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"THE INFLUENCE OF CERTAIN FACTORS AND IMPURITIES ON THE PRECIPITATION OF GOLD FROM CYANIDE SOLUTION BY ZINC DUST"

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A thesis presented in partial fulfillment of the requirements for the Degree of Master of Engineering.

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INTRODUCTION

The cyanide process as actually applied to the extraction of gold and silver from their ores is generally considered to have originated with British Patent nos. 14,174, Oct. 19, 1887, and 10,223, July 14, 1888, issued to J.S.MacAuthur, R.W. Forrest and W. Forrest.

The first patent emphasized the efficiency of cyanide as a solvent for gold and silver, and the superiority of dilute solutions. The dissolved gold was to be recovered from the solution by any conveniend way, " such as evaporating the solution to dryness and fusing the resulting saline residue, or by treating the solution with a sodium amalgam" (30). The second patent referred to the use of alkalins and, which is perhaps more important, to the use of zinc "in a state of fine division" as a precipitant for the noble metals dissolved in cyanide solutions.

Previous to this, however, other patents had been obtained and other investigations had been persued on the action of aqueous solutions of alkaline cyanide upon noble metals and the precipitation of these metals therefrom.

In 1840 Elkington (1) obtained a patent for a method of electroplating gold by using as electrolyte a solution made by dissolving gold in potassium cyanide with the aid of an electric current. It should be noted that the Elkington patent not only covered the dissolution of gold in cyanide solutions but

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also - and this probably did not occur to the patentee - a means of recovering the gold from the solution by electrodeposition.

That an electric current was unnecessary for the solution of gold was observed shortly after by Prince Bagration (2) who reported that the metal would dissolve slowly if placed in solutions of either sodium or potassium cyanide. He also noticed that gold could likewise be dissolved by a solution of potassium ferrocyanide but more slowly than with the simple salts. In both cases it was observed that heating and free access to the atmosphere hastened the dissolution of the metal. No means of recovering the dissolved gold was suggested.

About this same time, 1844, Glassford and Napier (3) determined the formula of the compound formed when potassium cyanide reacts with gold and found it to be potassium aurocyanide, KAu(CN)₂.

The same year A.P.Price (30) obtained a patent in Great Britain for precipitating gold and silver from solutions resulting from the treatment of ores by agitating the solution in contact with zinc in a fine state of division. It seems doubtful, however, if Price had in mind the precipitation of gold and silver from cyanide solutions. Moreover, previous to this, during the years 1862-4 (30), it had been pointed out that granular zinc would precipitate from solution most metals dissolved from ores. Two years later Elsner (4) made what is undoubtedly the

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first comprehensive study of the chemical reactions involved during the action of aqueous solutions of alkaline cyanides on metals, and in the case of gold proposed an equation which has since been known as Elsner's Equation:

 $4 \text{ Au} + 8 \text{KCN} + 0_2 + 2 \text{H}_2 0 = 4 \text{KAu}(\text{CN})_2 + 4 \text{KOH}$

oxygen, or its equivalent, forming an integral part of the reaction and being absolutely decessary for it to proceed. In the case of silver and of cadmium the equations were analoguous. Elsner, however did not propose any way of recovering the dissolved metals.

Wurtz seems to have been the first to sense the commercial possibilities of cyanidation and as early as 1866 he drew attention to the fact that the action of potassium cyanide solution upon gold might well be used to extract the metal from ores (5), but he does not seem to have followed up his idea.

A year later J.H. Rea obtained a patent in the United States (6) which covered the use of cyanide with the aid of an electric current for the extraction of gold from its ores, much emphasis being placed on the use of an electric current. The purpose of the electric current was twofold: firstly, to aid in the dissolution of the gold, and secondly, to precipitate the dissolved metal on cathodes of copper. The success of the process semms to have been both dubious and shortlived.

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Skey in 1875 (11) made some observations in connection with the use of cyanide as an aid to barrel amalgamation as was practised at the time. He noted that the gold dissolved by the cyanide was not precipitated by the mercury or the sulphides in the ore, and was lost. To remedy this he proposed passing the fluid coming from the barrels over copper plates. The copper being electropositive to gold and silver in cyanide solutions would precipitate these metals.

In 1877 Dixon (10) reported the results of some experiments on the solution of gold in potassium cyanide and ferrocyanide solution with the aid of an oxidizing agent. To recover the gold he suggested filtering the solution through finely divided metallic silver, and then precipitating the silver as a sulphide. He noted, furthermore, that both gold and silver could be precipitated by means of copper.

In 1885 Simpson and Parnell (7) were issued a patent for a process using solutions of potassium cyanide, ammonium carbonate and sodium chloride for the treatment of crushed gold ores. The patent also covered the use of zinc plates suspended in the solution to precipitate the dissolved gold.

Two years later, as already mentioned, the MacArthur-Forrest patents were granted.

MacArthur stumbled upon the cyanide process quite accidentally (8). In 1886 he had treated ores with a solution of potassium cyanide and had attempted ro precipitate any dissolved

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gold by means of hydrogen sulphide. When no precipitate formed he wrongly concluded that no gold had been dissolved by the cyanide. A year later, however, he had occasion to attempt to precipitate gold from a known solution by the same means but no reaction took place. It then occured to him that gold might have been dissolved during the tests of the previous year and that the hydrogen sulphide had failed to precipitate it. This proved to be the case, and zinc being electropositive to gold, suggested itself as a precipitant. Turnings of zinc were made by cutting discs on a lathe and these were placed in the solution.

About 1888 Julian, (30) in South Africa, made some investigations on the dissolution of gold in ores by chlorine, and by cyanide under high pressure, with subsequent precipitation by an electric current and sodium amalgam. These investigations resulted in several patent applications, and for certain oxidized ores the process appears to have been successful. By 1889 a plant has been erected at the Wemmer Gold Mining Company, Witwatersrand, to deal with this process.

