride in completely extracting lead from a complex nitrate solution eliminated these precipitating agents as a viable procedure for lead removal.

The next approach employed for the recovery of lead from a complex nitrate solution was Loebel's and Meissner's[82] sulfuric acid treatment process. In this operation, concentrated sulfuric acid supplies sulfate ions to the aqueous solution which causes the lead ions in solution to react with the sulfate ions to form lead sulfate, as shown by the following reaction:

$$Pb(NO_3)_2 + H_2SO_4 \rightarrow PbSO_4 + 2\,HNO_3.$$

The amount of sulfuric acid required to accomplish the precipitation of lead sulfate is approximately 40% of the overall solution volume. That is, for every litre of solution, 400 mL of sulfuric acid is needed. Under these conditions, the amount of lead remaining in solution was noted to be inconsequential.

Verification of the Loebel - Meissner process was undertaken by conducting experiments on a complex nitrate solution containing approximately four grams per litre of lead. These tests all used 25 mL of the original nitrate solution and varying amounts (1, 2.5, 5, 7.5, 10, 12.5, 15, 20 and 25 mL) of sulfuric acid. In a 100 mL Pyrex beaker, 25 mL of the original nitrate solution was added at a temperature of 20°C. After charging, one of the predetermined volumes of sulfuric acid was slowly added to the magnetically stirred solution. Slow addition was required to prevent the loss of solution [illegible] excessive amounts of sulfur dioxide or nitrous oxide fumes were emitted upon addition of sulfuric acid. This mixture was then allowed fifteen minutes for lead sulfate to precipitate from the complex nitrate solution. The temperature of the solution during this time interval rose anywhere between 5° and 70°C depending upon the amount of sulfuric acid added to the solution. The high and low temperature increases were reported at the largest and smallest sulfuric acid additions, respectively. After conversion, the charge was filtered with no washing of the solids. The filtered solution was then analyzed for lead content.

The extraction of lead from a complex nitrate solution with sulfuric acid was very successful. At the minimum sulfuric acid test amount, 40 mL acid per litre of solution, the lead concentration in solution decreased from approximately four grams per litre to one gram per litre. Further reduction in the lead concentration was noticed with additional increases in the sulfuric acid amount. For example, the lead concentration at a sulfuric acid addition of 200 mL and 400 mL was approximately 80 mg/L and 30 mg/L, respectively. At a sulfuric acid addition above 500 mL, all solutions solidified. After water washing the solid residue, minimal lead sulfate resolubilized as seen in Figure 5.16.

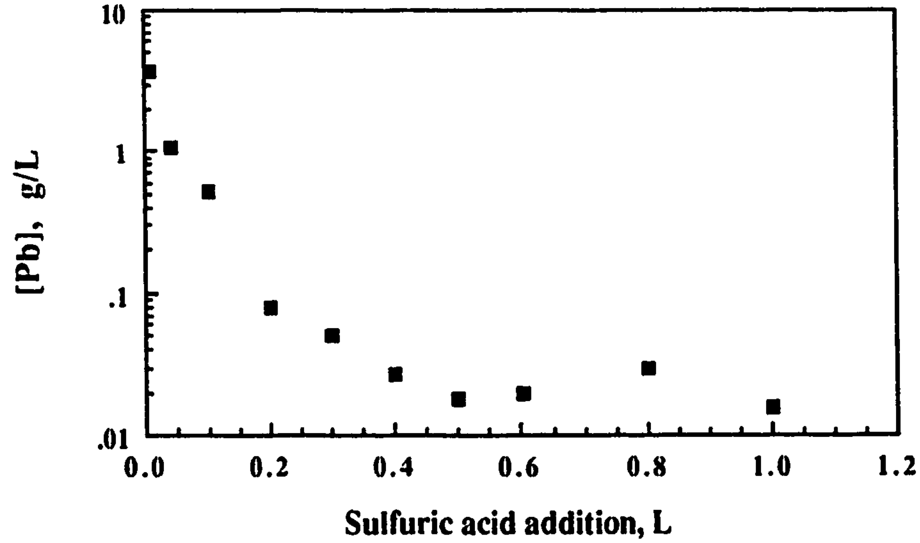

**Figure 5.16: Precipitation of lead from a complex nitrate solution using sulfuric acid.**

The success of sulfuric acid addition in almost completely extracting lead from a complex nitrate solution ratified this procedure as a viable method for lead removal. However, the problem encountered after lead removal, recovery of copper as an impure metallic product with excessive amounts (15 times the stoichiometric quantity) of particulate iron , suppressed the usefulness of the sulfuric acid process.

The next experiment undertaken was the recovery of lead from a copper free complex nitrate solution by sulfuric acid. The tests employed in this experiment were exactly the same as the ones used in the verification of the Loebel - Meissner process. The results of this test, presented in Figure 5.17, revealed that the lead concentration in solution steadily decreased from approximately 4 g/L at no sulfuric acid addition to less than 0.04 g/L at a sulfuric acid addition of 600 mL per litre of nitrate solution. The complete extraction of lead from this solution ratified this procedure as a viable method for lead removal.

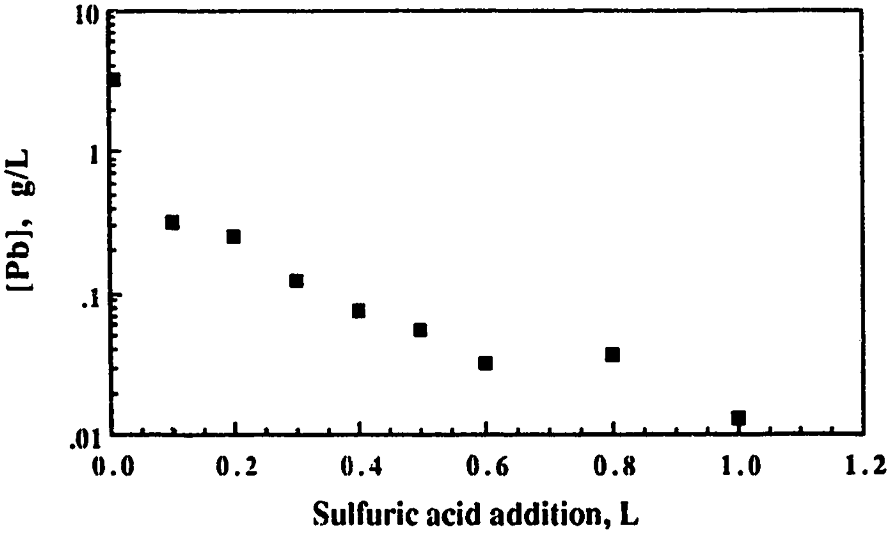

**Figure 5.17: Precipitation of lead from a copper free nitrate solution using sulfuric acid.**

### 5.3.3 Iron Recovery

In many hydrometallurgical processes, a common problem in the purification of solutions is the removal of iron contamination. A simple solution is the hydrolysis of the iron ions to form a hydroxide precipitate through the addition of sodium hydroxide.[112] The basic principle of this precipitation method is explained by the $M^{n+}$ - pH diagram, as shown in Figure 5.18, which highlights the dependency of the reaction upon metal ion concentration and solution pH. For example, the left hand side of each plotted line

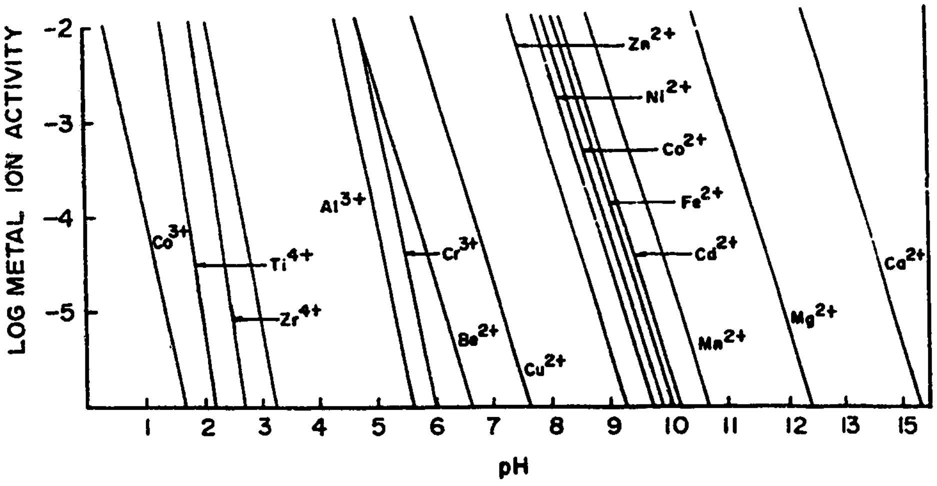

Figure 5.18: Precipitation diagram for metal hydroxides.[112]

represents the combinations of metal ion concentrations and pH values for which the concerned metal remains in solution. The right hand side of the line represents the conditions in which the concerned metal precipitates out of solution as a metal hydroxide. From this diagram, it is observed that ferric iron is selectively precipitated out of solution at a pH value between 3.5 and 5. This is not the case if iron is present in its ferrous state. In this form, iron does not precipitate until the solution pH is strongly basic. However, precipitation of the ferrous state is possible through air addition to convert ferrous iron to ferric iron. Once converted, iron hydroxide is easily precipitated at the desired solution acidity previously mentioned.

The nature of the iron hydroxide precipitate developed from a solution at pH 3.5 and room temperature is gel-like in character. The coagulated gel colloids settle very slowly and trap a significant portion of the nonferrous metal values present in the solution upon filtering. Therefore, repeated dissolution and precipitation are necessary to extract the entrapped nonferrous metal values from the iron hydroxide precipitate. These extra steps are undesirable from an economical point of view since they are costly and time consuming. A better approach to the selective removal of iron is to achieve the precipitate in a form that is coarse, dense and crystalline to ensure simple filtration and washing. Forms of favourable iron precipitates are: (1) geothite - FeO.OH, (2) jarosite family of compounds - $MFe_3(SO_4)_2(OH)_6$, where M stands for $Na^+$, $K^+$ or $NH_4^+$, and (3) hematite - $Fe_2O_3$.[113] These precipitates are developed at specific conditions of temperature, pH and presence of certain cations. Geothite precipitates at pH 2 to 3.5 and temperature of 70° to 90°C, according to the following reaction:

$$2\,FeSO_4 + O_2 + H_2O \rightarrow FeO.OH\,(\alpha\text{-form}) + H_2SO_4.$$

Jarosite precipitates from an acidic solution of a pH less than 1.5 at a temperature of 90° to 100°C in the presence of cations like $NH_4^+$ or $Na^+$ which is represented by the following mechanism:

$$3\,Fe_2(SO_4)_3 + 2\,(NH_4,Na)OH + 10\,H_2O \rightarrow 2\,(NH_4,Na)Fe_3(SO_4)_2(OH)_6 + 5\,H_2SO_4.$$

Hematite forms at 200°C in the presence of oxygen, as shown by the following reaction:

$$Fe_2(SO_4)_3 + 3\,H_2O \rightarrow Fe_2O_3 + 3\,H_2SO_4.$$

Iron recovery from a complex nitrate solution was attempted at the following conditions: solution acidity at a pH of 3.5; temperature of 80°C; and oxygen addition. Under these solution parameters, a coarse iron hydroxide product was precipitated.

### 5.3.4 Nickel Recovery

#### 5.3.4.1 Background Information

Methods for the recovery of nickel or nickel compounds from a sulfate solution are reduction, crystallization or precipitation. In reduction, the gaseous reductant, hydrogen, is used to reduce nickel ions in aqueous solution to nickel metal.[112] At the Port Nickel refinery, nickel metal is recovered from sulfate solution by this technique.[115] Before reduction, the sulfate liquor containing 50 g/L nickel is first purified to extract any impurities. Iron, aluminum, and chromium are precipitated as hydroxides by adjusting the solution acidity to a value in the range of 5 to 5.5 with ammonia, increasing the temperature to 82°C and then aerating. After filtering out the precipitate, the solution acidity is adjusted downwards to a pH of 1.5 with sulfuric acid. At this acidity, copper, lead and zinc are precipitated as their sulfides by passage of hydrogen sulfide through the solution. After filtration, the purified nickel liquor is adjusted to an acidity of 1.8 with ammonia, heated to 190°C, and then reduced in an autoclave at a hydrogen overpressure of 4.92 MPa. During reduction, the pH is held constant at the desired value of 1.8 by continual addition of ammonia which neutralizes the formed acid. The overall reduction is represented by the following reaction:

$$NiSO_4 + 2\,NH_3 + H_2 \rightarrow Ni + (NH_4)_2SO_4.$$

Crystallization is the physical process of separating salt in the form of crystals from an aqueous solution.[112] The three basic steps involved in this mechanism are: (1) supersaturation of solution, (2) nucleation of crystals, and (3) crystal growth. Saturation is critical to induce a salt to crystallize. This state is achieved when the solubility of the salt in aqueous solution is surpassed. The solubility data for nickel sulfate is presented in Figure 5.19. Note the increase in solubility as the temperature of the solution increases to the boiling point of water at which point, solubility peaks. Further increase in temperature results in a rapid decline of solubility. These two distinct stages suggest two possibilities of achieving nickel sulfate crystals. The first method is heating the solution in autoclaves at temperatures from 120° to 130°C to precipitate the salts almost quantitively. The second method is heating the solution at temperatures near the boiling point to entice saturation through evaporation followed by cooling the solution to room temperature or below to induce crystallization. Of these two methods, nickel sulfate is generally manufactured by evaporative crystallization.[115] The sulfate solution in this case is heated to near boiling to expel a portion of the water content through evaporation to achieve saturation. Upon solution coooling, spontaneous crystallization is attained at the temperature corresponding to supersaturation. The crystallized product is upgraded by eliminating major impurities such as iron, copper and zinc. Iron is removed by dissolving the crystals in hot water, oxidizing ferrous iron to ferric iron by aeration, and precipitating ferric hydroxide at a solution acidity of about five and a temperature of 77° to 82°C. The hot, iron free solution is subsequently cooled and reacidified to a pH of 1.5 with sulfuric acid. Addition of hydrogen sulfide gas to this solution precipitated both copper and zinc as their sulfides. After filtration, the purified solution containing 75 to 80 g/L nickel is crystallized after supersaturation at a normal operating temperature of 35° to 40°C.

