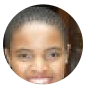
Zinc precipitation on gold recovery



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ZINC PRECIPITATION ON GOLD RECOVERY

Introduction

Zinc dust cementation for gold and silver recovery is one of the best known contact reducing processes in mineral processing. It is also known as Merrill-Crowe process from its founders, C.W Merrill of United States of America who started it and T.B Crowe from South Africa who added some important developments (Miller, 1981). Merrill-Crowe process is used for gold/silver precipitation from dilute sodium cyanide solutions and is favoured for gold cyanide containing high silver concentration. MINTEK researchers suggested that zinc cementation should be considered as a process alternative to electro winning for direct treatment of carbon eluate in the CIP process (Miller, 1981). The ore is leached before going through zinc precipitation. After zinc-dust cementation, the processed gold is taken for smelting then moulded into blocks ready for sale.

History of Zinc Precipitation

The zinc cementation process was introduced in 1890's and became an important part of the cyanidation process. C. W. Merrill as mentioned in the introduction was the first to use the application of the zinc cementation process at the Homestake Mine in Lead South Dakota in 1897 (Mular, 2002).

Zinc cementation was initially performed using long sloping boxes filled with bundles of coarse zinc shavings. Gold bearing solutions were passed through sand filters to remove suspended solids and then through the zinc boxes for metal precipitation. Vertical plates were installed in the boxes forming chambers to direct the flow of solutions through the beds of the zinc. The method proved to be effective but inefficient due to coating of the zinc surfaces with deposited metals or insoluble zinc hydroxide (Dorey, 1988).

Lead salts were introduced in 1894 to address the passivation problem. The bundles of zinc shavings were dipped in solutions of lead acetate before placing in the zinc boxes. The lead deposits on the zinc surfaces formed cathodic areas for the preferential precipitation of precious metals, leaving the adjacent anodic zinc surfaces exposed for dissolution (Atwood, 1985).

As a result, clarification was found to be a very important stage. If affects both metal recovery and precipitate grade. With suspended solids present, rate of precipitation was found to decrease which lowered the recoveries.

In 1918, the vacuum de-aeration tank was introduced by T.B. Crowe and was incorporated into the Merrill process to make the Merrill-Crowe process. This was the removal of dissolved oxygen, which caused zinc passivation making it almost impossible to filter (Mular, 2002).