At about the same time that Julian was carrying out his investigations, Dr. Siemens (30) applied for patents for the extraction of gold and silver from ores by means of cyanide solutions, with subsequent precipitation by means of an electric current, using iron anodes and lead cathodes. It proved to be suitable for low-cyanide solutions and was commercially applied in South Africa in 1893, where it became known as the Siemens-

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Halske process (12).

Some time before the introduction of the Siemens-Halke process, in 1890, Alfred James (9) introduced a system of zinc extractor boxes of his own invention in South Africa for the precipitation of gold from cyanide solutions.

The use of lead salt in conjunction with zinc was patented by MacArthur (13) in the early nineties and was first applied by him with success in the Transvaal about 1894. Mac-Arthur also proposed the use of zinc wafers for precipitation at about this time (12).

The lead-zinc couple was not adpoted elsewhere, however, until 1898 when it was brought forward by Betty (13) and Warter (40) as a substitute for the Siemens-Halske electrolytic process for the treatment of low-cyanide gold solutions. The use of the zinc-lead couple was very successful and soon displaced the electrolytic process of precipitation.

The use of aluminium as a precipitant for gold dissolved in cyanide solutions was patented by Moldenhauer in 1893. (13), and its use as an electrode for electrolytic precipitation was proposed by Sherard Cowper-Coles (20) and tried by Julian in the same year (31) with but little success. Julian also tried the use of aluminium in the form of plates and of shavings (31) as a substitute for zinc with unsatisfactory results.

B.C. Molloy (32) patented an electrolytic process of precipitation in 1892. which was a modification of the one previously proposed by Julian in 1888. It consisted of passing gold bearing solutions over mercury in which sodium was continuously deposited by electrolysis. The gold was precipitated on, and amalgamated by, the mercury (41). The process was employed for some months by Dr. A. Simon in 1892-3 (31) for the treatment of Witwatersrand tailings.

In 1895 Pfleger patented a process of electrolytic precipitation which was applied for a short time in the Transvaal. A short-circuited simple cell was formed by having zinc anodes in alkali or cyanide solution and iron cathodes in the gold bearing solution, the two solutions being separated by a porous membrane. The gold was deposited on the iron cathode.

Several other electrolytic methods of precipitating gold have been suggested, the main difference between these and the preceeding ones being in the use of different materials for electrodes. Zinc cathodes were tried by Andreoli (31), tinned iron was used for the same purpose at Minas Prietas, Mexico by Charles Butters (41), etc..

The use of zinc dust as a precipitant for gold and silver was patented in 1894 by Sulman and Pichard (22) and was first applied by them at the Deloro mine, Ont., The practive was to add zinc dust in amounts calculated to precipitate the metal to a tank of solution. The zinc dust was dispersed throughout the solution by air or mechanical agitation and was allowed to settle. The clear solution was decanted and the deposit filtered. The process was not very successful; decanta-

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tion losses were high and when just enough zinc was added redissolution occurred, while if zinc was in excess, zinc consumption became prohibitive.

The same year W.O. Johnston, of San Francisco, obtained a patent for the use of charcoal as a precipitant of gold from cyanide solutions although it has been tried some time previously with indifferent results by W. Actken at the Reefton mine, in New Zealand (12).

The following year, 1895, the use of cuprous salts as a method of precipitation was proposed independently both by ad Wilde and by Christy (41) but did not find any practical application, a serious objection being that the cyanide solution had to be acidified for precipitation to take place.

A year later the use of zinc dust was introduced into the United States by D.C. Jackling at the DeLamar-Mercur mine, Utah, and its use was perfected by C.W. Merrill in 1897 (9) at the Homestake mine. Merrill recognized the necessity of removing the zinc and the precipitated gold from the solution immediately on completion of precipitation. This was done by adding zinc dust to the suction of the pump carrying the pregnant solution, leaving the zinc in contact with the solution for a short time, and passing the solution through a filter immediately thereafter.

In 1897 the Pelatan-Clerici process made its appearance (23). This process attempted to dissolve, by cyanide, and

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precipitate, by electrolysis, the gold simultaneously. The pulp was agi+ated with cyanide solution in a wat the bottom of which was made up of copper sheeting, covered with mercury, and acting as a cathode. The agitator, made of iron, served as anode. Sodium chloride was added to increase the conductivity of the pulp. The gold precipitated on the mercury and was recovered as an amalgam. Aside from the mercury cathode, the process was very similar to the one patent by Rea thirty years previously.

The Pelatan-Clerici process was the forerunner of many similar schemes for the simultaneous dissolution and precipitation of gold in aurocyanide solutions. The Riecken process, first applied in 1900 in Western Australia, also made use of mercurycopper cathodes (41). The Gilmor-Young process employed at Nicaragua in 1898 consisted of agitating gold ores with cyanide and mercury in a pan. After some time copper and zinc amalgam were added to the pan and the agitation continued. The gold was recovered as amalgam.

From 1900 to 1910 very few innovations were developped if the introduction of Butters filters to clarify pregnant solutions is excluded.

In 1910 Kirkpatrick (13) introduced with success the use of aluminium dust as a precipitant for argento-cyanide solutions at the Deloro Smelter, Ont., The system was later installed at the O'Brien Mine in Cobalt. It was soon after applied, with modifications, at the Nipissing mill by Hamilton (13).

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The Merrill plate-and-frame filter press was first used in Mexico in 1911 (9). It had several advantages over the Butters filters and its use soon became popular in America and elsewhere.

Zinc threads were tried as a substitute for zinc dust by Carpenter in 1915, (26) but he reports inferior results.

The same year a patent was issued to Clevenger (27) for the use of zinc alloyed with 3 percent or less of sodium as a precipitant for gold or other metals dissolved in cyanide.

Sodium sulphide as a precipitant of silver from argento-cyanide solution was developed in 1916 at the Nipissing mill, Cobalt, to replace aluminium precipitation when, during the World War 1914-18, the price of aluminium became excessive. The silver was precipitated as silver sulphide which was subsequently reduced to metallic silver by a desulphurizing treatment (51).