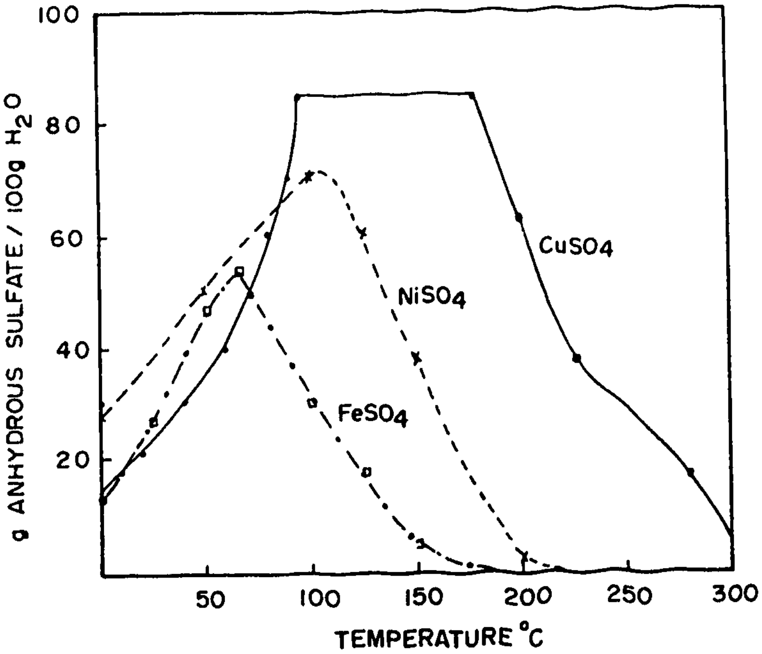

Figure 5.19: Influence of temperature on solubilities of sulfate salts of copper, nickel, and iron.[112]

Nickel is commonly precipitated from sulfate solutions in sulfide form. This is accomplished by introducing hydrogen sulfide gas to the solution. The gas provides sulfide ions for the precipitation reaction by dissolving in the aqueous solution, as shown by the following reaction mechanism:[112]

$H_2S_{(aq)} \rightarrow HS^- + H^+$

$HS^- \rightarrow S^{2-} + H^+$

$Ni^{2+} + H_2S \rightarrow NiS + 2\,H^+.$

The final expression states that the reaction is favoured in the forward direction under decreasing acidity of solution and elevated hydrogen sulfide gas pressure conditions. At atmospheric pressure, nickel sulfide is precipitated out of solution at pH's higher than 2.25, as shown in Figure 5.20 by the intersection of the nickel ion line with the hydrogen sulfide gas line. At pH's lower than this value, nickel remains in solution since the sulfide concentration is too low to facilitate precipitation. This is represented by the left hand side of the nickel metal ion line. In case the as-generated solution already contains the sulfide ion, then only the conditions have to be developed to induce the desired metal sulfide precipitation.

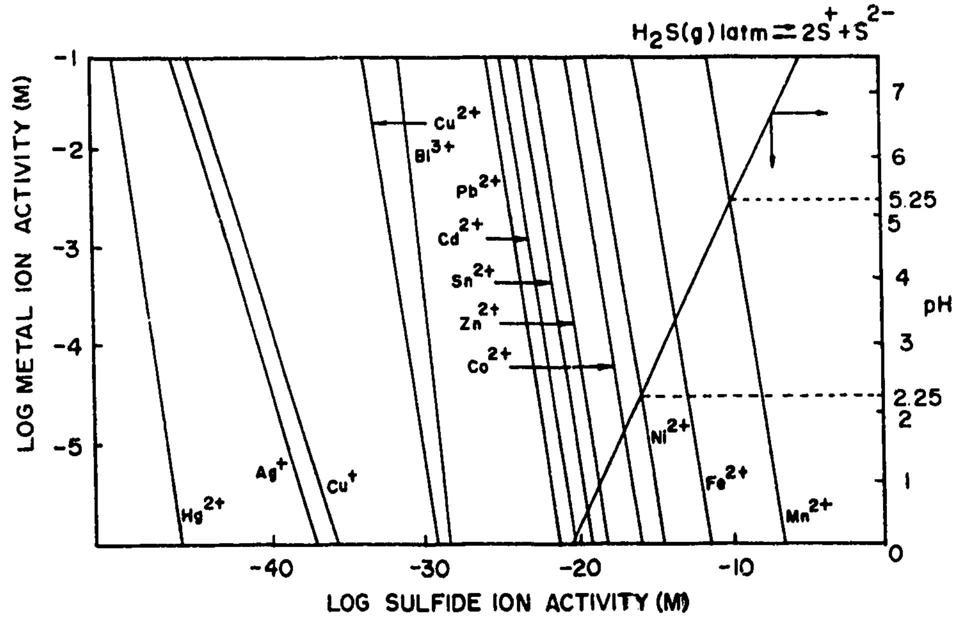

**Figure 5.20: Precipitation diagram for metal sulfides.**[112]

The Moa Bay sulfide process involves four key subdivisions, namely (1) dissolution of the ore by sulfuric acid pressure leaching, (2) precipitation of nickel-cobalt sulfide concentrate, (3) purification of the nickel-cobalt solution generated by pressure leaching of the sulfide with sulfuric acid, and (4) production of nickel and cobalt metals from the purified solution.[115] The second point listed is relevant in the present context taken to deal with sulfide precipitation. The leach liquor from the acid dissolution stage typically analyses: 5.95 g/L Ni, 0.64 g/L Co, 0.1 g/L Cu, 0.2 g/L Zn, 0.8 g/L Fe, 0.3 g/L Cr, 2.3 g/L Al, and 28 g/L free acid. The quantity of free acid remaining in the solution is critical to the overall success of the sulfide precipitation. An excess of acid hinders complete nickel precipitation while a deficiency of acid facilitates precipitation of iron, aluminum or other undesirable elements. This problem is further complicated by the fact that acidity increases as precipitation progresses. Thus, it is desirable to start with a sufficient quantity of free acid so that an excessively acidic condition is avoided at the end of precipitation. A satisfactory solution pH is between 2 and 2.5. This acidity is achieved by neutralizing the acidic leach solution with calcium carbonate. In the precipitating reaction, nickel combines with hydrogen sulfide at a temperature of 118°C and a pressure of 1.13 MPa to form nickel sulfide while producing sulfuric acid, as shown by the following reaction mechanism:

$$Ni^{2+} + SO_4^{2-} + H_2S \rightarrow NiS + H_2SO_4.$$

At this temperature, the above reaction is shifted towards complete precipitation. At the same time, pressure is required to ensure an adequate concentration of hydrogen sulfide in solution. Under these severe conditions, nickel sulfide precipitates almost completely out of solution except for a small fraction left behind due to a lower concentration of residual nickel along with a higher concentration of sulfuric acid in solution. Recovery of the residual nickel in solution is possible by addition of a nickel seed to induce instantaneous precipitation. Addition of a neutral salt such as magnesium sulfate is beneficial to the precipitation reaction since this compound is basic in nature and tends to neutralize a portion of the free acid developed during precipitation.

### 5.3.4.2 Experimental

The nickel recovery schemes presented in background information are unsuitable for application to computer circuit boards due to the deficiency of nickel generated from this material source. A procedure quite effective on lean nickel solutions is precipitation. Nickel is precipitated in the form of nickel oxalate by reacting the aqueous nickel sulfate solution with an excess oxalic acid at a pH in which the liquor becomes slightly supersaturated with respect to the oxalate of the metal so that precipitation of the oxalate is initiated.[116] Before precipitation, iron contamination is removed by doping the solution with sodium hydroxide to increase the solution pH to 3.5, increasing the temperature to 80°C, and aerating. After filtration, the purified nickel solution containing approximately one gram per litre of nickel is treated at a pH of 3.5 and a temperature of 80°C with a slight excess of oxalic acid and then boiled for 30 minutes to induce the formation of nickel oxalate. This compound is separated from the feed liquor by filtration and the filtrate containing less than 25 mg/L of nickel is transferred to secondary metal recovery.

### 5.3.5 Secondary Metal Recovery

The intention of the first and second leaching stage was to dissolve the base metals so that they would not contaminate the precious metal solution of the third leaching stage. In doing this, a raw leach liquor containing several base metals was obtained. Upon removal of the desired base metals such as, copper, lead, iron and nickel, the solution contained minor amounts of secondary base metals which must also be removed before the solution is discarded. Removal of these base metals from solution is easily undertaken by selective precipitation. In selective precipitation, the base metal impurities are removed by varying the pH of the solution with hydroxide. The addition of sodium hydroxide at a temperature of 80°C to alter the solution pH to highly basic resulted in the precipitation of these contaminants as hydroxides. In all cases, the metal concentration remaining in solution is less than 10 mg/L.

# Chapter 6

# Gold, Platinum and Palladium Separation

## 6.1 Third Stage Leach

The purpose of the third stage leach is to dissolve metallic gold from the second stage leach computer chip residue. The lixiviants used to dissolve this element are cyanide and aqua regia. Cyanide is generally used for the recovery of gold from low grade ores.[35] In the cyanidation process, gold is dissolved by an oxygenated sodium cyanide solution under alkaline conditions, as expressed in its simplest form by the Elsner equation:[28]

$$4\ Au + 8\ NaCN + O_2 + 2\ H_2O \rightarrow 4\ Na[Au(CN)_2] + 4\ NaOH.$$

Several practical problems, however, hinder the application of cyanide leaching to computer chip residue. First, cyanide is a deadly chemical, especially in the presence of acids which cause the production of hydrocyanic gas.[61] Prevention of gas emission is achieved by maintaining alkaline conditions in the leach solution by addition of calcium oxide or sodium hydroxide. Second, the spent cyanide leach solution is an environmental hazard which requires elaborate containment procedures to limit the emission of cyanide into the water table along with expensive chemical treatment with chlorine or hydrogen peroxide to destroy the cyanide in solution.[61] Third, cyanide solutions are unable to co-extract other valuable metal species such as platinum and palladium.[106] Fourth, long leach times are required with complex ores since dilute solutions are needed to limit the cyanide loss to base metals such as copper, iron, lead and zinc.[106] For these reasons, cyanide leaching of computer chips was not attempted.

The traditional medium for dissolving gold and the platinum group metals is aqua regia, a mixture of three parts concentrated hydrochloric to one part concentrated nitric acid. The combination of these two acids forms nitrous oxide and chlorine as shown by the following reaction:[36]

$$2\ HNO_3 + 6\ HCl \rightarrow 2\ NO + 4\ H_2O + 3\ Cl_2.$$

Problems hindering aqua regia leaching of scrap computer circuit boards are quite minor provided precautionary measures are undertaken. First, the purity of the precipitated gold is decreased by the presence of silver chloride in the residue, but a chemical wash with nitric acid before aqua regia leaching minimizes silver contamination in the gold precipitate. Second, metastannic acid hinders the dissolution of gold.[33] This acid is produced by the dissolution of tin from solder. Production of metastannic acid is limited by an initial leach with nitric acid. In nitric acid, lead dissolves, tin cracks and flakes, and gold remains inert. Third, aqua regia is ineffective for dissolving the secondary platinum group metals of iridium, ruthenium, rhodium and osmium.[106] This is not a concern since only minimal amounts of these metals are present in computer chips. Despite these potential problems, aqua regia leaching was selected for the recovery of gold, platinum and palladium from computer chips because of its flexibility, ease, low capital requirement, and ability to separate gold and silver from the platinum group metals.[106] The parameters investigated for the third leach stage were: (1) acid concentration, (2) temperature, (3) pulp density, (4) retention time, and (5) agitation.

### 6.1.1 Equipment and Procedure

The computer chip residue free of base metal contaminants was leached in aqua regia to determine the solubilization success of the following precious metals: gold, platinum and palladium in this medium. Experiments were undertaken in a 200 mL Pyrex beaker which was initially charged with 50 or 100 mL of aqua regia. After charging, the solution was allowed to stabilize at the predetermined temperature of 23°, 50°, 70° or 90°C. Elevated temperatures were achieved by using a hot plate. Upon temperature stabilization, a total of 25 g of crushed computer chips from the second stage leach were added to the solution in small increments to control the reaction rate and minimize the exothermic nature of the reaction. This overall weight was selected to provide a solid to liquid ratio of one gram of solid to either two or four millilitres of solution. A vigorous reaction was maintained throughout dissolution by the incremental addition of nitric acid. Upon completion of the test, the charge was cooled, filtered and washed with distilled water. The various products were then analyzed by atomic absorption.

### 6.1.2 Third Stage Leach Chemistry

Crushed computer chips were subjected to an aqua regia leach to solubilize gold, platinum and palladium but not the plastics or ceramics. The reactions that resulted between aqua regia and these metals were the following:[36]

$$2\,Au + 9\,HCl + 3\,HNO_3 \rightarrow 2\,AuCl_3 + 3\,NOCl + 6\,H_2O$$

$$Pt + 6\,HCl + 2\,HNO_3 \rightarrow PtCl_4 + 2\,NOCl + 4\,H_2O$$

$$Pd + 3\,HCl + HNO_3 \rightarrow PdCl_2 + NOCl + 2\,H_2O.$$

From these reactions, it was noted that nitrosyl chloride fomed upon reaction between hydrochloric and nitric acid as shown by the following reaction:[117]

$$3\,HCl + HNO_3 \rightarrow Cl_2 + NOCl + 2\,H_2O.$$

Of these reaction products, chlorine probably accomplishes most of the oxidation of the precious metal species even though nitric acid is added to act as the oxidizing agent. If the aqua regia solution was diluted with water, then chlorine and nitrosyl chloride recombined to form hydrochloric acid and nitric acid, as shown above by the reverse reaction mechanism.[117]

#### 6.1.2.1 Acid Concentration

The effect of acid concentration on the dissolution of gold, platinum and palladium from crushed computer chips was not examined experimentally for two reasons. First, it is desired to maximize the precious metal recovery. Dilution of aqua regia with water causes chlorine and nitrosyl chloride to combine and reform hydrochloric acid and nitric acid minimizing the amount of desired oxidant, chlorine, available for reaction with the precious metals. Second, dilution of the aqua regia increases the cost of the operation since an additional volume of water must be heated to the desired solution temperature.

### 6.1.2.2 Temperature

Before the effect of temperature on the dissolution of gold, platinum and palladium could be studied, the precious metal content of the computer chip residue was determined by the Aqua Regia Digestion method. In this procedure, 30 g of crushed computer chips were digested in 60 mL of aqua regia at 90°C. The dissolution of the computer chip residue was completed when the solution volume decreased to one half of its original value. Continued boiling past this point does not improve the results since the exposed precious metals readily solubilize under these conditions. This solution was then filtered to separate the computer chips from the dissolved metals, gold, platinum and palladium. The residue was discarded, and the filtrate was made up to 100 mL with the addition of distilled water. This filtrate was then analyzed for precious metal content with an atomic absorption spectrophotometer. The gold content of the computer chip residue was determined to vary between 60 and 80 ounces of gold per ton while the platinum and palladium contents were too low for determination by the atomic absorption spectrophotometer.

The computer chip residue was digested at 23°, 50°, 70°, and 90°C in aqua regia to determine the effect of temperature on the dissolution of gold, platinum and palladium. Gold was completely dissolved within one hour at 23°C and by one half hour for the other temperatures since at these times the gold in solution equalled the results from the Aqua Regia Digestion method. Detailed results for the four temperatures at various leach times are shown in Table 6.1. Complete dissolution occurred at all temperatures since hidden precious metals were exposed while dissolution barriers such as silver chloride or metastannic acid were prevented from forming on the gold's surface. Liberation of the precious metals from the computer chips and coagulated resin was accomplished in a jaw crusher - cone crusher series while the inhibiting compounds were removed from the computer chip residue by the second stage nitric acid leach. The differences in the rates of leaching between the four solution temperatures were due to the more rapid formation of chlorine at higher temperatures allowing the oxidation of gold to occur at a faster rate.

The effect of temperature on platinum and palladium dissolution could not be determined due to the minimal amount of these elements present in the computer chip residue.