<u>Merrill-Crowe Flow Sheet</u>

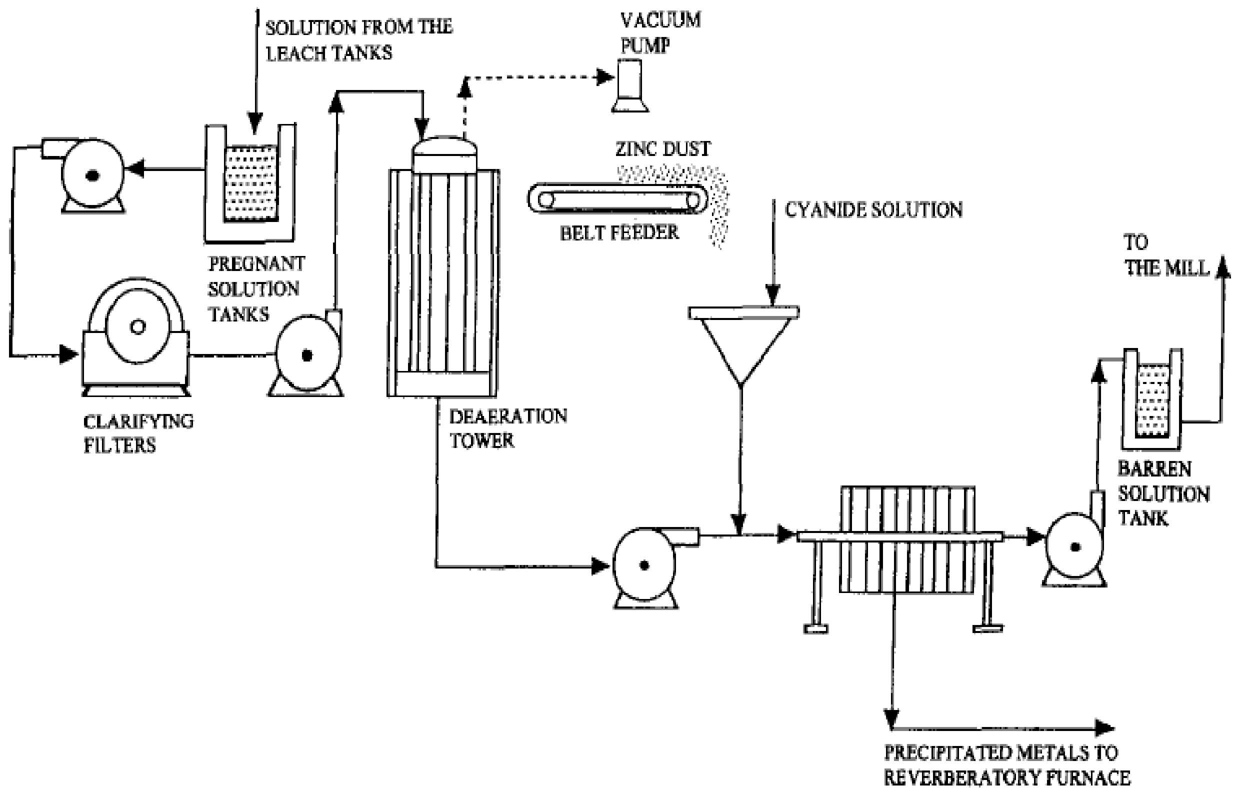

Figure 1: The flow sheet of recovery of gold/silver by Merrill- Crowe process (Chi, 1997).

A block diagram shown in the figure above is the simplified flow sheet of recovery of the precious metals by zinc cementation called Merrill-Crowe process. From leaching the pregnant solution is filtered off the solid particles that are suspended in it, expect for heap leaching where thickening is necessary. The clarified solution is de-oxygenated in a vacuum tower. Zinc dust is then added to a solution of gold cyanide using a belt conveyer according to the flow sheet above; vibrating tables could be used instead. This is where cementation reaction starts; it is completed as the zinc particles are trapped in the filter press. (Chi, 1997)

Merrill-Crowe Process Chemistry

This section deals with setting the gold free from the gold-cyanide solution. Main reactions are the deposition of gold on the surfaces of zinc particles. There are two half cell reactions representing this, the first one being the reduction of gold by zinc.

$$Au(CN)_2^- + e^- \rightarrow Au + 2CN^- \qquad (Primary\ reaction)$$

Gold cyanide loses an electron to form Au and CN^- ion. The zinc introduced then reacts with the cyanide ion. The second half cell reaction represents the oxidation of zinc. It loses two electrons to the cyanide anion to form zinc cyanide as shown in the equation below.

$$Zn + 4CN \rightarrow Zn(CN)^{2-} + 2e^- \ (Primary\ reaction)$$

There are also secondary equations which are the reactions of water with two electrons available from the reaction of zinc with cyanide.

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2$$

$$O_2 + H_2O + 4e^- \rightarrow 4OH^-$$

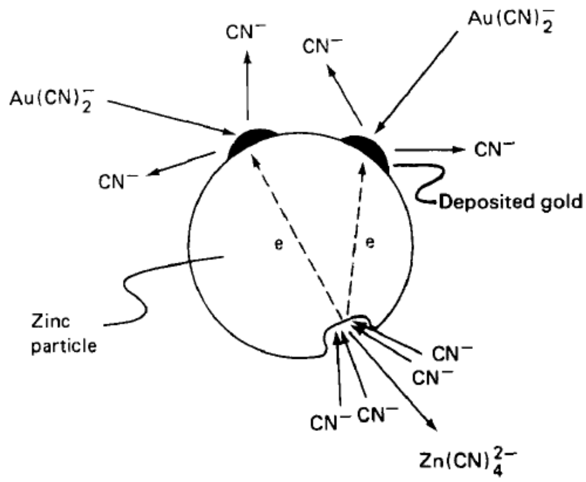

Figure 2: Schematic diagram showing gold deposition of gold onto surface of zinc particle (Gold metallurgy, 2011).