The Crowe process for the removal of dissolved oxygen by a vacuum from pregnant solutions was introduced in 1916 (24) and was undoubtedly one of the major innovations in zinc precipitation since that of Merrill in 1897.

The Merrill method of introducing zinc was soon combined with the Crowe procees of oxygen removal, and the use of this combination was quickly adopted by the gold-milling industry.

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Chemical methods of oxygen removal have been tried since the Crowe process (69) but have found no practical application due to cost as compared to the Crowe process.

In 1932 the Merrill-Crowe simultaneous clarificationprecipitation process came into being (50).

It is of interest to note that as recently as 1939 a process reviving, after a fashion, the idea of the Pelatan-Clerici process of simultaneous dissolution and precipitation of gold has been put forward (25). In this process charcoal is added to the cyanide pulp so as to adsorb the gold as soon as it is dissolved by the cyanide, the charcoal being later removed by flotation.

While the subject of gold and silver dissolutions in cyanide solution and the influence of different factors relating thereto has provoked much study and laboratory investigations by many experimenters such as Elsner (4), Julian and Smart (30), Bodlaender (66), White (67), Baisky, Swainson and Hedley (61), and Holmes (68), to mention only a few, one cannot say the same in regards to precipitation.

It is true that some investigators have devoted their energies to some of the problems involved, notably Christy (28) who, in particular, devoted much time to the electrodeposition of gold and silver from cyanide solutions; Gross and Scott (60) who investigated the efficiency of charcoal precipitation; White (29) who studied the solubility of zinc shavings in cyanide

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solutions; and others.

Operators have also reported from time to time observations made under working conditions.

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But most of these investigations and observations have been made prior to the inception of the Merrill-Crowe process which is today the method finding the most universal application for the precipitation of gold and silver from cyanide solutions.

It was therefore decided to investigate under controlled conditions and with pure solutions the influence of some of the factors which might have a bearing on the efficient precipitation of gold from deaerated solutions by zinc dust.

The writer is deeply indebted to Professor W.G. McBride who obtained for the author the Harrington Research Fellowship which made the investigation possible, to Professor J.U. MacEwan, under whose supervision the work was performed, for his many valuable suggestions, and to Professor J.W.Bell for the use of his constant-temperature laboratory and his interest in the work. My thanks are also due to Professor O.N.Brown for his encouragements and the free use of the Analytical Laboratory, and to Professor G. Sproule for the use of some of his equipment.

THE PROCESSES OF PRECIPITATION

As already mentioned five principal methods of precipitation have been used:

- 1. Electrolysis
- 2. Aluminium
- 3. Charcoal
- 4. Sodium sulphide
- 5. Zinc, a) shavings
 - b) dust

1. Electrolysis

This process is now of historical interest only and the principles involved will be discussed later under zinc precipitation.

2. Aluminium

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Aluminium has been used as a substitute for zinc especially in the precipitation of silver from cyanide solution. It differs from zinc precipitation in that aluminium does not replace the precious metals in the cyanogen compound but provokes complete decomposition with regeneration of the simple salt.

According to Moldenhauer the reaction is:

followed by,

 $2A1(OH)_3 + 2NaOH = Na_2A1_2O_4 + 4H_2O_1$

Hamilton (13), however, prefers the following equation:

 $2NaAg(CN)_2 + 4NaOH + 2Al = 4NaCN + 2Ag + Na_2Al_2O_4 + H$

The presence of caustic soda is essential as can be seen from the foregoing equations. Furthermore, lime must be absent or a low-grade precipitate difficult to melt into bullion will result due to the formation of insoluble calcium aluminate according to the following equation:

 $Na_{2}Al_{2}O_{4} + Ca(OH)_{2} = CaAl_{2}O_{4} + 2NaOH.$

Hamilton, already cited, obviated the difficulties engendered by the presence of lime by treating the solution with sodium carbonate before precipitation, the following reactions taking place:

 $Ca(OH)_2 + Na_2CO_3 = CaCO_3 + 2NaOH$ $CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$

Aluminium will not precipitate solutions containing gold only; a minimum of about two ounces of silver per ton of solution is necessary for the precipitation of both gold and silver to take place. Copper is precipitated at a very slow rate even when much silver is present.

3. Charcoal

The mechanism whereby gold is precipitated by charcoal was for a long time obscure. It was suggested at one time that a galvanic couple was formed, the carbon and the cyanide salt forming the poles. Later it was said that gases occluded in the pores were responsible for the precipitation, while others maintained that, although normally electronegative to it, carbon in this particular form could precipitate gold (12).

Allen (70) was the first to mention that precipitation was due to the phenomena of adsorption and subsequently discovered facts seem to bear him out.

The use of charcoal as a precipitant was the subject of study by Gross and Scott (60) and their conclusion was that the mechanism of precipitation involves adsorption accompanied by a chemical change. They consider that a monomolecular layer of cyanide is adsorbed on the charcoal and that for pine charcoal the chemical reaction is:

 $2KAu(CN)_2 + Ca(OH)_2 + 2CO_2 = Ca[Au(CN)_2]_2 + KHCO_3$

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while for sugar charcoal the reaction is:

$$Kau(CN)_2 + H_2O + CO_2 = HAu(CN)_2 + KHCO_3$$

The first product of the reaction is adsorbed and the second goes into solution.

The phenomena can, however, be much more simply explained by postulating that the charcoal is activated; that is, it carries a positive charge of electricity and that for this reason it adsorbs the negative aurocyanide ions present in the solution.

NaAu(CN)₂
$$\longrightarrow$$
 Na⁺ + Au(CN)₂
C⁺ + Au(CN)₂ \longrightarrow [C⁺ + Au(CN)₂]

This explains why gold adsorbed by charcoal from a solution is never metallic gold.

4. Sodium Sulphide

The sodium sulphide process is applicable to silver ores only as no gold is precipitated by this method in alkaline solutions as gold is a member of the arsenic-tin group. The silver is precipitated as silver sulphide with regeneration of cyanide.