**Table 6.1: Leaching of Computer Chips in Aqua Regia**

| Conditions | | Analysis | |
|---|---|---|---|
| Temperature (°C) | Time (hr) | % Gold | oz Au / ton |
| 23 | 0.5 | 0.170 | 49.6 |
| 23 | 1 | 0.279 | 81.2 |
| 23 | 2 | 0.155 | 45.2 |
| 23 | 3 | 0.313 | 91.1 |
| 50 | 0.5 | 0.209 | 60.9 |
| 50 | 1 | 0.218 | 63.4 |
| 50 | 2 | 0.070 | 20.4 |
| 50 | 3 | 0.239 | 69.7 |
| 70 | 0.5 | 0.206 | 60.1 |
| 70 | 1 | 0.214 | 62.2 |
| 70 | 2 | 0.250 | 72.9 |
| 70 | 3 | 0.163 | 47.4 |
| 90 | 0.5 | 0.266 | 77.6 |
| 90 | 1 | 0.241 | 70.3 |
| 90 | 2 | 0.266 | 77.6 |
| 90 | 3 | 0.250 | 72.9 |

### 6.1.2.3 Pulp Density

The amount of solution required for complete immersion of the computer chips was approximately two millilitres per every gram of computer chips. Precious metal dissolution in aqua regia at a temperature of 90°C was complete within 30 minutes as long as the computer boards were crushed to a particle size of 425 µm thereby ensuring the liberation of the precious metals from the ceramic and plastic components. For a pulp density of approximately four millilitres per every gram of computer chips, the rate or amount of precious metal solubilization was unchanged. Therefore, increasing the amount of acid used per gram of computer chips did not increase the leaching rate by a measurable quantity. This would not have been the case without the previous nitric acid leach which solubilized the base metals such as copper, iron, nickel and zinc. These base metals would have acted as acid consumers thereby increasing the amount of acid required for total precious metal dissolution.

### 6.1.2.4 Retention Time

The rate of precious metal dissolution in an aqua regia system was determined by immersing crushed computer chips in aqua regia at 23°, 50°, 70°, and 90°C to solubilize gold, platinum and palladium. In all cases studied, the extraction of gold was complete in approximately one hour. The rapid dissolution of this metal at each temperature was a result of the absence of metal barriers such as silver chloride or metastannic acid on the metal's surface. The rate of platinum and palladium dissolution could not be determined since all of the samples contained these metals in too low of a concentration to be detected by the atomic absorption spectrophotometer.

### 6.1.2.5 Agitation

The effect of agitation on the dissolution of gold, platinum and palladium was analyzed in aqua regia at 90°C. At this temperature, the agitated and nonagitated solutions dissolved the precious metals at approximately the same rate; dissolution was complete in both solutions within one hour. The behavior of the nonagitated solution closely resembled that of the agitated solution because of the self induced agitation brought about by the release of nitrous oxide and chlorine vapours causing bubbling and frothing of the solution.

Fresh reagent from the bulk of the solution was constantly brought to the gold, platinum and palladium surfaces in the nonagitated case. At the same time, the chloride species of these precious metals were constantly removed from the metal's surface. This solution transfer occurring in both cases allowed for complete dissolution of the precious metals.

## 6.2 Gold Separation - Theoretical

In the classical process for the recovery of gold from aqua regia solutions, as shown by Figure 6.1, the physical separation method employed is precipitation by reducing agents, such as metals, sulfides, ferrous salts, gas and organic compounds, or by oxidizing agents, such as peroxygens.

The metal customarily exercised in this reduction of auric chloride to metallic gold is zinc which is described by the following reaction:[36]

$$3\,Zn + 2\,AuCl_3 \rightarrow 2\,Au + 3\,ZnCl_2.$$

The principle underlying this mechanism is that the base metal upon introduction into a solution in which it is soluble dissolves while, at the same time, the ions of the noble metal precipitate out in metallic form. Actually, this reduction reaction occurs by a sequence of steps. First, the chloride ions are transferred to the zinc surface. After these ions are absorbed, the reduction reaction takes place at the zinc surface.[35] Following reduction, the gold is desorbed from the zinc surface and is transported to the bulk of the solution thereby completing the reduction reaction. The cemented gold is of low purity and requires further parting and purification since other metallic ions in solution also cemented out during this treatment.

Precipitation of gold from chloride solutions can be carried out using sulfide ions. The addition of hydrogen sulfide saturated water to the chloride solution at a temperature of 90°C converts the auric chloride to metallic gold by the following reaction:[36]

$$8\,AuCl_3 + 3\,H_2S + 12\,H_2O \rightarrow 8\,Au + 24\,HCl + 3\,H_2SO_4.$$

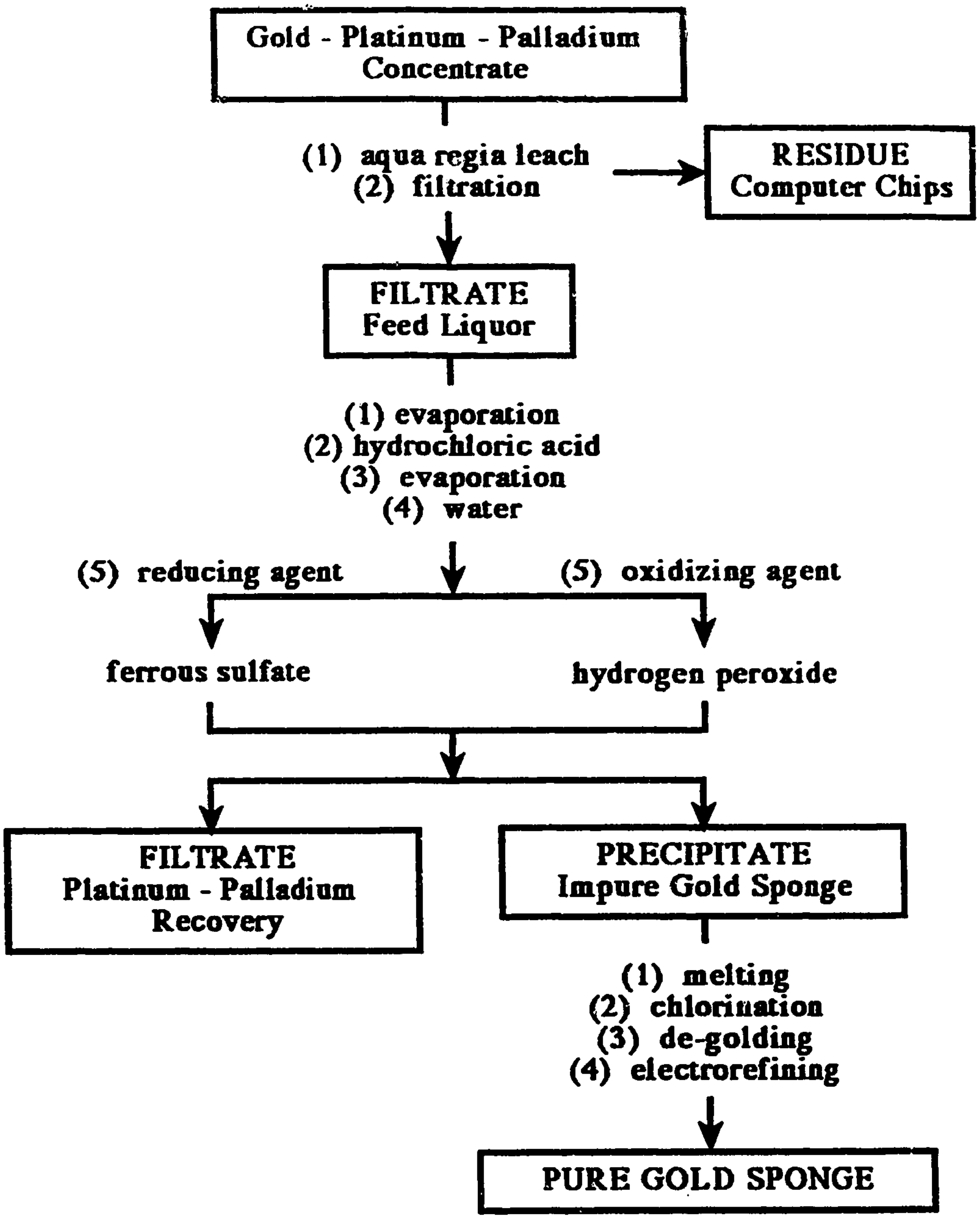

Figure 6.1: Classical process for the recovery of gold.

At temperatures of 38°C or less, auric chloride in water saturated with hydrogen sulfide is converted to gold disulfide instead of metallic gold as shown by the following reaction:[36]

$$8\,AuCl_3 + 9\,H_2S + 4\,H_2O \rightarrow 4\,Au_2S_2 + 24\,HCl + H_2SO_4.$$

A ferrous salt commonly used to precipitate gold from aqua regia solutions free of nitric acid is ferrous sulfate, as shown in the following reaction:[36]

$$AuCl_3 + 3\,FeSO_4 \rightarrow Au + Fe_2(SO_4)_3 + FeCl_3.$$

The amount of ferrous sulfate required to carry out this reaction is approximately seven grams per every gram of gold.[106] Before addition of this reducing agent to the gold solution, it is dissolved in hot water and treated with small increments of concentrated hydrochloric acid until the solution is a clear, apple green. This solution is then added slowly to the gold containing solution to precipitate gold as a fine, dark brown precipitate cloud which is allowed to settle overnight. During precipitation, the emission of brown gas bubbles indicates nitric acid is still prevalent in the solution. In this case, extra ferrous sulfate is added to compensate for the ferrous sulfate lost during exhaustion of nitric acid. After the solution is partially settled, a sample is removed from the ferrous sulfate treated solution to test for gold in solution. Testing is accomplished by immersing a crystal of ferrous sulfate into the designated sample. The presence of a brown cloud around the crystal indicates incomplete precipitation of gold. In this case, the gold containing solution is retreated with extra ferrous sulfate. After precipitation, the cystal test is redone. The lack of a brown cloud around the crystal indicates the complete removal of gold ions from solution. The gold sediment is separated from the barren solution by filtration and is then transferred to a cleaning dish. In cleaning, the gold is washed with hot water, stirred, allowed to settle, and then separated from the clarified solution. After two wash cycles, the gold is treated with boiling concentrated hydrochloric acid to dissolve the light yellow mud obtained from the ferrous sulfate. The gold, free of yellow mud, is separated from the solution by filtration and washed with hot water. A final acid wash along with two hot water washes yielded gold of a reasonable high fineness of approximately 99%.

Sulfur dioxide is an outstanding oxidizing and reducing agent commonly used to precipitate gold from aqua regia solutions since it provides a very good selective precipitation of gold from complex solutions.[106] Before addition of sulfur dioxide, the aqua regia solution is boiled down to the thickness of syrup and resolubilized with hydrochloric acid. This procedure is repeated two or three times before the final solution is diluted with three or four volumes of water. The resultant solution, free of nitric acid and sediment, is treated with sulfur dioxide at a rate of approximately one bubble per second to precipitate gold. The evolution of brown nitrous oxide fumes at this stage indicates the presence of nitric acid in the solution. Nitric acid is purged from the solution by continual addition of sulfur dioxide. Once the nitric acid is expelled, the gold precipitates. The lack of precipitation at this point indicates that the solution pH is too acidic. This situation is remedied by the addition of excess water or sodium bicarbonate to increase the solution pH. After precipitation, the gold powder is separated from the solution by filtration, washed with hot water, boiled with concentrated hydrochloric acid to solubilize any copper or other base metals, washed with water again and finally dried.

An organic compound commonly employed to precipitate gold from aqua regia solutions is oxalic acid, a white crystalline powder dissolved in hot water. Generally, this acid is used only on high quality aqua regia solutions with minor base metal impurities since it is quite expensive in comparison to the other methods presented for gold recovery.[106] Its use is usually considered as a repurification by precipitation process. In this operation, gold powder precipitated by another reducing agent such as sulfur dioxide is redissolved in aqua regia, boiled down to expel nitric acid from the solution, dissolved with water, and then precipitated with an oxalic acid solution, as shown by the following reaction:[106]

$$2\,AuCl_3 + 3\,H_2C_2O_4 \rightarrow 2\,Au + 6\,HCl + 6\,CO_2.$$

Before reduction is undertaken, equal amounts of both solutions, the aqua regia solution and oxalic acid solution, are individually boiled. Once boiling, the gold solution is slowly poured into the hot oxalic acid solution which results in the immediate precipitation of gold. This new precipitate is deficient in base metal impurities.

Oxidizing agents, on the other hand, have not been utilized as precipitating agents for gold even though peroxygens in contact with gold oxide reduce the metallic oxide to metal while simultaneously forming water and oxygen.[118]

$$Au_2O_3 + 3\,H_2O_2 \rightarrow 2\,Au + 3\,H_2O + 3\,O_2.$$

In a similar manner, gold solutions in contact with hydrogen peroxide auto-reduce by yielding metallic gold and evolving oxygen at the same time.[118]

$$2\,AuCl_3 + 3\,H_2O_2 \rightarrow 2\,Au + 3\,O_2 + 6\,HCl.$$

This reaction of hydrogen peroxide with gold compounds occurs quite readily in either acidic or alkaline solutions. Other peroxide solutions which act in the same manner as hydrogen peroxide are sodium peroxide and calcium peroxide.[118]

$$2\,AuCl_3 + 3\,Na_2O_2 \rightarrow 2\,Au + 3\,O_2 + 6NaCl$$

$$2\,AuCl_3 + 3\,CaO_2 \rightarrow 2\,Au + 3\,O_2 + 3\,CaCl_2.$$

After precipitation, the impure gold sponge is upgraded in purity by a sequence of operations which consist of melting, refining, de-golding, and electrorefining, as shown by Figure 6.1. Melting of the impure gold sponge is undertaken in an induction furnace under neutral or slightly oxidizing conditions at a temperature of 1200°C.[35,119] An addition to this melt is fluxing agents, such as soda ash, borax, silica, fluorspar and nitre, to ensure protection of the melt from contamination by the furnace atmosphere and combustion products of the fuel; insulate the melt; accept unwanted liquid and solid components; and alter the fluidity of the slag. After the entire charge is molten, excess fluxing agents are added to achieve a low slag viscosity which minimizes the amount of precious metals entrapped in the slag layer.

Once the impure gold sponge is molten, gold refining is undertaken by the Miller process. In this process, chlorine gas is injected into the molten bullion to react with the base metal impurities to form volatile or nonvolatile metal chlorides.[35,120] The volatile chlorides are lost to the atmosphere as gas while the nonvolatile chlorides are transported by flotation to the slag layer, thereby causing an overall upgrade of the gold bullion. This upgrading is actually carried out in three stages. The first stage eliminates the volatile base metal chlorides such as iron, lead, and zinc which causes high turbulence in the melt. Loss of gold during this stage is prevented by minimizing turbulence through the slow addition of chlorine gas. The second stage commences upon the reduction of turbulence in the melt and formation of a liquid chloride slag consisting of silver and copper. The last stage results when most of the copper and silver exists in the slag and the turbulence of the melt increases due to the formation of volatile gold chlorides. During this stage, gold losses are minimized by halting chlorination at a gold fineness of 99 in the melt.

In de-golding, the slag contaminated with the nonvolatile silver and base metal chlorides is melted with sodium carbonate to recover any contained gold.[35] During melting, silver chloride reacts with sodium carbonate to form molten silver, as shown by the following reaction sequence:

$$2\,AgCl + Na_2CO_3 \rightarrow Ag_2CO_3 + 2\,NaCl$$

$$AgCO_3 \rightarrow Ag_2O + CO_2$$

$$2\,Ag_2O \rightarrow 4\,Ag + O_2$$

while the base metal impurities react with soda ash to form metal oxides. In the melt, silver settles and scavenges gold while the base metal oxides float to the surface of the slag. The molten silver - gold alloy is then recycled to the Miller process.

The bullion from the Miller process undergoes electrorefining by the Wohlwill process.[35,120] The anode sheets are gold while the cathode sheets are titanium. The electrolyte is an aqueous chloride solution prepared by dissolving gold with chlorine gas in the presence of hydrochloric acid, as shown by the following reaction:

$$2\,Au + 3\,Cl_2 + 2\,HCl \rightarrow 2\,HAuCl_4.$$

During electrorefining, gold dissolves from the anodes and is selectively plated at the cathode. Silver forms insoluble silver chloride which precipitates out of solution while platinum and palladium forms soluble chlorides which are removed from the solution after electrorefining by precipitating agents such as ammonium chloride and sodium chlorate, respectively. The Wohlwill electrorefining process produces gold of at least 999 fineness at the cathode.