Gold is then recovered in the precoat filters which are then smelted and shaped into blocks ready for market.

Merrill-Crowe Unit Operations

Merrill-Crowe process is the technique used to separate gold from a cyanide leach solution. It is cementation using zinc powder. The unit operations of the Merrill-Crowe process include; solid-liquid separation, clarification, vacuum de-aeration in packed towers, zinc addition and filtration of precipitated gold and silver using pressure filters (Sepor Inc., 2010).

Solid- liquid separation

Heap leaching is the only leaching that needs a solid-liquid separation, with other leaching methods the pregnant solution goes straight to the clarifying tank. Separation uses the Counter Current Decanter (CCD) thickeners before being clarified. From the leaching tanks where cyanide solution is added to gold, the slurry is sent to the CCD tank, shown in figure 5 below, the pregnant solution and solids separate. The pregnant solution contains water with minerals and cyanide and solids that go in the downstream contain slurry with low value minerals. The efficiency of the decanters can be increased by improving the washing efficiency, increase the clarification at the thickener overflow and reduce the overflow of minerals (Mular, 2002).

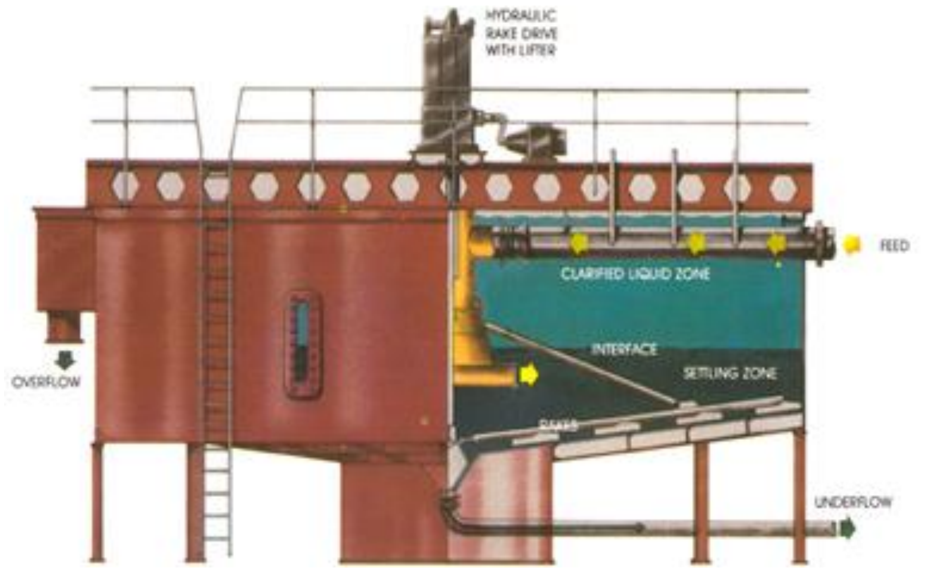

Figure 3: A counter current decanter thickener tank showing how liquid and the settled solid are separated (Gold metallurgy, 2011).

The process of filtration includes delivering solids contaminated with solvent-soluble contaminant into the decanter centrifuge and directing a liquid solvent through a selected portion of the helical blade to the internal surface of the drum to mix with the solids and dissolve contaminant there from.

The drum is rotated at a sufficient rotational speed so as to form a layer of solids along the internal surface of the drum, separate the liquid solvent from the solids within the rotating drum, and move the liquids toward the liquid outlet. The helical conveyor is rotated at a rotational speed which is slightly different than the rotational speed of the drum so that the helical blade pushes the layer of solids toward the solids outlet.

The solids are then discharged from the drum at the solids outlet of the decanter centrifuge and the liquid solvent is discharged from the drum at the liquid outlet of the decanter centrifuge. As seen in the figure below the pregnant solution stays at the top and the solid slurry settles at the bottom.