About 0.06 lb of sodium sulphide at 60 per cent purity is required per troy ounce of silver in solution. The reaction is as follows:

 $2NaAg(CN)_2 + Na_2S = Ag_2S + 4NaCN$

The silver sulphide is desulphurised by agitation in contact with caustic soda and aluminium ingots (50).

Most of the sodium sulphide used in precipitation is regenerated during the desulphurising process.

5. Zinc

a) Shavings

At present, plants using shavings are few and usually small and are fast disappearing. It is safe to say that today no new plant of any importance would be designed to use zinc shavings.

b) Dust

The improvements of Merrill and of Crowe, which have fesulted in the Merrill-Crowe Simultaneous Clarification-Precipitation process, in the use of zinc dust have made this substance such an efficient precipitant that it is today of almost universal application.

Briefly, the Merrill-Crowe process consist of complete clarification and deaeration of the pregnant solution before the addition of zinc dust, with subsequent separation of the precipitate from the solution by means of filters, the whole operation taking place without contact with the atmosphere. Clarification is accomplished by means of vacuum clarifying leaves after which the solution is deaerated in a tank under a vacuum of 22 inches of mercury to an oxygen content of about 0.5 mg. per liter.

Zinc dust is added by means of a mixing cone so arranged that no air is introduced with the zinc.

The gold and silver and excess zinc is separated from the barren solution by means of pressure filters, either bag or leaf type.

Fig. I illustrates a possible arrangement with the bag type of filters.



Fig. I

PHEORETICAL A SPECTS OF PRECIPITATION BY ZINC

Whether or not a metal will go into, or will deposit out of, solution under an impressed voltage depends on the electrode potential between the electrode and the solution. This theory was first put forward by Nernst in 1889.

According to this theory, the atoms of an electrode have a tendency to lose electrons and form ions, and, in opposition, the ions in solution have a tendency to gain electrons and deposit themselves on the electrode as atoms. The first tendency is determined by an hypothetical pressure which Nernst called the "electrolytic solution pressure, P", and the second tendency is determined by the effective ion concentration. In dilute solution the ion concentration is proportional to the osmotic pressure "p" due to the ions in the solution (72).

Three conditions are possible:

(1) P > p

The metal will send positively charged ions into the solution and will continue to do so until opposed by the accumulated charges in the solution. The solution will acquire a positive charge, and the metal a negative charge; that is, a difference of potential will be established between the metal and the solution.

(2) P = p

No action will take place, and no difference of potential will built up between the metal and the solution.

 $(3) \underline{P < p}$

The metallic ions in the solution give up their positive charges; that is, gain electrons and separate as atoms on the electrode. This will continue until the accumulated charges oppose further action. The metal acquires a positive charge and the solution a negative one. As in (1) a potential will be established between the metal and the solution but in the opposite direction.

From the preceeding we see that the processes of dissolution and deposition are closely allied but act in opposite directions.

When equilibrium is established, with an electrode for which P p, the metal is negative to the solution and is surrounded by a layer of positively charged ions. This layer of ions on the electrode is known as the Helmholtz "electrical double layer". It prevents the dending of more ions into solution by the metal.

If, however, electrons are withdrawn from the metal through an electrical circuit, the double layer is ruptured, the electrolytic solution pressure asserts itself and some ions will pass from the metal into the solution; that is, the metal will dissolve and will continue to do so so long as the circuit is closed. If the removal of electrons is stopped the double layer will again be formed, and dissolution will cease.

When the metal is positive to the solution, i.e. P p, the electrical double layer will be formed as before but in the reversed order, the metal being surrounded by a layer of negatively chraged ions. If now electrons are withdrawn from the solution or furnished to the electrode, by means of an electrical circuit, as before, the double layer will be broken, the osmotic pressure of the solution will become active, and the ions in the solution will deposit out of solution. The deposition will continue as long as the circuit is closed and ions remain in solution.

When the electric reaction is reversible, Nernst showed that

$$E = \frac{RT}{nF} \ln p \qquad (1)$$

where E = Electrode potential of the metal
 R = Ideal gas constant
 n = Valency of the metal ion
 F = 1 Faraday, or 96,500 coulombs
and the convention used is to state the potential difference of the
metal with respects to the solution.

Equation (1) may be written thus:

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At constant temperature the expression RT/nF = ln Pis constant for a given metal, hence

 $E = \frac{RT}{nF} \ln p + (constant) \dots (3)$

The equation may be simplified by using common logarithms and substituting the values for R, and F; furthermore, by taking the temperature at 18[°]C, we obtain:

where a is the active ion concentration. The value of E_0 for monovalent gold is 1.5 volts (59).

Gold, in the form of NaAu(CN)₂, dissolved in dilute solutions, ionizes thus,

the long arrow indicating that the ionization is almost complete.

The equilibrium constant is given by the following equation,

$$K_{1} = \frac{[Na^{T}] \times [Au(CN)_{2}]}{[NaAu(CN)_{2}]}$$
(6)

and as the degree of ionization is large, K1 is large.

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The complex aurocyanide ion is in turn ionized into gold and cyanide ions,

the ionization constant being,

$$K_{2} = \frac{[Au^{\dagger}] \times [CN^{-}]^{2}}{[Lu(CN)_{2}]} = 1 \times 10^{-28} (71) \dots (8)$$

As the ionization is small $\operatorname{Au}(\operatorname{CN})_2$ can be made equal to one.

Substituting in equation (4), we have for gold,

$$E = 1.50 + .059 \times -9$$

=+0.97 volts, in reference to the

standard hydrogen electrode.

The above, however, does not take into account the "free" cyanide present in gold cyanide solutions. If the solution contains say one pound per ton of free cyanide in terms of NaCN; that is 0.00098 moles per liter; and gold to the extent of 0.25 ounce of metal to the ton, or 0.000125 moles $Au(CN)_2$ per liter, the total concentration of CN- ions in the solution is (0.000125 x 2+0.00098) 0.00123 moles per liter, or $[CN]^2 =$ 0.123 x 10⁻².