As a separation scheme, the classical approach has a few drawbacks. First, the leaching process is not efficient because of substantial alloying between the platinum group metals and base metals, and the vast differences in leaching rates for pure metals.[120] Second, the precipitation process is not selective enough because of entrainment of mother liquor and coprecipitation of base metals. Third, the precipitated metal is low in purity and requires upgrading by redissolution and reprecipitation. Fourth, the poor selectivity of the separation stages leads to an process requiring many unit operations and numerous recycle streams. Fifth, the process is slow and tedious. However, for all its shortcomings, the classical approach is still used due to its simplicity.[120]

The efficiency of metal separation and purification is improved immensely in the modern solvent extraction process for the recovery of gold from solutions. Solvent extraction offers greater selectivity, cleaner separations, improved first pass yields, continuous operation, reduced recycling of residues, and higher overall recoveries than precipitation methods.[121] In the Inco process, shown in Figure 6.2, the concentrate is first immersed in a hydrochloric acid - chlorine gas leach medium at 90°C.[122] After filtration, the liquor acidity is adjusted to three to four molarity of hydrochloric acid to ensure that all gold is oxidized to the auric state. This aqueous solution is then treated with dibutyl carbitol to extract the gold into the organic liquid phase. The loaded organic is then physically separated from the aqueous phase and transferred to the stripping process. In stripping, the organic phase is subjected to a hydrochloric acid wash which transfers the gold into an aqueous solution. The gold bearing strip solution is treated with aqueous oxalic acid to precipitate metallic gold. This reduction reaction results in an organic upper layer which is purified and recycled, a spent oxalic acid aqueous middle layer, and a solid

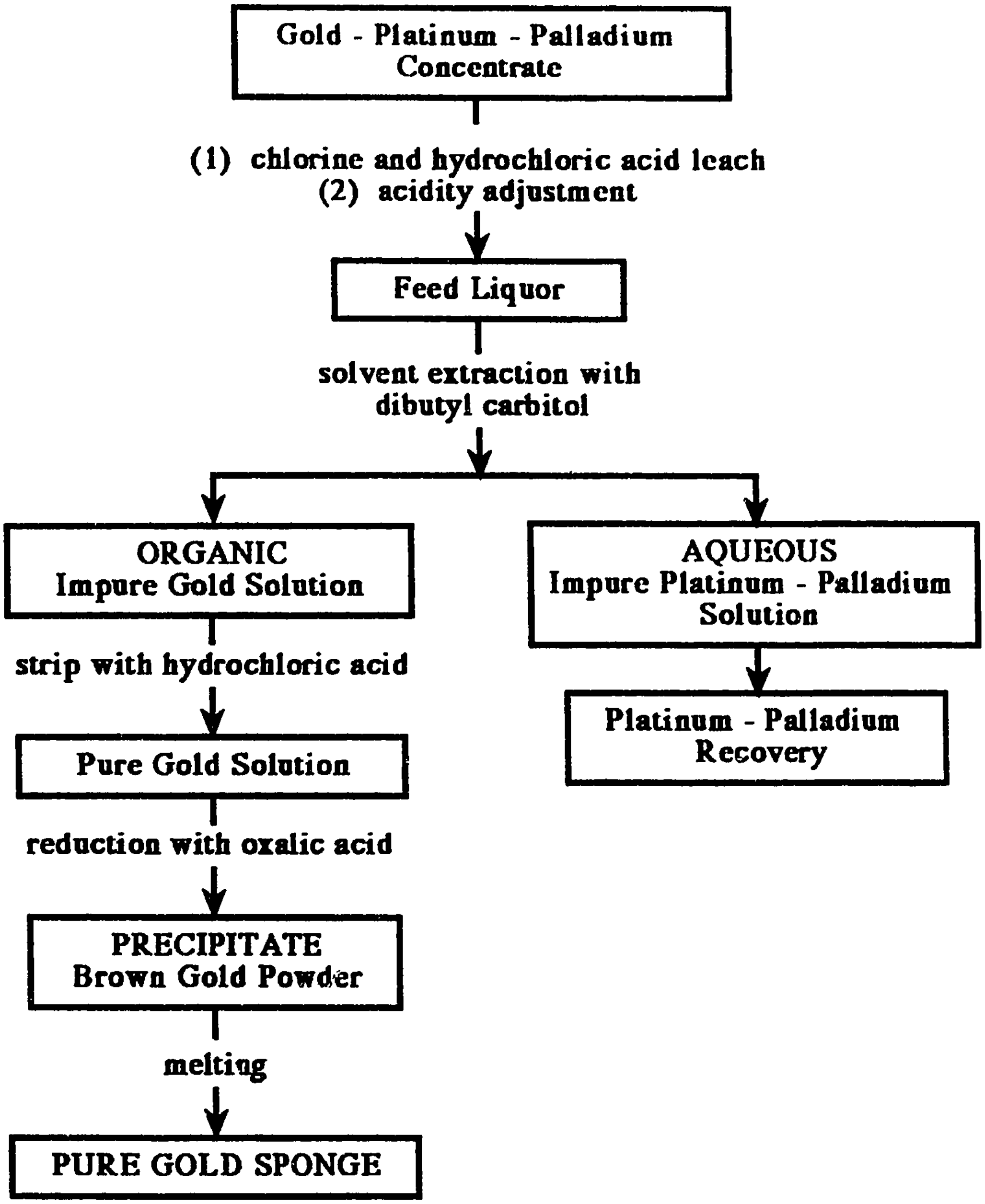

Figure 6.2: Modern process for the recovery of gold.

'brown gold' powder bottom layer. The gold powder is then upgraded in purity by melting and the aqueous phase is transferred to palladium solvent extraction.

The Matthey Rustenburg Refiners process uses methyl isobutyl ketone, MIBK, as the gold extractant.[120] Before extraction in this case, the free hydrochloric acid concentration of the pregnant filtrate is adjusted to a molarity of six. Upon addition of MIBK, the gold is extracted into the organic phase from the filtrate. This organic phase is then treated with a mixture containing hydrochloric acid and oxalic acid to directly precipitate a metallic gold sponge. After filtration, the aqueous phase is transferred to palladium solvent extraction.

### 6.2.1 Gold Separation - Experimental

In precious metal recovery, the coagulated resin - computer chip residue developed from leaching scrap computer circuit boards with a nitric acid - water mixture (noted in Chapter 4, page 85) was treated with aqua regia, a solution containing three parts hydrochloric acid and one part nitric acid, to separate gold, platinum and palladium from the residue. Leaching was conducted by first charging a 250 mL Pyrex beaker exposed to the atmosphere with 50 mL of aqua regia and allowing the solution temperature to stabilize at 70°C. A temperature below the boiling point of water was necessary to ensure minimal solution evaporation and gas emission during leaching. After solution charging, 25 g of residue was added to the Pyrex beaker in 2.5 g increments to minimize the exothermic nature of the reaction between aqua regia and the metallics, and to inhibit excessive solution frothing caused by the evolution of chlorine and nitrosyl chloride fumes from the reaction. A small amount of frothing was beneficial to the overall leach process since solution mixing removed the soluble metal species away from the surface and transported fresh reagent from the solution bulk to the metal's surface thereby allowing the dissolution reaction to proceed at a rapid rate. As the reaction proceeded, gas emission peaked and then subsided in approximately fifteen minutes. At this point, extra nitric acid was added to the slurry to maintain a vigorous but controlled reaction. After one hour of leaching, the precious metals were completely solubilized from the coagulated resin - computer chip residue and hence leaching was discontinued. The resulting slurry was filtered to segregate the solution from the crushed chips and resin intermixed with a silicon oxide precipitate contaminated with trace amounts of iron oxide, aluminum hydroxide and titanium oxide. These precipitates were identified by EDX analysis, as shown in Figure 6.3, and supported by x-ray diffraction. The solid residue was consequently washed with water to remove any absorbed soluble chlorides and then disposed as waste. The washings were united with the previous filtrate to procure a third stage chloride solution for precious metal recovery. Atomic absorption analysis of this solution sample of 100 mL, shown in Table 6.2, identified a net deficiency of precious metals. This prohibited further solution treatment for precious metal recovery without sample adaption.

In adaption, the coagulated resin - computer chip sample size was increased to 250 g and doped with gold containing components. This residue was then leached with 500 mL of aqua regia. After leaching, the solid constituents were separated from the chloride solution by filtration, water washed to remove any absorbed soluble chlorides and disposed as waste. The two solution fractions, chloride filtrate and water washings, were united to form an one litre precious metal solution. Curing the solution overnight resulted in the precipitation of barium nitrate, as shown in Figure 6.4. This precipitate was identified by EDX analysis and supported by x-ray diffraction. The cured solution was consequently filtered to remove the particulate matter. Atomic absorption analysis of the clarified solution determined that the gold content was 535 mg/L. This amount was sufficient to continue processing the solution for precious metal recovery.

In the treatment stage, the clarified aqua regia solution is converted to a chloride solution since free nitric acid in this original solution hinders precipitation by redissolving precipitated gold and then holding the gold ions in solution. This conversion is undertaken

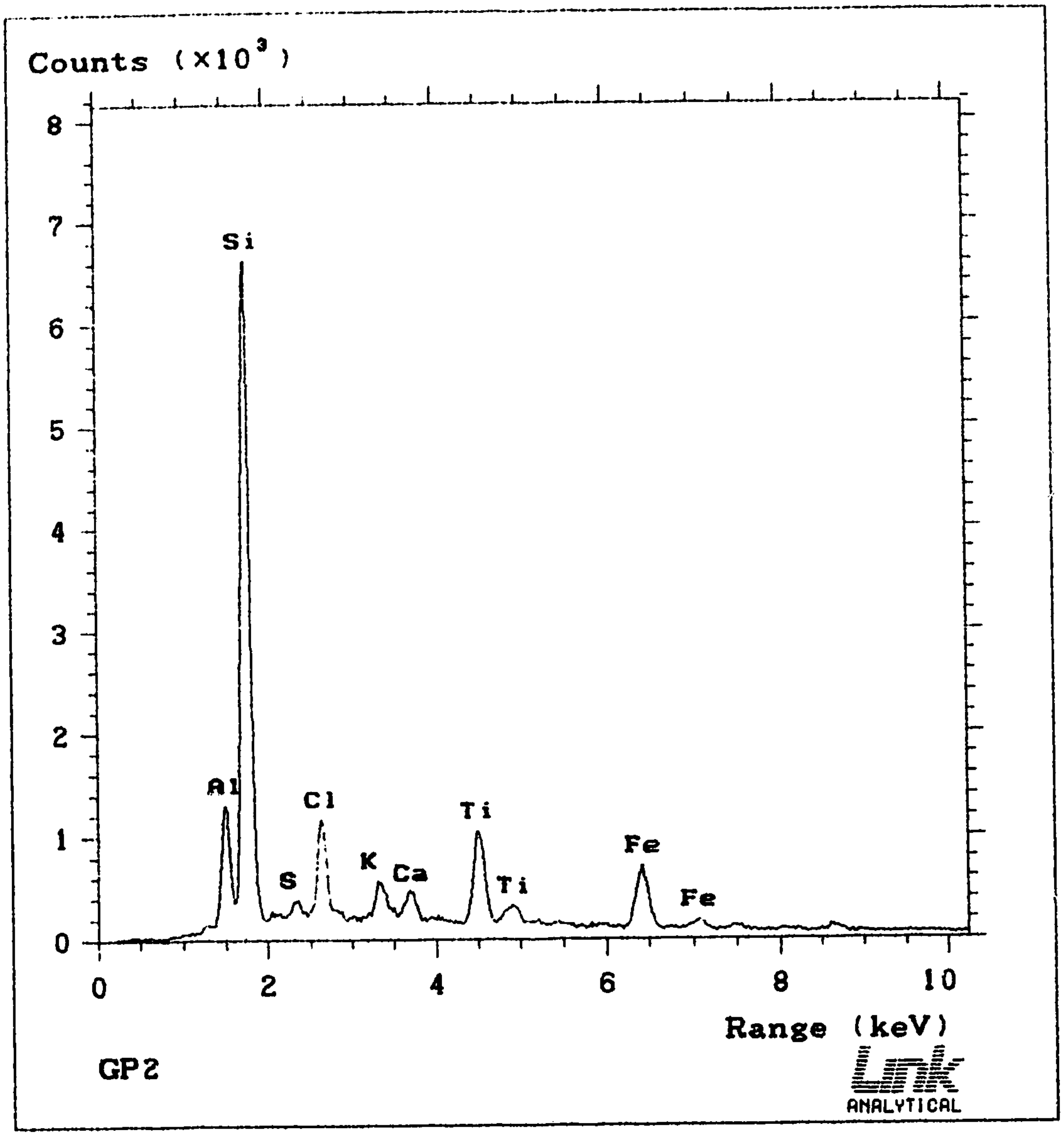

Figure 6.3: EDX analysis of the elements incorporated in the silicon oxide precipitate which was developed from aqua regia leaching.

**Table 6.2: Atomic Absorption Analysis of the Third Stage Leach Solution.**

| Base Metals | | Third Leach (mg/L) | Third Leach (%) | Precious Metals | | Third Leach (mg/L) | Third Leach (%) |
|---|---|---|---|---|---|---|---|
| Aluminum | Al | 570 | 0.326 | Gold | Au | 67.0 | 0.0383 |
| Chromium | Cr | 550 | 0.314 | Palladium | Pd | 12.5 | 0.00714 |
| Copper | Cu | 1500 | 0.857 | Platinum | Pt | 2.5 | 0.00143 |
| Iron | Fe | 2400 | 1.371 | Silver | Ag | 8.0 | 0.00457 |
| Lead | Pb | 24 | 0.0137 | | | | |
| Magnesium | Mg | 95 | 0.0543 | | | | |
| Manganese | Mn | 80 | 0.0457 | | | | |
| Nickel | Ni | 585 | 0.334 | | | | |
| Tin | Sn | 0 | 0. | | | | |
| Titanium | Ti | 825 | 0.471 | | | | |
| Zinc | Zn | 15 | 0.00857 | | | | |

by boiling down the aqua regia solution on the hot plate while constantly stirring the solution with a magnetic spin bar. At first, the liquid volume is rapidly reduced but as the solution thickens, liquid evaporation is decreased. During the latter stages of solution reduction, spattering is usually prevalent due to overheating. This is avoided by decreasing the temperature to minimize the rate of evaporation. Heating is discontinued when the solution resembles a thick syrup. At this point, the thickened liquid is diluted with hydrochloric acid and then re-evaporated to a syrup consistency. The evaporation, liquification with hydrochloric acid and re-evaporation steps is undertaken at least twice and preferably three times to ensure that the solution is free of nitric acid. After the last evaporation, the solution is diluted with hot water to three or four times its original bulk and allowed to cure overnight. Curing results in the precipitation of either a brown precipitate which contains mainly iron, titanium and tin, as shown in Figure 6.5, or a white precipitate which contains only titanium, as shown in Figure 6.6. The compounds