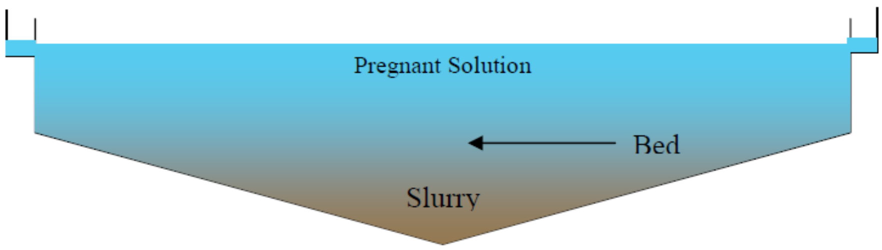

Figure 4: Simplified counter current decanter thickener tank (Gold metallurgy, 2011).

The main aim of the separation is getting the solids out of the gold cyanide solution and remaining with the cyanide solution. It is very important to remove as much solid as possible otherwise it will impair the clarification of the finer particulate solids at the interface liquid and solid layers.

The reason for the solid removal is to make the zinc performance successful as it will not work in a solution with solids –this will be discussed at a later stage when talking about addition of zinc dust.

Clarifying

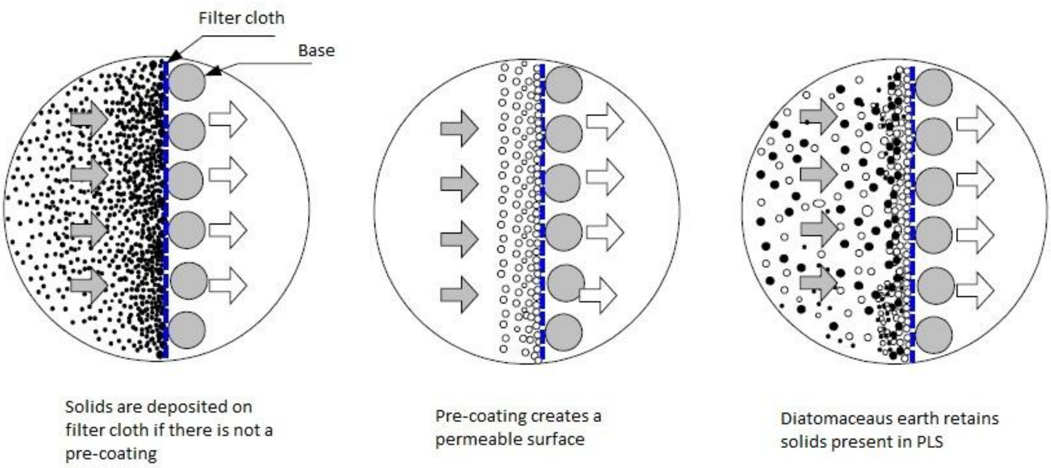

Figure 5: simple diagrams of how circular leaf clarifying tanks work (Gold Metallurgy, 2011).

After separating the solids, the pregnant solution passes to a storage tank which can function as a settler –to help remove smaller particles which could not be removed earlier- from which it is then pumped to the canister precoat type filter clarification units where undissolved solids are removed. This happens in other cases that preliminary settling may extend to the use of two or three conical bottom tanks and sometimes have a mechanical device to remove sediments. The overflow goes to a storage tank or sump ahead of the clarifiers and the underflow is returned to the filtration circuit for recycling.

Figure 6: Display of circular clarifiers (Gold Metallurgy, 2011).

With other leaching methods, agitation leaching and percolation leaching, the pregnant solution goes straight to the clarifying tank. Clarifiers comprise leaf clarifying tanks, which consist of canvas filter leaves arranged in either rectangular or circular tanks. Circular canvas filter leaves are explained in figure 2 above and figure 4 shows the rectangular filter leaves.

Figure 7: Rectangular leaf filter (Gold Metallurgy, 2011).

Leaf sizes are normally 1.8 m wide by 2.15 m deep or 2.0 m wide by 1.2 m deep. Most commonly, 50 leaves are contained in individual tanks. A variation is the use of Merrill precipitation units with 45-48 radically placed leaves at 20 m wide and 2.4 m deep. The latter arrangement is preferred over the earlier because it has the advantage of flexibility and standardization since any particular unit can be used either as a clarifier or as a precipitator (Severing, 2008).