Substituting this value in equation (9), we obtain

$$[Au^{f}] \ge 0.123 \ge 10^{-2} = 10^{-28}, \text{ therefore,}$$

$$[Au^{f}] = 81 \ge 10^{-27} \qquad (10)$$
The amount of gold present in the solution in the
form of simple gold ions is seen to be extremely small.
Substituting this value in (4), we obtain,

$$E = 1.50 + .059 \times \log 81 \times 10^{-27}$$

= 1.50 - 1.6, approx.
= -0.1 volts.

That is, the potential electrode of gold is negative towards the solution at this dilution for a pure gold cyanide solution.

If gold is to be precipitated from such a solution the precipitant must have greater electrode potential than gold; that is, in a dilute cyanide solution such as postulated above, the potential developped must be more than minus 0.1 volts. Zinc fulfills this condition and, therefore, it will precipitate gold from the solution if there are no interfering elements.

The mechanism whereby gold is displaced or deposited from solution is essentially one of electrodeposition, and can

perhaps best be understood from the study of the deposition of copper sulfate from an acid solution by means of zinc.



fig. a

the circuit.

Suppose that a zinc plate and a copper plate are immersed in a solution of copper sulphate dissolved in dilute sulphuric acid, fig. a. If the zinc and the copper plates are electrically connected, electrons will flow, through the exterior circuit, and a current will flow in the

opposite direction as will be seen if a galvanometer is placed in

Zinc will dissolve and will displace copper ions from the solution, the copper being deposited on the copper plate.







fig. c

Suppose now that a bar one part of which is zinc and the other copper is immersed in the copper sulphate solution, fig. b. As before electrons will flow from the zinc to the copper, and copper will be deposited on the copper end of the bar.

Suppose, further, as shown at fig. c, that a zinc bar is now placed in the solution. Copper will be deposited on the zinc in a spongy mass, and the

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deposition will continue so long as diffusion of the ions through the sponge is possible.

If we substitute sodium aurocyanide for copper sulphate and sodium cyanide for the sulphuric acid in the above, a gold sponge instead of copper will be deposited on the zinc. Such is the mechanism of gold precipitation from dilute cyanide solutions by zinc.

The chemical change occuring during precipitation of gold by zinc is (13),

:

$$\mathbf{2}\operatorname{NaAu}(\operatorname{CN})_{2} + \operatorname{Zn} = \operatorname{Na}_{2}\operatorname{Zn}(\operatorname{CN})_{4} + \operatorname{ZAu} \quad \dots \quad (a)$$

Reaction also takes place, however, between excess zinc and the cyanide in solution so that parallel with (a) we have,

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$$4 \text{NaCN} + 2n + H_2 O = \text{Na}_2 2n(\text{CN})_4 + 2 \text{NaOH} + H_2$$
 (b)

and the over-all reaction is (42),

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 $NaAu(CN)_2 + 2NaCN + Zn + H_2O = Na_2Zn(CN)_4 + Au + H + NaOH ...(c)$

PREVIOUS WORK ON ZINC PRECIPITATION

White (29) in 1919 performed some experiments on the solubility of Zn strips in cyanide solutions, with and without gold present in the solutions. With the following conditions obtaining: Au = 7.0 mg./l (.222 oz/T); Oxygen = 0.75 mg./l; temperature = 24-27°C, White obtained the results shown in table I.

Test No.	KCN ld/T	Na OH 16/T	Au pptd mg.	Zn dissolved mg/sqcm 24 hrs	Au recovery per cent	Remarks
A	0.000	0.016	0.00	0.08	0	Zn only
В	0.420	0.040	1.76	0.68	25.2	Zn-Pb couple
C	0.000	0.096	0.15	0.13	2.15	Zn-Pb couple
D	0.540	0.032	0.56	0.53	8.00	Zn only
E	0.000	0.096	0.00	0.10	0	Zn only

TABLE I

Note: 1 lb KCN x 0.753 = 1 lb NaCN; 1 lb NaOH x 0.70 = 1 lb CaO.

The conclusions drawn from these results were: 1) No gold is precipitated by zinc in the absence of free cyanide. 2) A Zn-Pb couple can precipitate gold even in the absence of free cyanide.

- 3) Zinc can precipitate gold in the presence of some free cyanide.
- 4) The best results are obtained by mean of a Zn-Pb couple in the presence of free cyanide.
- 5) In the absence of free cyanide very little zinc is dissolved.
- 6) While the precipitation of gold is increased threefold with a Zn-Pb couple, the amount of zinc dissolved is increased but slightly.
- 7) The amount of zinc dissolved is greatly in excess to the theoretical amount necessary to precipitate the gold. In test D it is 18 times this amount.

White's results, however, are open to some criticism because of the fact that the alkalinity was not maintained constant so that the tests are not strictly comparable.

Robertson (14) found that for good precipitation on shavings the free cyanide should be in excess of 0.02 per cent KCN (0.4 lb/T KCN or .3 lb/T NaCN) and the protective alkalinity less than 0.007 per cent NaOH (0.1 lb/T CaO).

Treating zinc shavings with a cold solution of caustic soda and sodium cyanide for 5 minutes is said by Kasey (52) to reduce the amount required per box.

Sherwood (15) noted that cadmium in zinc dust has little effect while the presence of one or two per cent of lead is an advantage.

Carpenter (16) reported that poor precipitation by

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shavings may be due to muddy solutions, absence of free cyanide, absence of protective alkalinity, the presence of copper in the solution, the presence of alkaline sulphides, thiocyanates, ferricyanides, etc. or coating of zinc oxide on the zinc.

Julian and Smart (31) mention reducing agents, such as sulphides and organic matter, as being detrimental to precipitation. As a result of experiments they report that Na₂S has a profound effect; even such small quantities as 0.011 lb per ton of solution reduced efficiency 6.5 per cent, 0.088 lb by 11 and 0.62 lb by 32 per cent. They also state that precipitation is markedly affected if the solution becomes acid: if the solution is neutral precipitation is bad while if it is made acid by a strong acid (H_2SO_4) precipitation is "fairly rapid and perfect".