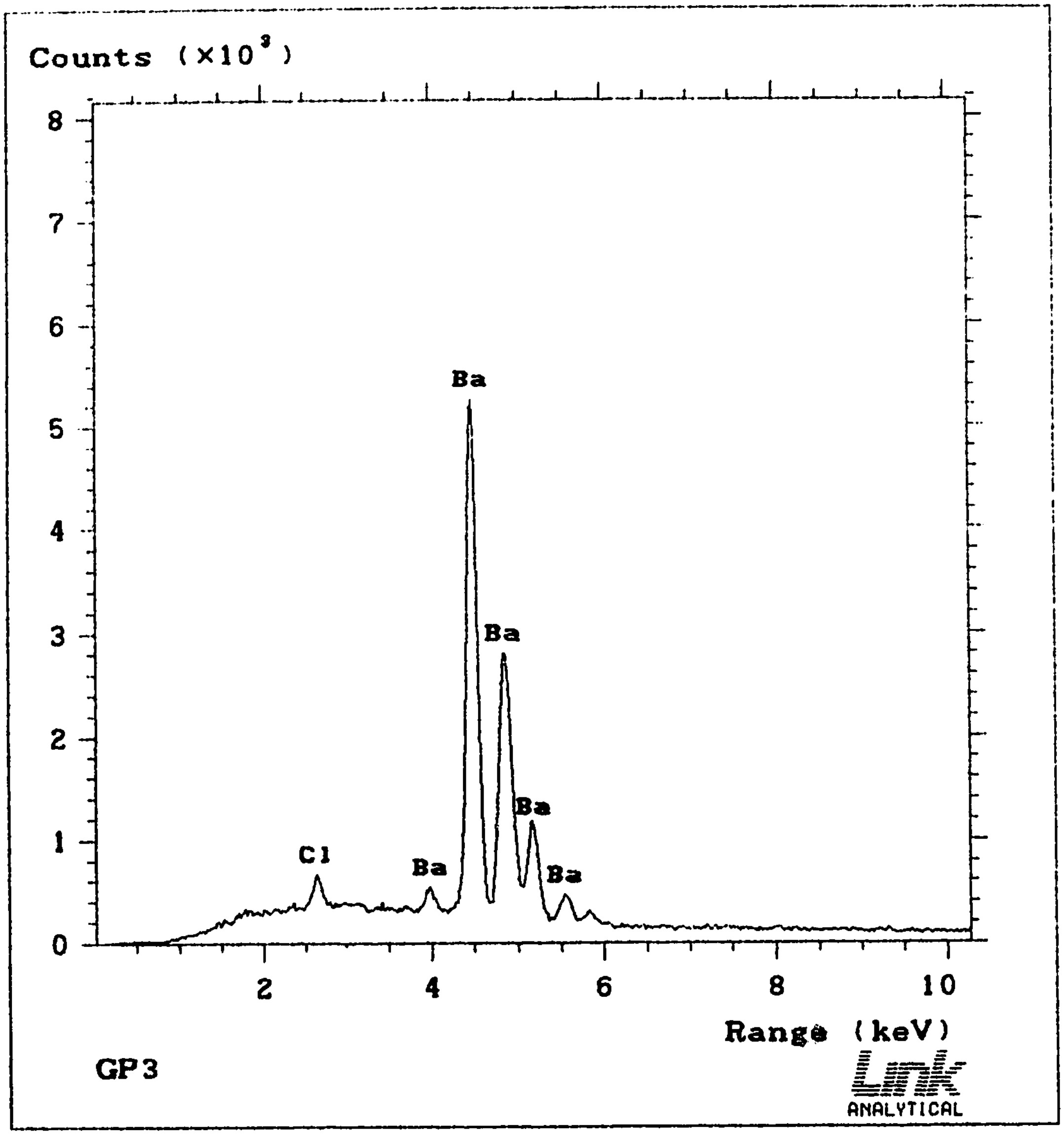

**Figure 6.4:** EDX elemental analysis of the barium nitrate precipitate which was developed from curing the aqua regia leach solution.

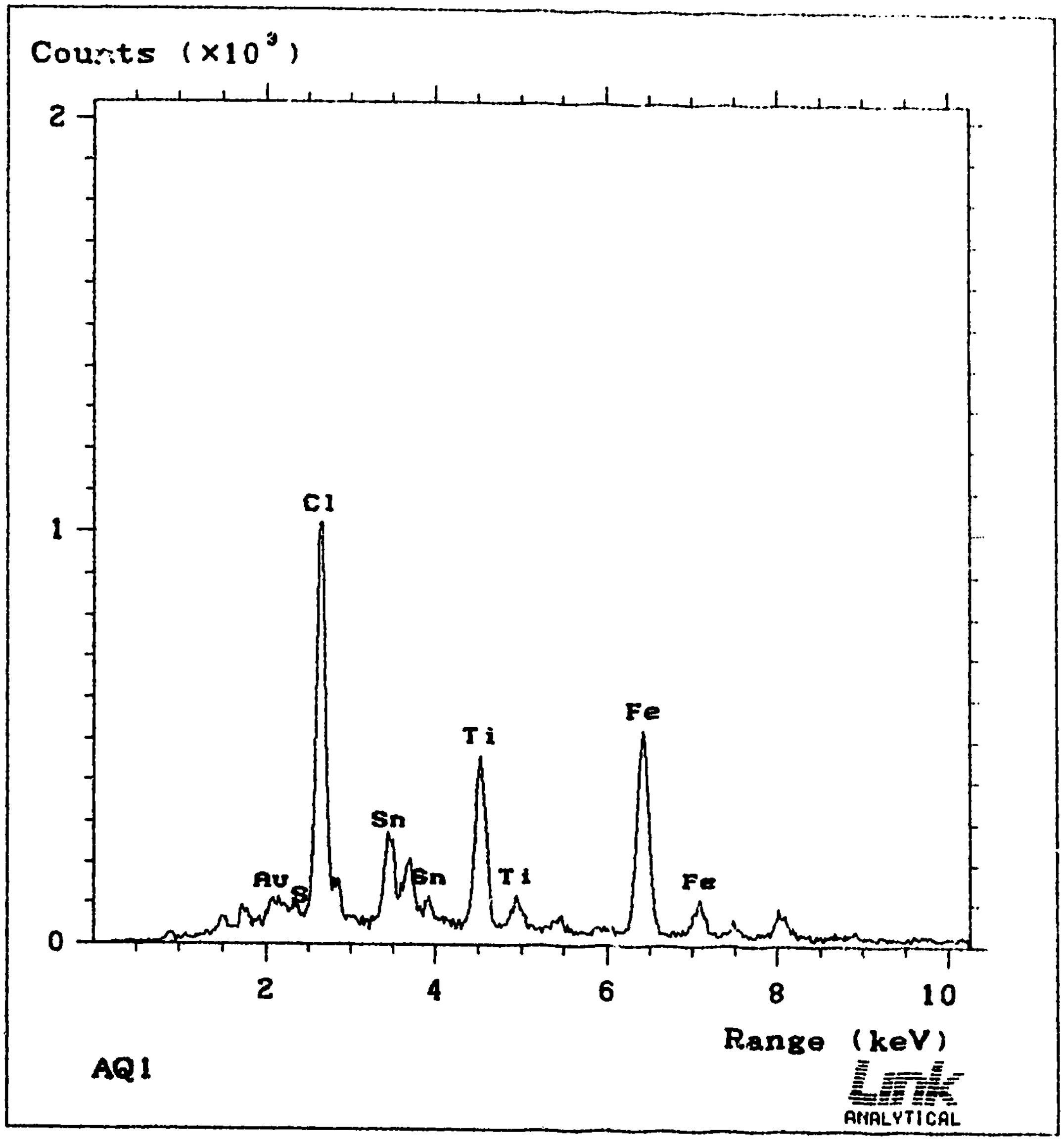

Figure 6.5: EDX elemental analysis of the brown precipitate which was developed after resolubilization of the chloride syrup with hot water.

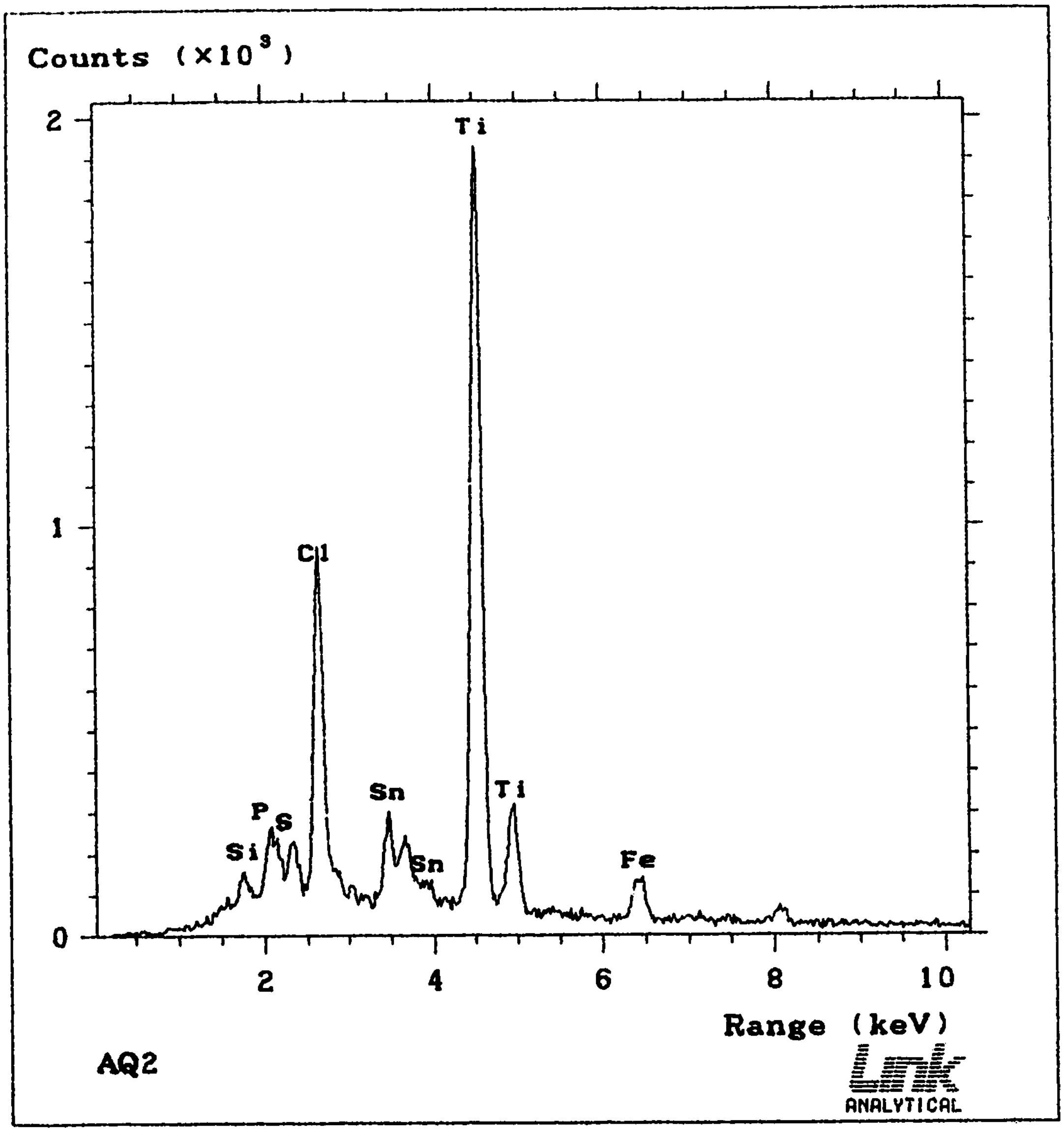

Figure 6.6: EDX elemental analysis of the white precipitate which was developed after resolubilization of the chloride syrup with hot water.

corresponding to these attained elements were iron oxide, titanium oxide and tin oxide; identified by EDX and x-ray diffraction analysis. The cured solution is then filtered to remove the particulate matter which would contaminate the gold precipitate developed at a later stage. This solution containing gold, platinum and palladium as soluble chlorides is now ready for precious metal recovery.

There are several ways of precipitating gold from the solution, one of which is ferrous sulfate. The amount of this compound required to carry out gold precipitation is approximately seven grams per every gram of gold.[106] Therefore, the one litre solution containing approximately 535 mg of gold needs 3.75 g of ferrous sulfate to precipitate impure gold. A detailed description of this precipitating reagent is presented on page 161. After precipitation, the gold flakes were contaminated with titanium, tin, antimony and silicon, as shown in Figure 6.7, and intermixed with a barium sulfate precipitate, as shown in Figure 6.8. Gold is separated from these undesirable contaminants by retreating the precipitates with the aqua regia digestion - ferrous sulfate precipitation procedure.

## 6.3 Platinum Separation - Theoretical

The classical approach for the recovery of platinum from an aqua regia solution involves a series of precipitations, as shown in Figure 6.9. From a solution at 90°C, platinum chloride is precipitated as insoluble ammonium chloroplatinate by the addition of ammonium chloride which is produced from dissolving 214 g of ammonium species in hot distilled water and then diluting the solution to a volume of one litre.[120,121] This reaction mechanism between the two chloride species is designated by the following:

$$PtCl_4 + 2\ NH_4Cl \rightarrow (NH_4)_2[PtCl_6]$$

and requires approximately 0.6 grams of ammonium chloride for every gram of platinum. The precipitate is a bright orange - yellow colour. It is washed with water and dried. This impure salt requires purification since other platinum group metals are coextracted during precipitation. The purification process involves the calcination of the impure salt to a crude

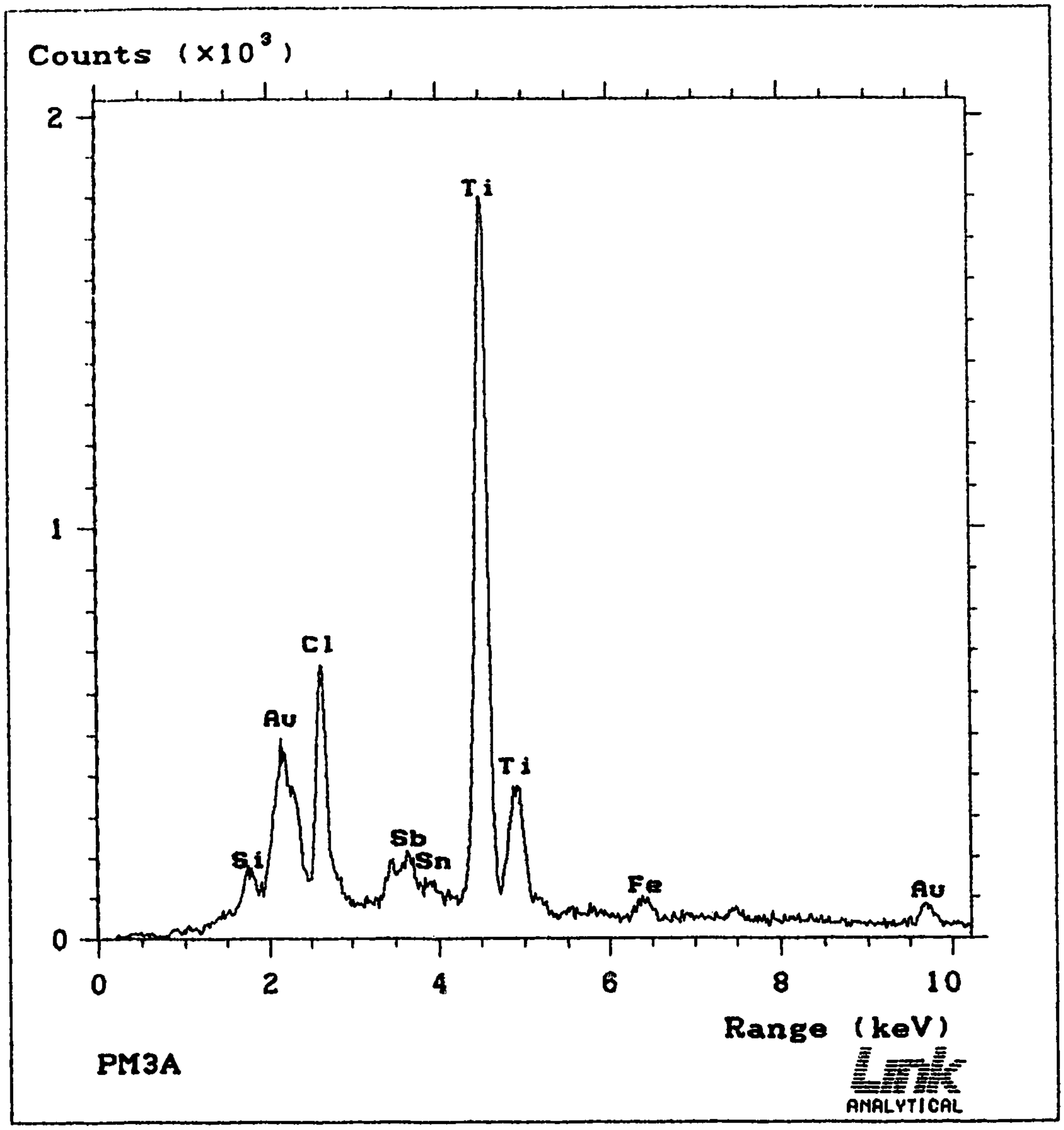

Figure 6.7: EDX elemental analysis of gold flakes which were obtained from a chloride solution through ferrous sulfate treatment.