For canvas leaf clarifiers the throughput of solution is of the order of 10 tons per square meter per 24 hours and the filtrate contains less than 10 ppm of solids. Pre-coating of leaves is invariably practiced and the material used may consist of either residue slime or diatomaceous earth. Back washing or hosing down of the accumulated sludge is conducted weekly unless excessive slime is produced. As in the case in most filtration units, lime deposits from alkaline cyanide solution have to be removed periodically from the canvas or synthetic cloth by washing with dilute hydrochloric acid solution.

De-aeration

The filtered pregnant solution flows through the de-oxygenation chamber with 4 to 8 ppm of dissolved oxygen removed. Typically water has 6 to 8 ppm of dissolved oxygen in it. De-oxygenation is conducted by passing the clarified solution through a Crowe tank, which usually has a cylinder of 2 m diameter by 3.5 m height in which some grids are arranged horizontally with the object of dispersing the incoming solution into relatively fine films as it flows down through the tank. As a result, virtually all the solution is freely exposed to the vacuum in the cylinder and thus the dissolved oxygen is removed. The quantity of removed air varies from 20 to 40 mg per litre depending on ambient temperature.

Figure 8: A picture showing three de-aeration towers

The Crowe tank can be positioned at a sufficient height to counter the barometric head imposed by the vacuum and thus permit the gravitation of the de-oxygenated solution to the emulsifying tank ahead of the precipitation unit.

The cost of such Crowe de-aeration operation is low as it consists almost entirely of electric power to elevate gold bearing solution to a height of approximately nine meters and power to operate a vacuum pump of 600-700 m^3 per hour capacity. In all about 8 kW is involved for the treatment of 290-310 tons of solutions per hour. Alternatively the use of a pump with a liquid gland seal permits a lower elevation of the Crowe tank.

Addition of zinc dust

The filtered, de-oxygenated solution flows through the zinc mixing chamber where zinc dust is blown through the cyanide solution. Zinc is added to solidify gold. Zinc is added at a steady state using a slow moving feeder belt or a vibrating feeder. Zinc feeders are normally 80-100 cm in diameter and 100-120 cm deep. At the stage lead nitrate in crystal form or concentrated solution form if it was not added before aeration (Triwood1973, 2007).

It is important to balance the zinc-lead addition, the amounts added per tonne of cyanide solution passing through the precipitator ranges from 15 to 38 grams of zinc and 5 to 12 grams of lead nitrate as said in the chemistry section (Gold Metallurgy, 2011).

Figure 9: Addition of zinc and lead nitrate (Gold Metallurgy, 2011)

According to Chi, 1997 a laboratory investigation was carried out in which data from three gold/silver operations were analysed by regression analysis. Zinc effeciency is defined as the stoichiometric zinc requirement for the gold/silver precipitation divided by the total amount of zinc added. Table 1 below was taken from the same source and it lists the operating parameters from the three plants studied and the corresponding zinc efficiencies on annual average basis. It is expected that zinc efficiency is dependent on these operating variables and varies significantly from plant to plant.

The investigation was aiming at impovements in Merrill-Crowe precipitation by using zinc effeciency within the scope of practical possibility. This technique was used to identify which variable exert significant influence on zinc effeciency.

Table 1: Annual plant operating parameters taken in 1990 (Chi, 1997)

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Plant	Pregnant grade, Ag (g/t)	Flow rate (gpm)	Zn addition (kg/day)	NaCN (g/t)	Zinc efficiency (%)
1	39.18	1934	322.06	815	62.1
2	13.04	4733	575.62	665	20.2
3	4.05	1797	176.45	305	8.2

Filtration of precipitated gold/silver

After precipitating the gold/silver, the press filters are used to separate the precious metals from the solution.

Figure 10: A diagram of the filter press (Gold Metallurgy, 2011)

Several filter presses are arranged in parallel so that one filter can be cleaned while the others are in operation normally in a weekly routine. After a cycle has completed the cake is blown with air to dry it, the pressed is opened and most of the filter cake is discharged into a wheeled tray placed beneath the press. The remaining cementation cake is removed using scrapers. According to Chi, 1997 it is evident that most cementation occurs in the feed pipe and in the plate-and-frame filter press. Parga, Wan and Miller's research show that 10% of the silver is precipitated in the pipe while the remaining 90% is removed in the filter presses as the solution passes though the cake. (Chi, 1997)

Mathematical Modelling

SPSS/PC+ is a software used for modelling and analysing several analysis to know the closeness of the predicted and actual variables from the three gold/silver plants discussed in the zinc addition above. The model devised in the example below covered the period January 1990 to December same year and four variables listed below were covered and the operating data for the four variables were taken monthly.