Toombs (17) noted that if calcium sulphate is present in pregnant solution in amounts that approach the saturation point (about 4 lb/T) it interfers with precipitation on shavings due to the fact that it coats the zinc.

Common salt dissolved in pregnant solutions in the proportion of 5 lb per ton is said by Johnston (45) to improve precipitation on shavings. Laboratory tests showed improved recovery of about 4 per cent.

Soluble or colloidal silica is reported by Johnson (18) to be precipitated by a zinc-lead couple. It is suggested that the silica is occluded by zinc hydroxide, $Zn(OH)_2$ present in the solution and when the latter precipitates it brings down the

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silica. This coats the zinc and affects precipitation adversely. It is thought that the precipitation of $2n(OH)_2$ is a result of "very low cyanide strength" and consequently low pH". Another factor in bad precipitation is said to be PbSO₄ formed by the action of sulphates on lead compounds. The "white precipitate" formed in zinc boxes at the City and Suburban Plant, South Africa, contained 53.47 per cent MgCO₃, 15.36 per cent CaCO₃, 11.93 per cent $2n(OH)_2$, 8.76 per cent Fe₂O₃ and Al₂O₃, 4.03 per cent insolubles, 3.57 per cent Na₂SO₄, and 2.85 per cent chloride, alkali, and cyanides, Gold is said to be occluded in this precipitate to the extent of 9.6 dwt. (0.48 oz) per ton of precipitate.

Newton and Fewster (19) report that with zinc dust and deaeration the best results are obtained with a free cyanide content of at least 0.017 per cent KCN (0.34 lb/T KCN or 0.256 lb/T NaCN) and about 0.02 per cent CaO (0.4 lb/T). The elimination of Pb(NO_3)₂ reduced the zinc consumption to 0.10 lb per ton milled, while deaeration further reduced the zinc consumption to 0.06 lb per ton.

On the other hand Shoemaker (32) recommends that if the ore treated does not contain lead, precipitation is improved by adding $Pb(NO_3)_2$ to the extent of 0.002 oz. per ton.

Scott (33) reports that when gold and silver are precipitated from a $Ca[CN)_2$ solution by means of zinc dust the reagent consumption are: Zinc, 0.045 lb per ton of solution, and lead acetate, 0.01 lb. The presence of chromates in pregnant solutions is reported by Bell (34) to be detrimental to precipitation by zinc dust owing to the zinc becoming with chromium. All chromium salts have to be precipitated by a lead salt and removed from the solution before the gold can be recovered. The precipitated chromates do not occlude any gold. Because of their relative positions in the electromotive series it meens highly improbable that chromium would deposit on the zinc. What probably occurs is that the chromates in solution coat the zinc, thereby preventing contact between the zinc and the solution.

The addition of starch, 0.0107 lb per ton milled, and caustic soda, 0.0053 lb, improved the settlement of silica gel at the Dome mill (35) and resulted in better gold precipitation by zinc dust.

The effect of temperature is said to be more marked with weak than with strong solutions, the higher the temperature, within reasonable limits, the more rapid and complete the precipitation. Ehrman (36) reports that as much gold can be precipitated by shavings in two hours at 35°C than in twenty-four at 20°.

Discussing the practice of precipitation by zinc shavings Clennell (40) states that the cyanide strength of the solution entering the extractor boxes should never be less than 0.2 per cent KCN (4 1b/T KCN or 3 1b NaCN) when no lead salt is present.

When lead is added Carter (37) found that solutions titrating as low as 0.008 per cent free cyanide (0.16 lb/T) could

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give 90 to 95 per cent gold recovery.

The presence of other salts than cyanide was reported by James (38) to improve precipitation in certain cases, even when the free cyanide content is very low or absent.

Again according to Clennell, "a certain minimum of free alkali is found to be essential for good precipitation. On the other hand, a larger excess should be avoided."

Dorr (50) in his book; "Cyanidation and Concentration of Gold and Silver Ores", mentions that precipitation takes place only in the presence of free cyanide, is always accompanied by the liberation of hydrogen, and that the alkalinity of the solution is increased during precipitation.

In the same book L.D. Mills, states that with the Merrill-Crowe process the efficiency of gold precipitation is generally independent of the cyanide or alkali content, of the solutions, and that substantially complete precipitation can take place with solutions containing no more than 0.05 lb NaCN or CaO per ton of solution. For silver ores, the cyanide and alkali content must be higher. He further states that the principal detrimental effect of high cyanide and alkali is the wasteful consumption of zinc.

Still according to Mills an excess of lead salt is to be avoided because the zinc becomes coated with enough lead, to retard, or even stop, galvanic action between the zinc and the gold. Also the amount of lead dissolved and precipitated may cause excessive zinc consumption and give a low-grade precipitate.

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About 10 per cent of the weight of zinc dust used is said to be the right amount if no soluble lead is present in the ore.

Sodium bisulphite is stated to be a precipitant activator, 0.10 lb being required per ton of solution. The alkalinity must not be in excess of pH 6.6.

According to the Merrill Company (39) solutions titrating 0.1 lb or more NaCN per ton are readily precipitated and that successful pfecipitation has been reported with as little as 0.05 lb. The cyanide strength, however, should be raised when copper is present in the solution. The presence of copper is said to be no more detrimental than to increase the zinc consumption and lower the grade of precipitate produced when the Merrill-Crowe process is used. Only enough lime to ensure the solubility of lead salt as alkali plumbite is necessary while the zinc consumption is from 0.02 to 0.06 lb/T, according to the same source.

On the other hand Crowe (44) mentions that precipitation is difficult if the solution titrates over 0.1 lb CaO (protective) and that the pH of the solution should not be above 8.4 unless the cyanide strength is at least 0.25 lb NaCN per ton of solution.

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APPARATUS AND PROCEDURE

Briefly, the procedure followed was to deaerate one liter of pure gold cyanide solution to which controlled amounts of reagents and "impurities" had been added. After deoxydation zinc dust, with or without lead salt, was added and left in contact with the solution for a definite time after which the solution was filtered.