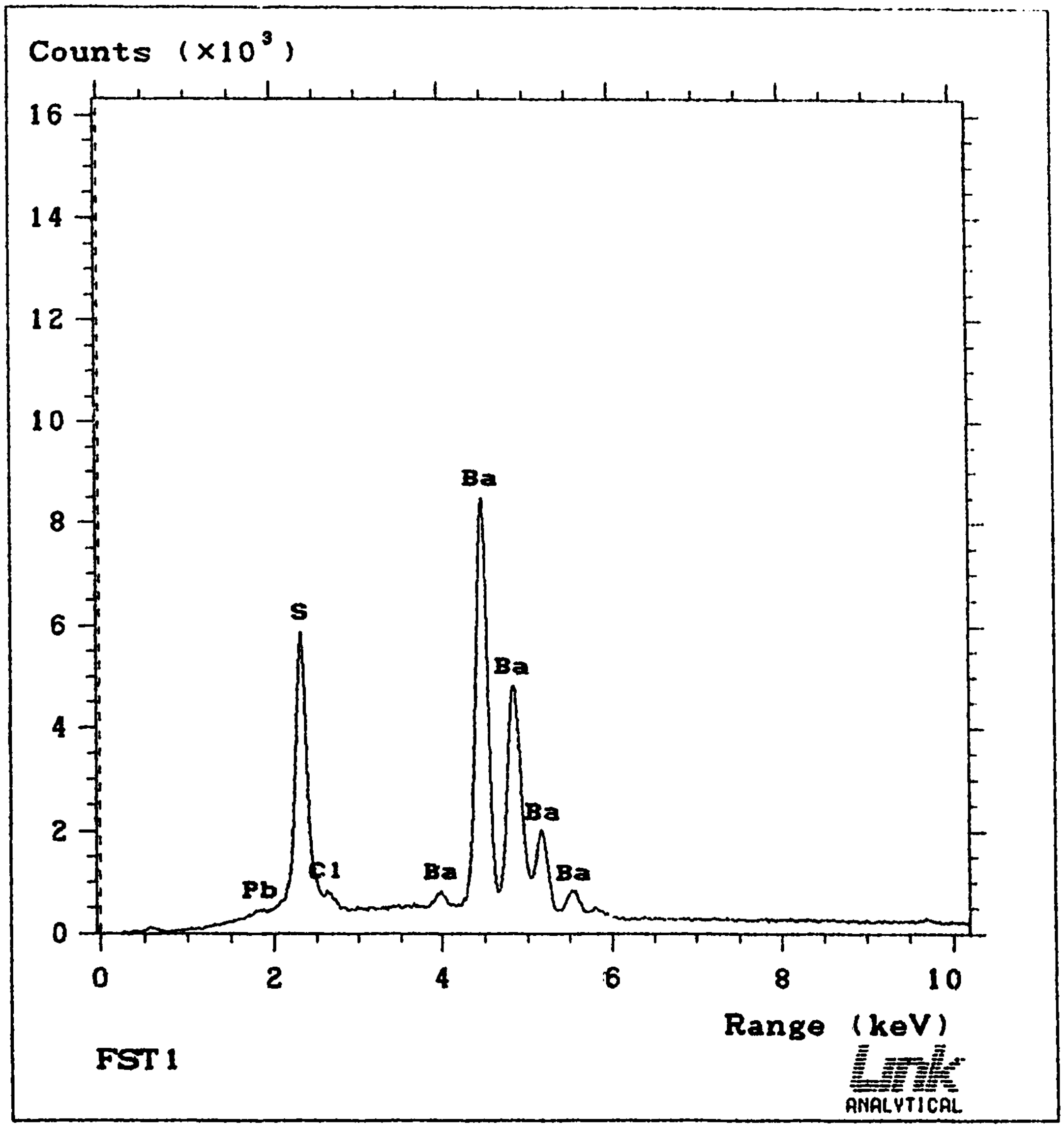

**Figure 6.8:** EDX analysis of barium sulfate precipitate which was obtained from a chloride solution through ferrous sulfate treatment.

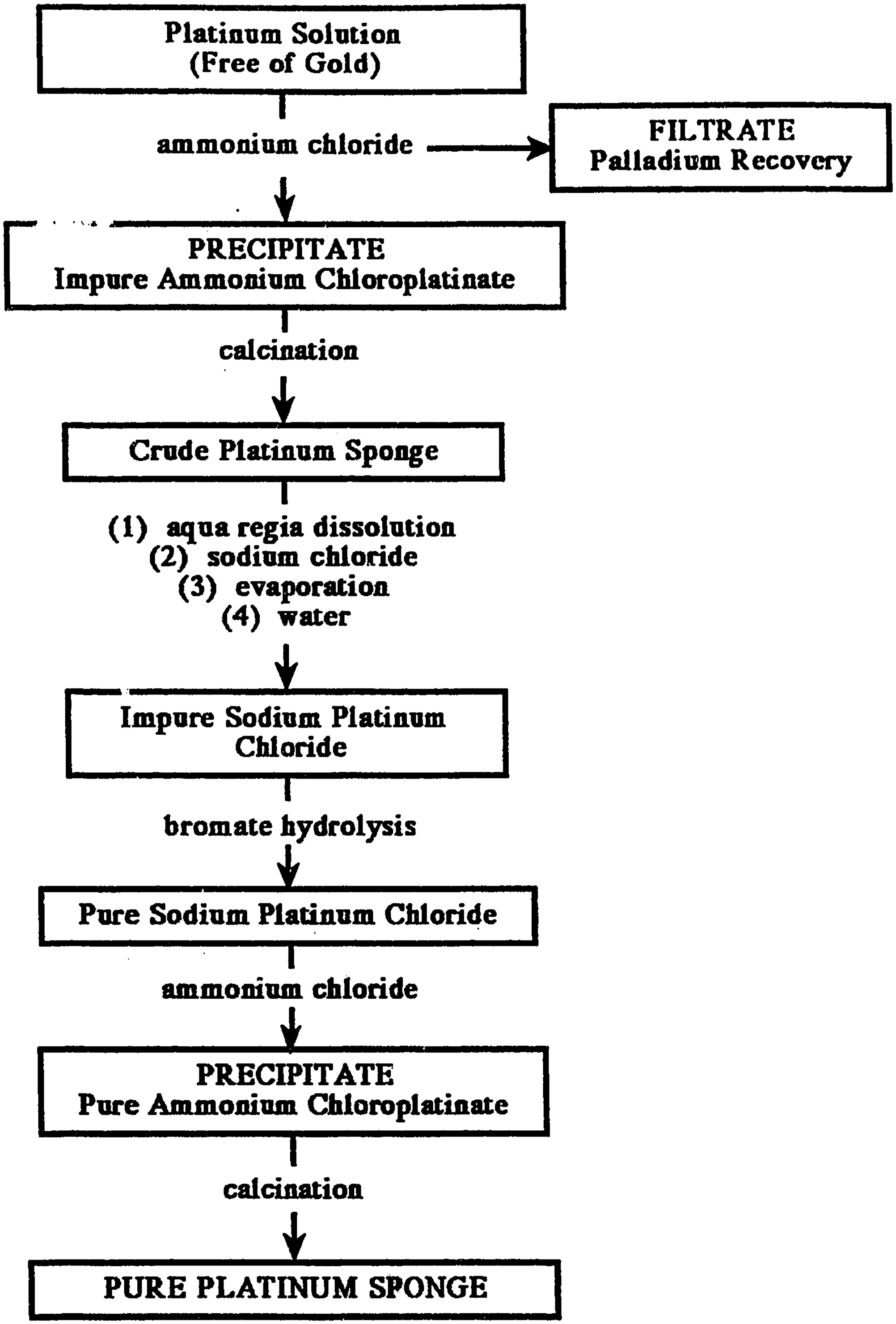

Figure 6.9: Classical process for the recovery of platinum.

platinum sponge followed by dissolution in aqua regia. After filtration, the filtrate is doped with sodium chloride and hydrochloric acid, then evaporated. The produced sodium chloroplatinate residue is resolubilized with water. This slightly acidic solution is subjected to bromate hydrolysis to precipitate the contaminants as hydrated oxides.[123] During this process, ruthenium is removed as volatile ruthenium tetroxide and iridium, rhodium and palladium are converted to valency states amenient for subsequent precipitation with hot sodium bromate. After hydrolysis, the excess bromate is destroyed by boiling the pure platinum solution with hydrochloric acid. This solution is treated next with ammonium chloride to precipitate platinum as ammonium chloroplatinate. This salt, after drying, is roasted at 1000°C to give a pure platinum sponge of 99.99% purity.[28,120]

The modern approach for the purification of platinum from solution is based upon solvent extraction, as shown by Figure 6.10. Before platinum extraction, the solution is treated with a reductant, normally sulfur dioxide, to reduce possible platinum contaminating elements such as the minor platinum group metals into the trivalent oxidation state. During this process, platinum remains in solution as the $PtCl_6^{2-}$ complex. This impure aqueous solution is then acidified to a hydrochloric acid molarity of five or six. After acidity adjustment, the solution is treated with tributyl phosphate, TBP, or a secondary ammine to extract the platinum into an organic liquid phase.[120] The organic, loaded with platinum, is then physically separated from the aqueous phase and transferred to the stripping process. In stripping, the platinum is transferred back to the aqueous solution thereby obtaining a purified, upgraded platinum solution. The TBP organic extract is stripped with water while the amine organic extract is stripped with a dilute caustic solution. The platinum bearing strip solution is further upgraded in purity by the bromate hydrolysis procedure. After upgrading, platinum is precipitated from solution by treatment with ammonium chloride. The pure ammonium chloroplatinate is converted to a 99.98% pure platinum sponge by calcination at 450° to 500°C in air.

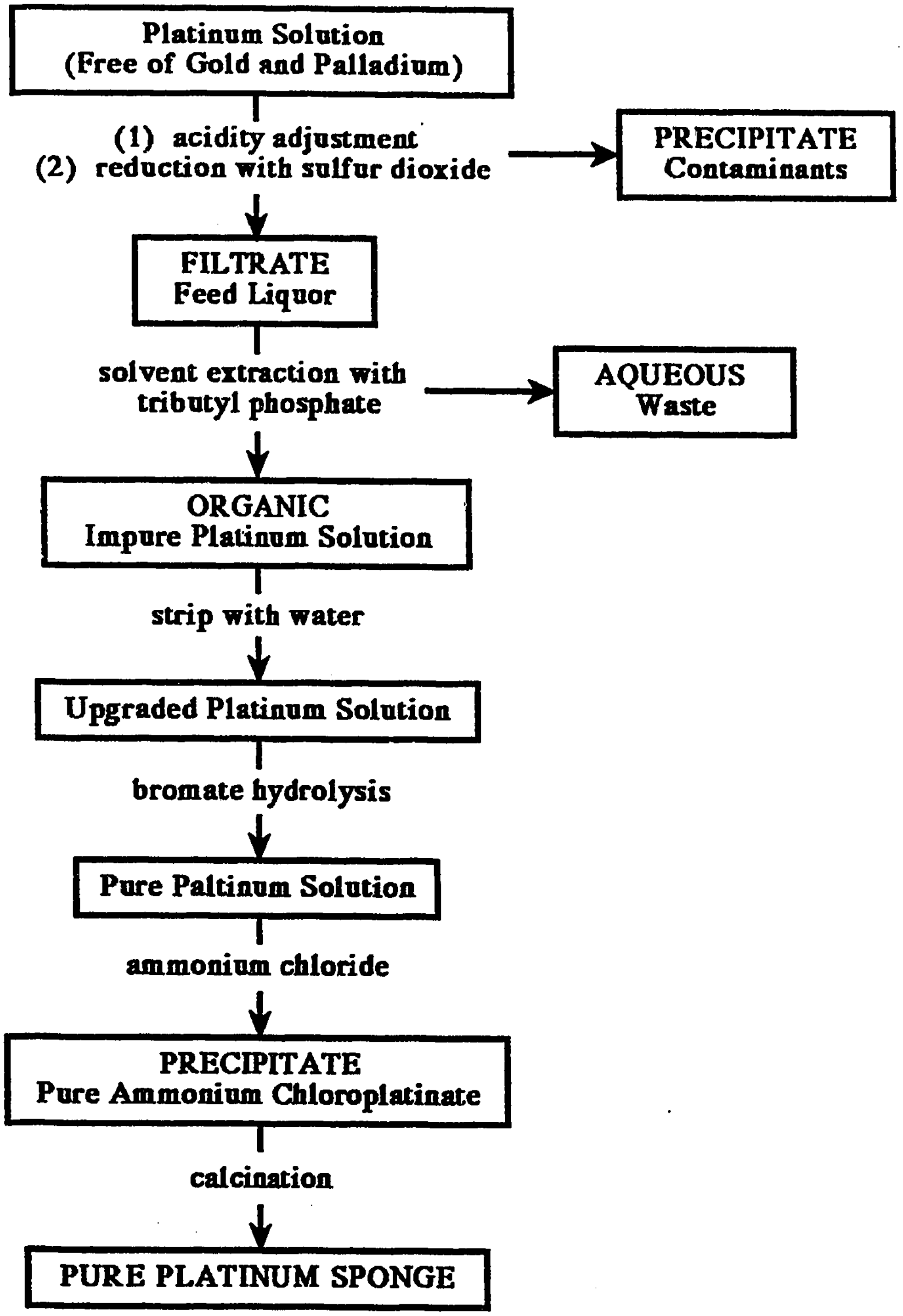

Figure 6.10: Modern process for the recovery of platinum.

The recovery of platinum from an aqua regia solution could not be attempted due to the minimal amount of this element in the computer chip residue.