- Grade: The grade of gold/silver in pregnant solution (g/ton)
- Add: Daily zinc addition (g)
- Flow: Flow rate (g/min)
- NaCN: Concentration of sodium cyanide (g/ton)

Again zinc effeciency, ZE

$$ZE(\%) = \frac{Stoichiometric\ zinc\ required\ for\ gold\ \&\ silver\ precipitation}{Total\ mass\ of\ zinc\ added} \times 100\%$$

Table 2 below lists mathematical models in terms of the above parameters which describe the three Merrill-Crowe circuits. From these models, individual plant predictions can be made as shown by the multiple regression, R^2, that 92% of the operating data can be represented by equation 1 in table 2 for plant 1, and 99% of the operating data represents equations 2 and 3 from the same table for plants 2 and 3 (Chi, 1997).

Table 2: A table for multiple regressions (Chi, 1997)

Equation		Multiple R^2
Plant 1	$ZE = (38.34 \times Grade) + (5.02 \times 10^{-2} \times Flow) - (59.05 \times NaCN) - (1.06 \times 10^{-1} \times Add) + 91.89$	0.9175
Plant 2	$ZE = (44.19 \times Grade) + (4.44 \times 10^{-3} \times Flow) - (5.99 \times NaCN) - (1.68 \times 10^{-2} \times Add) + 8.31$	0.9915
Plant 3	$ZE = (55.96 \times Grade) + (3.99 \times 10^{-3} \times Flow) - (0.24 \times NaCN) - (1.9 \times 10^{-2} \times Add) + 0.64$	0.9915

Figure 10 below shows the comparison between the actual plant data and the predicted zinc efficiency in a form of a graph which interprets that the prediction is good.

The mathematical model for each plant reflects plant operating experience. The influences of the four operating variables are determined by their corresponding correlation coefficients with dependent variable. As seen from table 2 all three models show a consistent effect of these four parameters on zinc efficiency.