The solution was tested for "free" cyanide, "protective" alkalinity, pH, and gold before deoxydation, and for "free" cyanide, "protective" alkalinity, pH, gold and zinc after precipitation and filtration.

The methods of analysis employed are described in Appendix II page

Unless otherwise stated the temperature of the solution was 20°C. This constancy of temperature was made possible by performing the experiments in a thermostatically controlled room designed by Professor Bell.

The "impurities" added were, for the most part, solutions prepared from Merck C.P. reagents and in the case of the gold cyanide it was prepared by dissolving refined gold metal in pure cyanide solution, both of which were prepared by the writer (see Appendix I page).

The zinc used was Merillite Zinc Dust and save when stated otherwise 4 mmol per liter (or 0.524 lb per ton) were added for precipitation after being conditioned with lead nitrate. As the gold content of the solutions was fixed at 0.04 mmol per liter except for the tests bearing on the influence of the gold contact the molecular ratio of zinc to gold was therefore 100 to 1.

Deoxydation of a solution may be accomplished by

a) Mechanical or Physical means

b) Chemical agents.

a) Mechanical or Physical Means

1) Heating or boiling the solution.

Heating a solution is said by Hausen (43) to accomplish the same result, as regards removal of air, as applying a vacuum. However, this method was rejected by the writer because of the possible reactions which might take place at a high temperature between the compounds in solution.

2) Submitting the solution to a vacuum.

This is the basis of the Crowe process, and was the method adopted for the majority, of the tests reported herewith.

A laboratory apparatus which would remove air by submitting a very thin stream of solution to a high vacuum was designed and is illustrated in figures 2 and 3 page 36.

It consists of a glass separatory funnel (A) of about 2 1/2 liters capacity fitted with a perforated stopper (a), and an Erlenmeyer flask (B) of 4 liters capacity, the two being fitted together by a rubber cork (j).

By means of a short length of rubber tubing a piece of glass tubing (p) drawn out to a small nozzle at one end was fixed to the discharge of funnel (A).

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Fig. 2. Photograph of funnel (A) and flask (B) shown in Fig. 3.



Fig. 3. Dearation Apparatus.

A glass tubing (g) was passed through the rubber cork (j) and was joined to the glass tubing going through cork (i) at the top of the funnel by a piece of rubber tubing on which was attached a pinchcock (b).

The side opening (f) of the flask was connected to a vacuum pump (E) by means of heavy rubber tubing, a calcium chloride tube (D) being placed between the two to absorb any water vapour resulting from the evacuation or descration of the solution in the flask.

Furthermore, a three-way stopcock (d) on the vacuum line permitted the evacuation of the funnel at will, by means of tubing (F), independently of the Erlenmeyer.

A mercury gage (C), graduated in inches, connected to the vacuum line at (e) showed at all times the pressure obtaining in the apparatus, i.e. flask (B), or funnel (A), or both.

(c), (k), (l), (m), and (n) are pinch cocks whose use will be apparent presently.

Preliminary tests showed that the size of the nozzle used was important and that the finer the nozzle the more perfect the deaeration. However, when the nozzle was extremely small the time required to evacuate the solution became very long. A test was also performed with a solution heated to 35°C but this did not materially improve deoxydation. The arrangement finally adopted was to use a fairly small nozzle and to pass the solution twice through the apparatus with minimum contact with the atmosphere. In this way the oxygen content of a saturated solution could be reduced to 0.52 mg. per liter within reasonable time, about 55 minutes. Winkler's method was used to determine the oxygen present in the solution (see Appendix II page 101).

The results of these tests are shown in Table II

Test No.	Temp. oc	Nozzle used	Time req'd	0 ₂ -m	g/l	No of times	Water evaporated
			min.	bef.	aft.	passed	gm•
1	18°C	large	7	9.6	2.15	1	10
2	20°C	very fine	110	9.7	0.60	l	16
3	21 °C	fine	15	9.0	1.26	l	13
4	35 °C	fine	15	9.0	1.20	1	16
5	20 °C	fine	55	9.1	0.52	2	15

TABLE II

Note: Vacuum for all tests, 29.6 ins. Hg Volume of solution used, 1000 ml.

The manner in which the apparatus was used is as follows:

 The filtered solution - water white - was placed in (A), stopper (a) being closed and (c) opened. (d) was turned so as to shut off (F) which was disconnected from (A) at (c), (K) being closed as an added precaution. (b) was closed.

- 2) The vacuum pump connected to (E) was started, (n), (m), and
 (1) were opened and the vacuum was allowed to rise to the maximum, 29.6 to 29.8 ins. mercury.
- 3) (a) was opened and the solution was allowed to be drawn into (B) by passing through (p) coming out as a fine jet.
- 4) When all the solution in (A) had been drawn into (B) stopper
 (a) was closed. With (c) opened to the atmosphere 15 minuted
 were required to pass 1000 ml of solution from (A) to (B).
- 5) Tube (F) was now connected to (A) at (c), (k) was opened,
 (d) was turned so as to shut off (B) and connect (F) to the vacuum line. In this way (A) was evacuated.
- 6) After evacuation (1) was closed and (B) was disconnected from the vacuum line at (o). (b) was now opened, a minimum quantity of air was admitted into (B) by opening (1) for a second or two, and the solution in (B) was forced through (g) and (h) back into (A).
- 7) When all the solution had been forced in (A), (b) was closed as well as (c) and (k). Tube (F) was now disconnected from (A) at (c).
- 8) (1) was opened and air admitted into (B). Cork (j) was now removed from (B) and zinc dust was placed in (B).
- 9) Cork (j) was now replaced on (B), the latter was connected once more to the vacuum line at (o), (d) being turned so as to shut off (F) and connect (B). In this way (B) was once more evacuated.