## 6.4 Palladium Separation - Theoretical

In the classical approach, palladium is recovered from the aqua regia solution after removal of gold and platinum. The aqua regia solution is treated with ammonium hydroxide, as shown in Figure 6.11, to convert the palladium (II) state into the tetrammine complex by the following:[28,120,121]

$$PdCl_2 + 4\,NH_3 \rightarrow [Pd(NH_3)_4]Cl_2.$$

Conversion of the tetrammine complex into an insoluble diammine complex, an orange - yellow salt, is made possible with the addition of hydrochloric acid by the following reaction mechanism:

$$[Pd(NH_3)_4]Cl_2 + HCl \rightarrow [Pd(NH_3)_2]Cl_2 + NH_4Cl + NH_3.$$

The insoluble diammine complex is converted to an impure palladium sponge by calcination. Upgrading of the sponge purity is done by dissolution in aqua regia. The nitric acid is removed by numerous evaporations with hydrochloric acid, the last evaporation being carried almost to dryness. The palladium chloride is then dissolved in water before ammonium hydroxide addition to convert the chloride into a tetrammine chloride. Palladium diammine chloride is precipitated from solution by the addition of hydrochloric acid. This salt is then converted to palladium black by reduction with formic acid. A high grade palladium metal sponge is produced by calcination.

In the modern approach, palladium recovery is based upon solvent extraction techniques. Palladium is recovered from the aqueous phase from methyl isobutyl ketone solvent extraction, as shown by Figure 6.12, by use of dialkyl sulfide, $R_2S$, which functions by a ligand exchange mechanism.[120] Before palladium extraction, the acidity of the aqueous phase is reduced by partial evaporation and water dilution. The organic, loaded with palladium, is then stripped with an ammonia solution which results in the

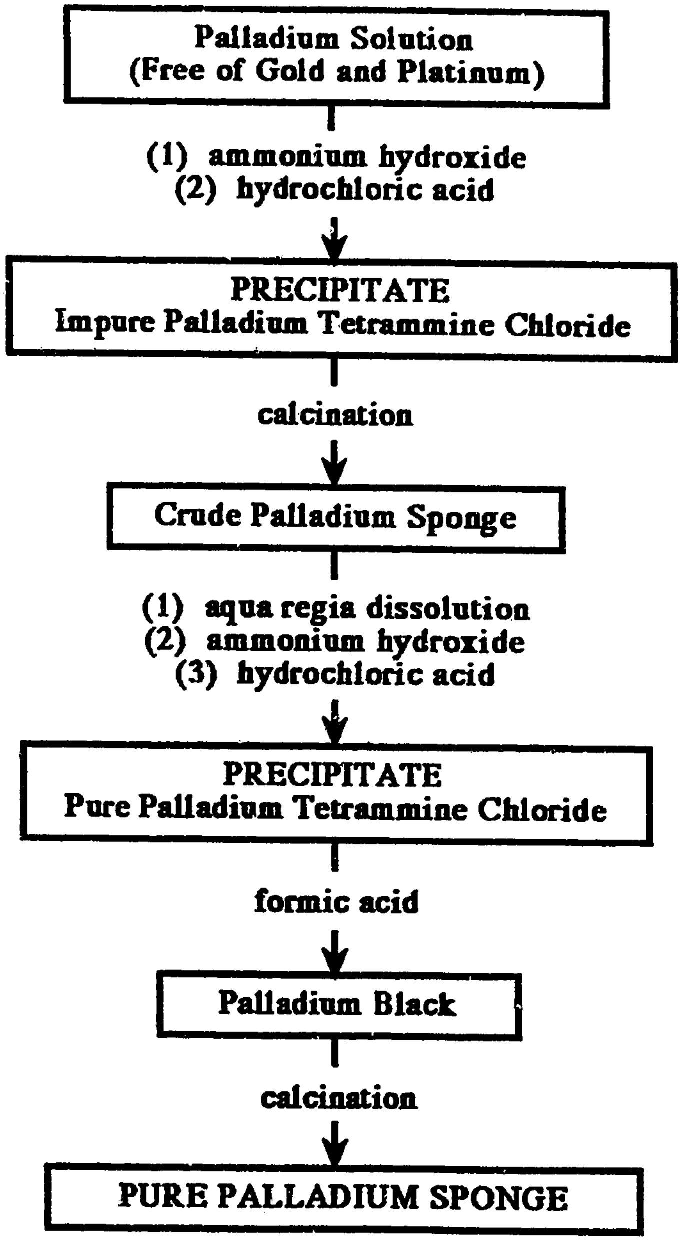

Figure 6.11: Classical process for the recovery of palladium.

substitution of the ammonia for the dialkyl sulfide and chloride, as shown by the following reaction:[120]

$$PdCl_2(R_2S)_2 + 4\,NH_3 \rightarrow Pd(NH_3)_4^{2+} + 2\,R_2S + 2\,Cl^-.$$

The aqueous solution obtained from the stripping operation is a purified palladium solution with a higher palladium ion content. The further addition of a controlled quantity of ammonium hydroxide causes the precipitation of palladium diammine chloride. This salt is calcined at 450° to 500°C in air to yield a 99.98% pure palladium sponge. The aqueous raffinate is transferred to platinum solvent extraction.

The recovery of palladium from an aqua regia solution could not be attempted due to the minimal amount of this element in the computer chip residue.

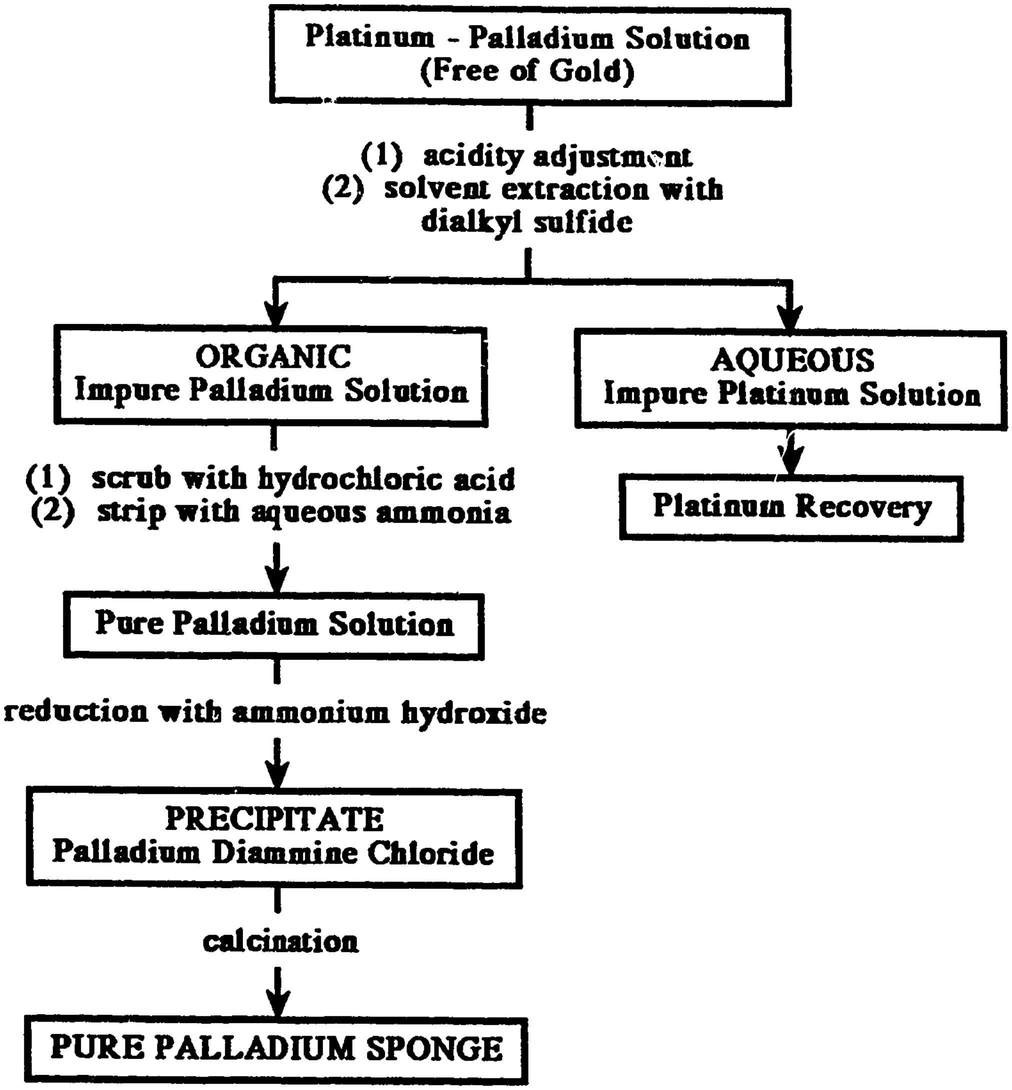

Figure 6.12: Modern process for the recovery of palladium.

# Chapter 7
# Conclusions

The results obtained through this study of the influence of nitric acid and aqua regia leaching on the solubilization of base and precious metals from scrap computer circuit boards and the effectiveness of the precipitation of these metals from nitrate and chloride solutions allow the following conclusions to be drawn:

(1) The preferred flow sheet for the treatment of as-received scrap computer circuit boards, as shown in Figures 7.1 to 7.3, involves the following stages: (1) leaching in nitric acid - water system, (2) mechanical crushing of computer chips and coagulated resin, (3) leaching in nitric acid - water system, (4) stripping of silver from leach solution with chloride ions, (5) cementation of copper with particulate iron, (6) precipitation of lead with sulfuric acid, (7) precipitation of iron with sodium hydroxide, (8) precipitation of nickel with oxalic acid, (9) leaching of solid residue in an aqua regia system, (10) precipitation of gold with ferrous sulfate, (11) precipitation of platinum with ammonium chloride, and (12) precipitation of palladium with ammonium hydroxide and hydrochloric acid.

(2) The following nitric acid leach conditions maximize metal dissolution, but minimize fiberglass decomposition: acid concentration - one part nitric acid to two parts water, temperature - 70°C, pulp density - three millilitres of solution per one gram of solid, and retention time - one hour. Under these conditions, the computer chips readily separate from the fiberglass boards.

(3) Recovery of gold, as a solid metallic residue, from gold plated base metal substrates results in the one:two nitric acid:water mixture by dissolution of the interior base metal by chemical tunnelling.

(4) Mechanical crushing completely liberates base and precious metals contained within the plastic or ceramic protective computer chip cases. An one:two nitric acid:water leach readily cleans the crushed computer chip - coagulated resin product of base metals, which would contaminate the gold precipitate.

(5) Silver precipitates completely from a complex nitrate solution as silver chloride with the addition of sodium chloride or hydrochloric acid. Leaching the precipitate with ammonium hydroxide dissolves silver chloride, but, not the contaminant, lead chloride. A high purity silver chloride product precipitates from the resultant solution by altering the pH to acidic with nitric acid.

(6) Silver chloride converts into metallic silver by a two step process consisting of silver oxide formation and decomposition. Oxide formation occurs by immersing silver chloride into a solution containing 25 times the potassium hydroxide stoichiometric requirement. Addition of hydrogen peroxide to this suspension results in the decomposition of the oxide to metallic silver.

(7) Elemental silver in the form of fine powder results by mixing sodium carbonate with silver sulfide at a molar ratio between 1.40:1 and 1.75:1, and heating this mixture in the range of 550° to 600°C to effect a solid state reaction within three hours.

(8) Cementation of copper from a copper nitrate solution at a pH of -0.25 and a temperature of 25°C is 99.8% complete with 2.25 times the iron stoichiometric requirement. Higher temperatures hinder cementation since the cemented copper redissolves to some degree. For example, at 40° and 55°C, the recovery of copper is 92.5% and 0%, respectively. Solution acidity's above a pH of -0.25 result in the complete cementation of copper at 25°C, but iron hydroxide contaminates the cemented product.

(9) Lead completely precipitates from a complex nitrate solution as lead sulfate with the addition of concentrated sulfuric acid at an acid to solution ratio of 1:2 and a temperature of 80°C.

(10) Lead partially precipitates from a nitrate solution by addition of hydrochloric acid or sodium chloride. Resolubilization of the precipitated lead chloride occurs in solutions containing excessive amounts of chloride ions.

(11) Recovery of iron as a crystalline, coarse hydroxide occurs by treating the highly acidic solution with sodium hydroxide to increase the solution pH to 3.5, increasing the temperature to 80°C, and aerating.

(12) Nickel readily precipitates in the form of nickel oxalate by reacting the aqueous nickel sulfate solution at a pH of 3.5 with a slight excess of oxalic acid and boiling for at least 30 minutes.

(13) An aqua regia leach at 70°C for one hour separates metallic gold from the tin oxide, computer chip and resin mixture. Addition to the chloride solution, free of nitric acid, of at least seven grams of ferrous sulfate per every gram of gold completely precipitates gold as an impure metallic product.

(14) Platinum completely precipitates from a chloride solution at 90°C by addition of 0.6 g of ammonium chloride per every gram of platinum.

(15) Palladium recovery from a chloride solution results by treating the chloride solution with a slight excess of ammonium hydroxide to convert the palladium (II) state into the tetrammine complex. Conversion of this complex into an insoluble diammine complex occurs by adding hydrochloric acid to the solution.