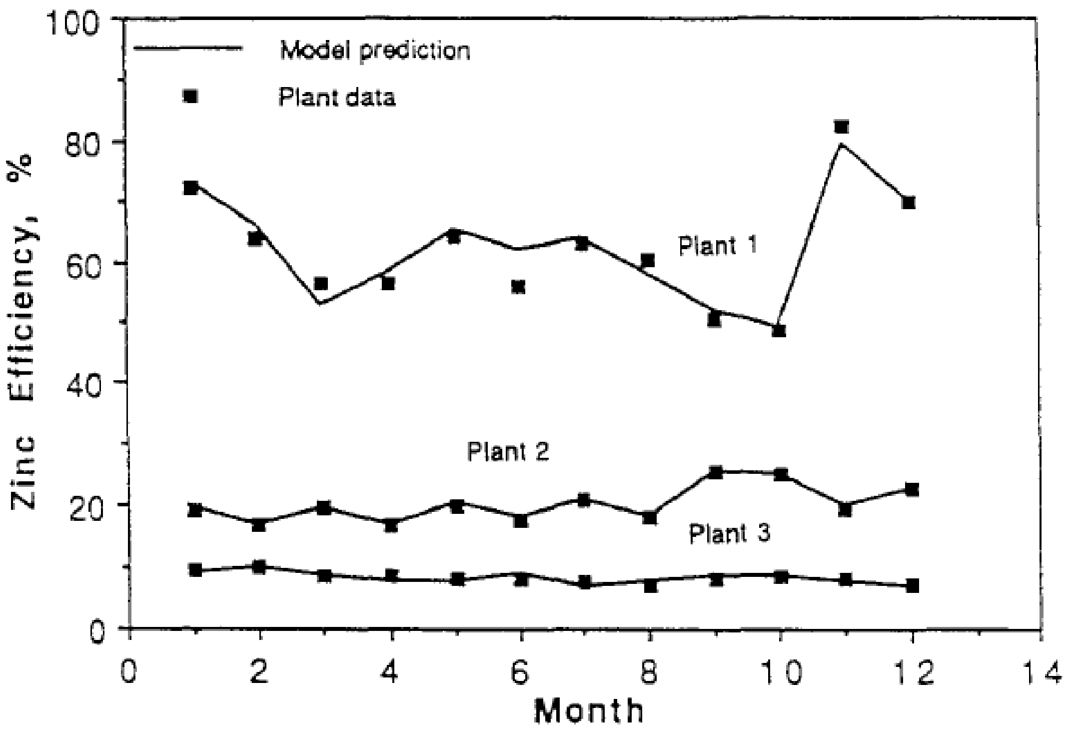

Figure 11: Prediction of plant performance using mathematical modelling (Chi, 1997)

Interpretation of Mathematical Models

1. Grade

Grade means the concentration in the feed of the pregnant solution. The effect of the silver grade of the pregnant solution is significant in the plant operations. Equations 1 to 3 above shows that the grade of silver is the only variable that exerts a similar effect on the zinc efficiency in the three different plants (Chi, 1997).

2. **Flow Rate**

Equations 1 to 3 show that increasing flow rate rate shud benefit zinc efficiency though efficiency would decrease due to filtration and not enough time of stay in the filter papers. A higher flow rate would result in increased packed bed mass coefficient (Chi, 1997) hence reaction rate would increase with increased flow rate.

3. **NaCN Concentration**

Increased cyanide solution that is more than the required amount is thought to affect zinc efficiency negatively. According to Chi, 1997 the solubility of zinc dust increases significantly with increase in NaCN concentration which says high cyanide concenration is not always advantageous. When cyanide concentration is in excess of the value required, to avoid any significant formation of zinc hydroxide and ensure free cyanide is present to maximize the rate of gold/silver precipitation then excess zinc will dissolve which results in a decreased zinc efficiency. An economic benefit could be achieved by reducing the cyanide concentration but making sure it does not come insufficient.

4. **Zinc Addition**

Depending on the operating efficiency and composition of the solution, zinc dust should be added 5 to 30 times the stoichiometric coefficient of the precious metals requirement. An increase in the daily addition of zinc in Merrill-Crowe process results in decrease in zinc efficiency according to equations 1, 2 and 3. This also means the increased zinc addition will increase the consumption of zinc for the same amount of precious metals precipitated. Improved zinc efficiency can be achieved by reducing daily zinc consumption with caution. (Chi, 1997).

Process Selection- choice of Merrill-Crowe process

There are two main processes currently in use for the recovery of previous metals from cyanide leach solutions which are the ones covered in this reports, and those are zinc precipitation and carbon adsorption. According to Fleming, 1998 the carbon in leach process has in most cases proved to be more efficient and to have 20 to 50 percent lower capital and operating costs than Merrill-Crowe process. In 1998 when Fleming wrote gold processing, carbon adsorption was used over 70 percent in the world’s gold production.

Carbon in leaching has an advantage over Merrill-Crowe when ores contain significant levels of organic carbon, high base metal concentrations and when the ore contains high clays which are difficult to filter.

The selection of carbon adsorption or Merrill-Crowe process in based on economical considerations and the problem is the precious metal values increase and so the inventory of carbon is higher. This causes plants to be expanded to process more activated carbon. This as though that at some points it will be less economic to operate a carbon adsorption process than a Merrill-Crowe process. (Gold Metallurgy, 2011).

Merrill-Crowe process has some advantages over the carbon adsorption process in cases of high metal concentration like ore containing significant amounts of silver; high silver to gold ratios. As gold ore grades increase and silver content goes over 30 ppm, Merrill-Crowe process is a good option. (Gold Metallurgy, 2011). Zinc cementation can also be used for recovery of precious metals from carbon strip solutions as an alternative to direct electro winning.

Mines which use Merrill-Crowe process are Newmont Mining Company- Minera Yanacocha mine and Barrick Gold’s Pierina Mine in the same district in Peru, Placer Dome’s La Coipa Mine in Chile, Goldfields Operating Company, chimney creek- carbon strip circuit, FMC Paradise Peak- Carbon strip circuit and Equity Silver Mine, British Columbia- carbon strip circuit. (Fleming, 1998).

Merrill- Crowe Precipitation Unit

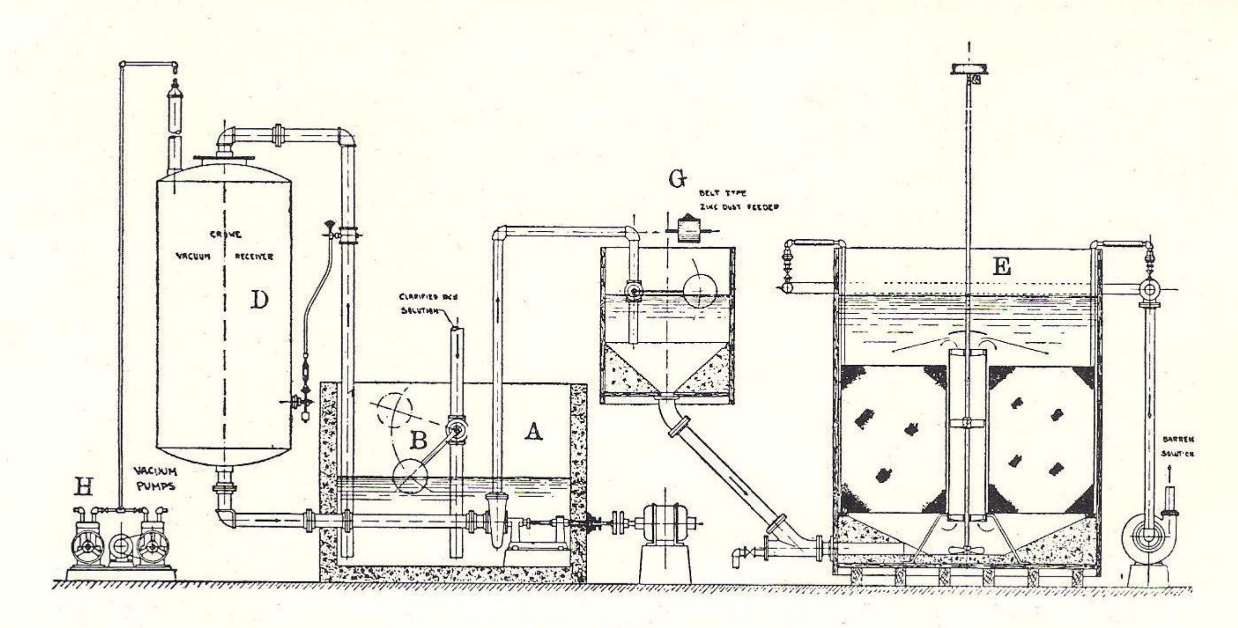

Figure 12: Merrill Crowe Precipitation Unit (Pryor, 1965)

Table 3: A table showing Merrill -Crowe precipitation unit and descriptions of each part (Pryor, 1965).

UNIT	DESCRIPTION
A	It is a clarifying tank, pregnant liquor runs into it. Solution is drawn through by vacuum. After this it goes to D.
B	Hung filtering leaves which act like floaters. It works to keep the a constant level in A.
D	De-aeration tower where the sparklingly clear liquid flows under automatic control over grids which expose it to vacuum. The de-aerated cyanide solution is drawn from the bottom of the tank by a pump sealed against air leakage to G.
G	Where zinc dust is added which is lead activated. Precipitation happens rapidly. The solution then goes to the precipitation press filter, E.
E	Excess zinc and gold slime are arrested and held until the next clean-up.

Conclusions

It was found out that:

- Grade of the precious metals is the most significant parameter in controlling the zinc efficiency in Merrill-Crowe process.
- An increase in the grade and flow rate of the pregnant gold/silver increases the zinc efficiency.
- An increase in NaCN concentration decreases the zinc efficiency due to dissolution of zinc.
- A reduction in daily zinc addition will certainly increase zinc efficiency determined by actual plant condition.
- Mathematical modelling helps in the decisions of the plant operation.
- Merrill-Crowe process is one of the oldest methods of gold/silver recovery and best for low grade precious metals.
- This process is ideal for large volume gold and silver operations.

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