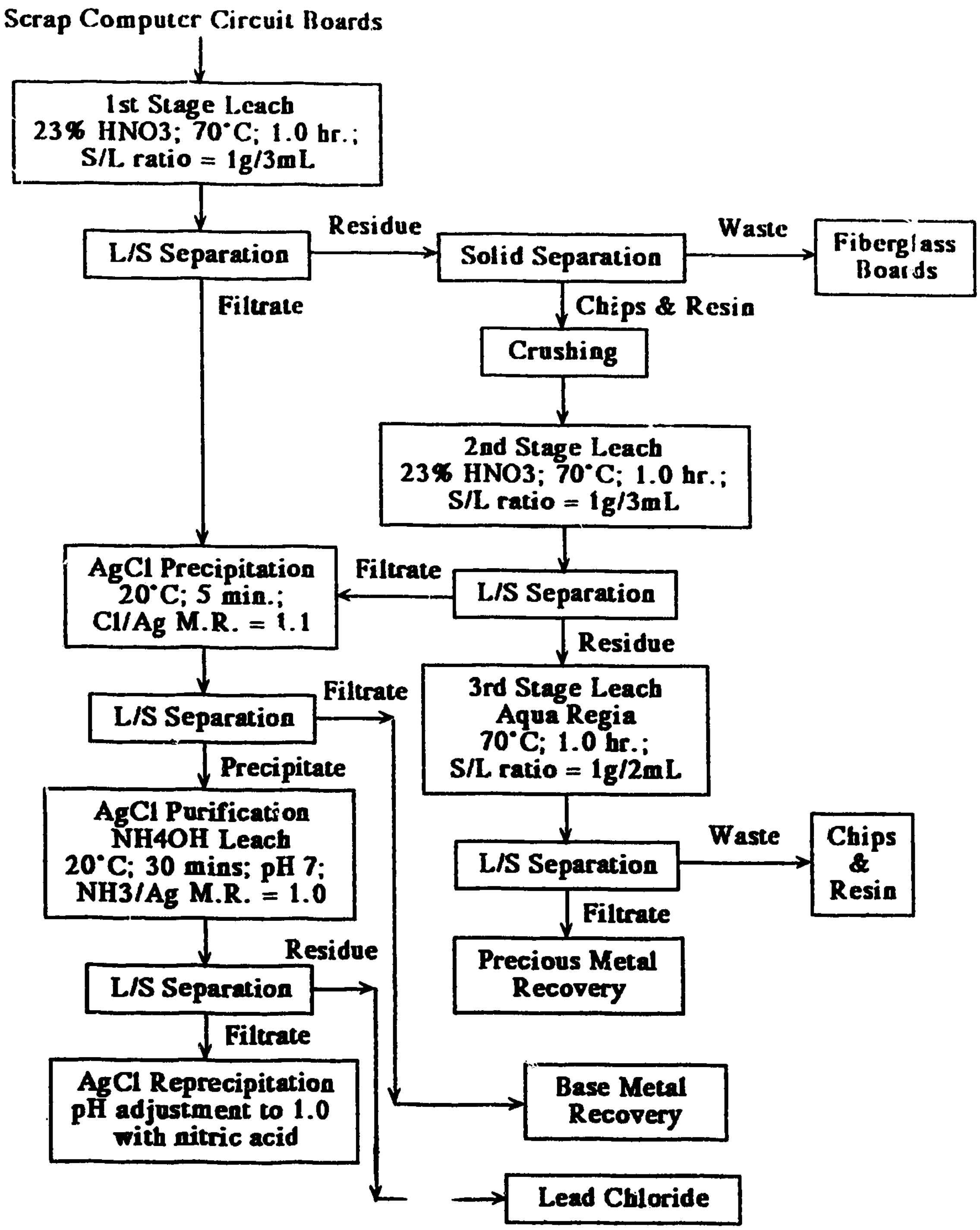

**Figure 7.1:** Flow sheet for leaching base and precious metals from scrap computer circuit boards.

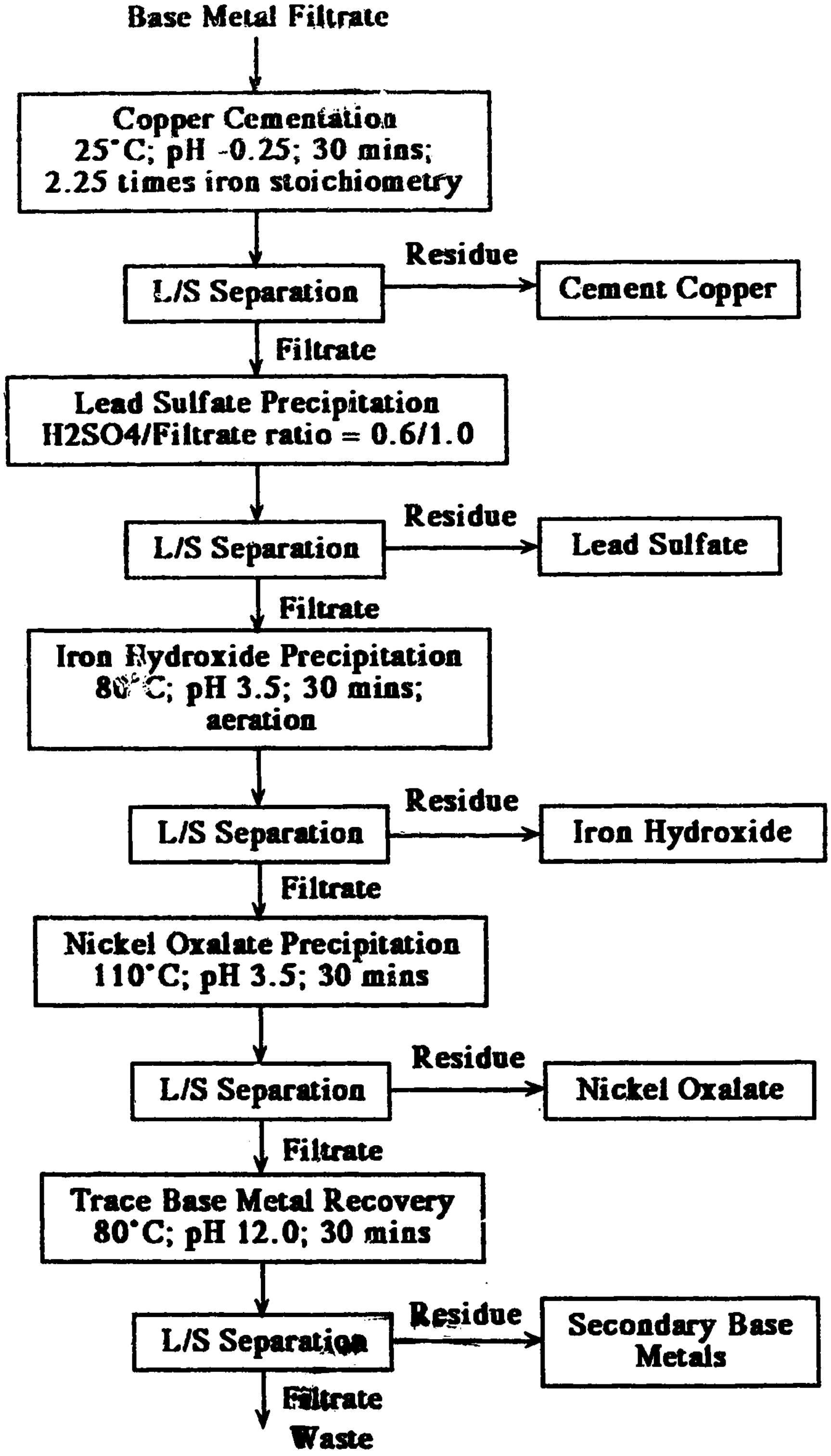

Figure 7.2: Flow sheet for the recovery of base metals from a complex metal nitrate solution.

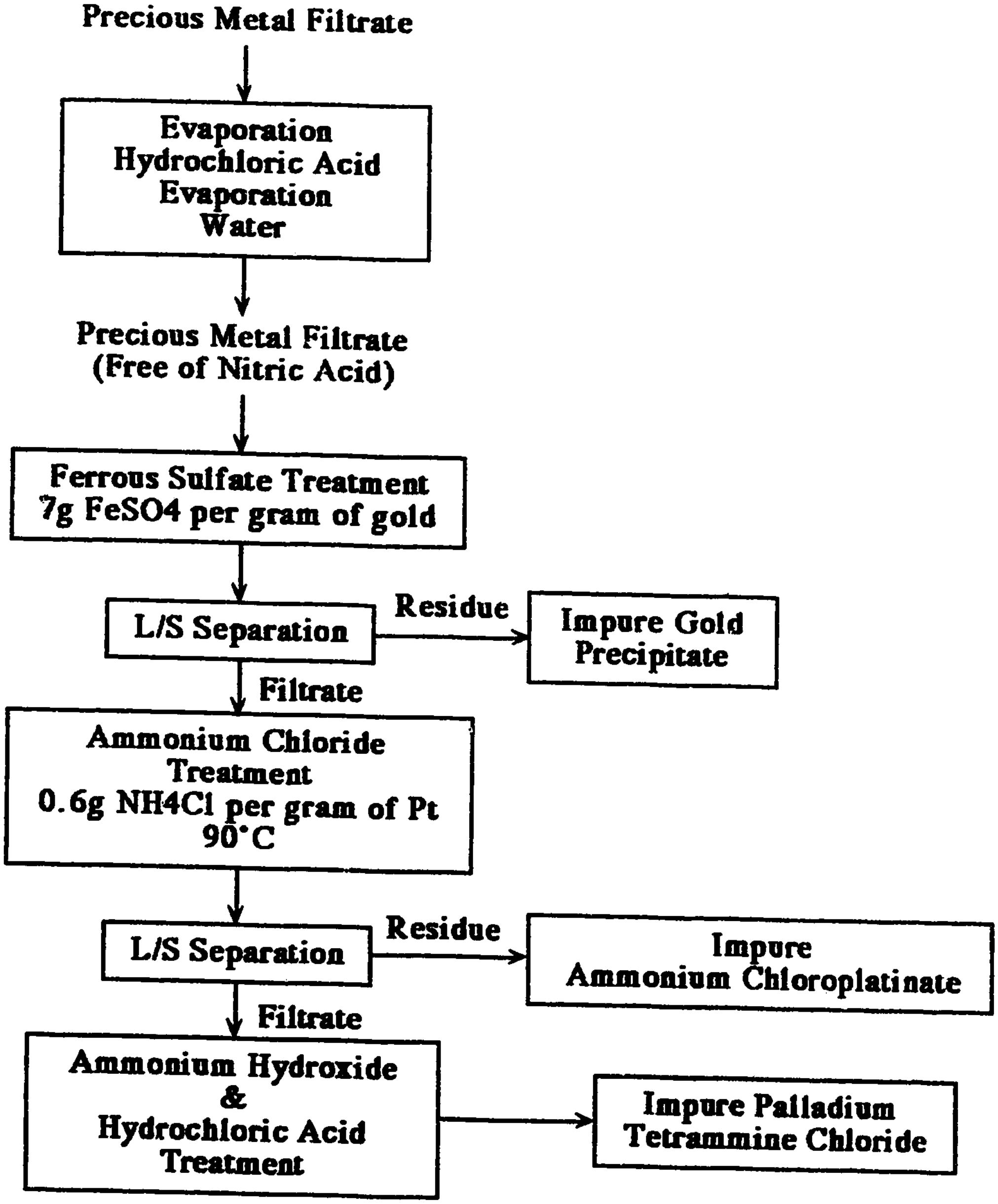

Figure 7.3: Flow sheet for the recovery of precious metals from a complex metal chloride solution.

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# Appendix A

# The Rapid Method for Precious Metal Analysis

The Rapid method was used to determine the precious metal content of the various sized fractions of crushed computer circuit boards. Before employment of the Rapid method,the sized fractions must be effectively reduced from their overall quantity to a representative sample size. A sample is hence defined as a quantity of material taken from a larger quantity for the purpose of estimating the properties of the larger quantity. Accurate sampling of metals from any scrap material is a very difficult task. The difficulties arise mainly from the fact that scrap is usually heterogeneous. Accuracy of the analysis relies upon the sample which is selected. Statistical reliability is achieved through the quantity of particles in the sample. That is, for finer particles, the surface area of the sample is greater and hence the sample becomes more homogeneous. Thus, there is a relationship between the largest material size and the quantity of material required for proper representation. In a chemical analysis, the sample size required for accurate analysis is between one and thirty grams depending upon the particle size. For an one gram sample, the material should be all minus 200 mesh; whereas, for a thirty gram sample, the material should be all minus 35 mesh.

The reduction of the overall sample size of each fraction to a representative size was accomplished with a Jones riffle. This splitter is an open V-shaped box in which a series of chutes is mounted at right angles to the long axis giving a series of rectangular slots of equal area alternately feeding two trays placed on either side of the trough. The crushed computer circuit board sample was poured into the series of chutes and split into equal portions by the slots. Before one of the halves was discarded, the pouring and splitting stage was employed three times to ensure proper mixing of the overall sample. This procedure was continued until a sample size of approximately 40 to 50 g was achieved.

From each representative sample, a grab sample of 10.00 g was removed. A grab sample is a small quantity of material chosen at random from different spots in the large bulk (representative) sample. The grab sample was then placed in a 500 mL Erlenmeyer flask. To the flask, 150 mL of hydrochloric acid was added. Dissolution of the crushed computer circuit boards was further enhanced through the application of heat. Heat was supplied by a hot plate at a temperature of approximately 150°C. This mixture was slowly digested down to approximately 50 mL. At this point, nitric acid and sulfuric acid were both added in 25 mL portions to the solution. Great caution must be exercised during the mixing of these acids since they not only produce harmful vapours but also boil over if mixed quickly together with the heated hydrochloric acid - crushed computer circuit board mixture. This new mixture was then digested down to approximately 25 mL. After digestion, the walls of the flask were throughly cleaned with a distilled water spray. The flask was then returned to the hot plate where it was allowed to boil for a few minutes. After boiling, the solution and solids were transferred to a teflon beaker. The solution was then returned to the Erlenmeyer flask. To the retained solids approximately 10 mL of hydrofluoric acid was added. Utmost caution must be employed while using hydrofluoric acid since it is highly corrosive to the skin and the fumes are highly toxic. This hydrofluoric - crushed computer circuit board mixture was slowly digested to dryness. Hydrofluoric acid ensured complete exposure of any precious metals contained within the solid. Solubilization of the residue resulted upon addition of 25 mL of aqua regia (three parts hydrochloric acid to one part nitric acid). This solution was poured back into the original flask while the remaining solid crushed computer circuit boards was discarded. Solution digestion was then carried out at approximately 150°C. This step was continued until strong sulfur trioxide fumes were emitted or the solution reached dryness. The dry salts were solubilized upon addition of 75 mL of hydrochloric acid at elevated temperatures. These solubilized salts were diluted with distilled water to produce a 300 mL solution. This diluted solution was then boiled before 10 mL of tellurium tetrachloride was added.

Tellurium tetrachloride was made by adding 25 mL of hydrochloric acid to 0.625 g of tellurium metal. Complete metal dissolution was accomplished through the addition of small increments of nitric acid. After all the metal was dissolved, the solution was dried twice. Between each evaporation, 12.5 mL of hydrochloric acid was added to the beaker to ensure the formation of chloride species and the removal of the presence of nitric acid. After the last digestion, the salts were boiled with 50 mL of one part hydrochloric acid to one part distilled water. This solution was bulked to 250 mL with distilled water.

Coagulation of the precious metals in a precipitate occurred through the addition of stannous chloride to the dilute solution containing tellurium tetrachloride. The amount of stannous chloride necessary to ensure complete precious metal precipitation was between 15 and 20 mL. Better stannous chloride control was achieved by adding the stannous chloride drop wise until the metal precipitated. After precipitation, 10 mL excess stannous chloride was added to the dilute solution. Gentle boiling of the solution for 15 minutes ensured complete removal of the precious metals from solution.

Stannous chloride was manufactured by boiling 125 mL of one part hydrochloric acid to one part distilled water solution in a beaker. Once this solution was gently boiling, a total of 125 grams of stannous chloride was added in five portions. The solution was constantly stirred during addition of the solid. Complete dissolution of the stannous chloride powder was evident by a change in solution colour from milky to clear. After dissolution, the final stannous chloride solution was produced by bulking with enough distilled water to make 250 mL.

The precipitate was separated from the dilute solution free of any precious metals by filtration. After filtering, the solution was discarded while the precipitate was washed several times with a one part hydrochloric acid - three part distilled water solution. These washings were not discarded since they contain precious metals solubilized by the acid.

The remaining precipitate was completely solubilized with warm aqua regia and then rinsed with distilled water. These various solutions were joined together to produce a precious metals solution.

The precious metal solution was boiled to dryness in a beaker covered with a dish plate. Seven millilitres of aqua regia were added to solubilize the dry salts. This solution was then transferred to a 25 mL volumetric flask. Two solution buffers, cupric chloride and lanthanum chloride, were also added to the flask. Finally, distilled water was added to raise the solution volume to 25 mL.

Lanthanum chloride buffer and cupric chloride buffer are required reagents for atomic absorption. Lanthanum chloride is produced by mixing 15 mL of distilled water with 7.5 g of lanthanum oxide ($La_2O_3$). While slowly stirring this mixture, hydrochloric acid is constantly added until the lanthanum oxide is completely dissolved. At this point, an extra 5 mL of hydrochloric acid is added. After letting the solution cool, enough distilled water is added to bulk the final solution to 50 mL.

Cupric chloride is made by mixing together 30 mL of a solution containing one part hydrochloric acid and one part distilled water with 6.25 g of metallic copper. Dissolution of metallic copper is enhanced by adding small increments of nitric acid. After dissolution, nitric acid is removed from the solution by evaporation. Solubilization of the salt occurred upon the addition of a solution containing 10 mL of hydrochloric acid and 20 to 30 mL of distilled water. Finally, the solution is bulked to 50 mL with additional distilled water.

For atomic absorption spectroscopy analysis, the 25 mL solution containing the precious metal ions, cupric chloride and lanthanum chloride buffers plus the make-up distilled water was analyzed for gold and platinum with a Perkin Elmer 4000 Atomic Absorption Spectrophotometer.