- 10) (c) was slightly opened, for about a second, till the vacuum in (A) had dropped to 27 in. and (a) was then opened again allowing the solution to pass through (p) into (B). Under the pressure now obtaining, about 2 1/2 in., 35 minutes were required for 1000 ml. of solution to pass from (A) into (B).
- 11) After all the solution had been drawn into (B), (a) and (1) were closed and (B) was disconnected from the system at (o). (A) and (B) now formed a separate unit which could be removed and shaken in order to mix thoroughly the zinc dust and the solution in (B). A contact of half an hour, with frequent shaking, was permitted to take place between the zinc and the solution.
- 12) The solution was then filtered twice through a Buchner filter using a No 50 Watman paper for the first filtration and a No 2 for the second. The second filtration was done in order to be quite certain that no small particle of zinc would inadvertantly pass into the barren solution.

b. Chemical agents

Deoxydation by the addition of reagents has been suggested by White (69) who showed that tannin had an efficiency of almost 100%.

The Merrill Company prefers the use of sodium hydrosulphite as a deoxydation agent and the method of procedure suggested is as follows (44): "To 1000 cc. of pregnant solution, add 100 mgs. sodium hydrosulphite. When dissolved add 100 mgs zinc plus 10 per cent Pb(NO₃)₂. (More zinc if solution contains copper or silver) and stir gently for 30 minutes. Filter and assay filtrate".

The above procedure was modified somewhat by the writer in that more zinc was added, 4 mmoles per liter or 0.262 gm. per liter. Consequently the amount of lead salt added was proportionally increased.

It is also suggested that the zinc should be conditioned with the lead nitrate in a small beaker with about 20 ml. of water before adding it to the solution. A one per cent solution of lead nitrate - containing 10 mg or 0.030 mmoles per ml was prepared and 5 ml. of this solution were added to the zinc. After the lead had deposited on the zinc, and the zinc had settled to the bottom of the beaker, the clear solution was decanted and the zinc added to the gold solution.

This method of conditioning zinc was also employed when the solution was evacuated and, unless mentioned otherwise, the quantity of lead added was 0.15 mmole per liter. 15 ml. of water were used to wash the zinc from the beaker into the flask, preliminary tests having shown that this was the quantity of water vapour removed from the solution during evacuation. No correction for the quantity of water removed was therefore necessary.

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Deoxydation by hydrosulphite is very thorough: tests made by the writer showed only slight traces of oxygen remaining in the solution after the addition of the reagent.

The method is very attractive in that it is quite rapid. However, it was felt that the addition of a reagent might provoke unwanted reaction within the gold solutions which would influence precipitation in a manner uncontrolled, i.e. an unknown factor would be introduced. For this reason the slower, but more controllable method of evacuation was used, with the exception of a few tests relating to the influence of time of contact between the zinc and the solution.

The influence of the following was investigated: A: Influence of "Free" Cyanide B: Influence of "Free" Cyanide with lead salt added C: Influence of Lead Salt, with cyanide constant D: Influence of Lime, with cyanide constant E: Influence of pH greater than 9.0 with NaOH F: Influence of pH less than 9.0 with HCN G: Influence of Free Cyanide with lime constant H: Influence of Sulphide with lime added I: Influence of Sulphite with lime added K: Influence of Thiosulphate with lime added L: Influence of Free Cyanide with lime added M: Influence of Ferrocyanide with lime added N: Influence of Zinc cyanide with lime added

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- O: Influence of Temperature on a gold solution containing lime
- P: Influence of Gold concentration of cyanide solution containing lime
- R: Influence of Molecular Zinc-Gold ratio
- S: Influence of H, I, J, K, L, M, and N, without lime
- T: Influence of H, I, J, K, L, M, and N, with NaOH to maintain pH
- U: Tests on an unknown working cyanide solution
- V: Influence of Time of Contact between the zinc and the gold

A tests

The object of these tests was to determine the influence of the "free" cyanide content on the precipitation of gold from a pure gold cyanide solution by zinc alone.

The results are shown in Table A. and by Graph A. where the quantities are reported both in mmoles per liter and 1b per ton of solution. The notation "CN" and "CaO" used in the table indicates the "free cyanide" in terms of sodium cyanide and the "protective" alkalinity in terms of calcium oxyde respectively. This notation is followed throughout.

Test No	"C mmo	N" 1 e/1	ľ	H	Zn dissolved	Recovery per cent
	bef.	aft.	bef.	aft.	mmore/r	per cent
A-1	0.10	0,08	7.2	6.8	0.1888	15.30
A~2	0425	0,20	8.0	7.4	0.2455	15.30
A-3	0. 80	0.50	9,3	9.3	0.3775	63.20
A-4	1.35	0.75	9.7	9 .9	0.6040	86,80
A-5	3.15	2.00	10.0	10.5	0.8305	89.30
A-6	5.80	4.00	10.05	10.6	1.0570	86,50
A-7	12.60	8,70	10.3	10,9	1.3590	81.00
, A- 8	49.50	43.00	10,5	11.0	1.7743	48,5
Note:	Mmoles	NaCN pe	er liter	x 0.098	= 1b per ton	

TABLE A

Mmoles Zn per liter x 0.1308 = 10 per ton

Conclusions

- 1. The recovery is influenced by the amount of "free" cyanide present in the solution.
- 2. The recovery reaches a maximum for a "free" cyanide content of about 3.2 mmoles per liter (0.31 lb NaCN per ton).
- 3. A lack or an excess of "free" cyanide is prejudicial to recovery, the limits being approximately not less than 1.35 mmoles per liter nor more than 5.80 (0.13 to 0.58 lb NaCN per ton respectively).
- 4. The presence of a large ambunt of cyanide is almost as bad as too little.
- 5. The pH of the solution is decreased by precipitation when the cyanide content is low, remains unchanged for a cyanide concentration of about 0.8 mmoles per liter (approx. 0.08 lb NaCN per ton).
- 6. Good recovery is, within limits, accompanied by a rise in the pH of the solution.
- 7. The quantity of zinc dissolved increases with increased cyanide content, but there is no direct relationship between the amount of zinc dissolved and the gold recovery.
- 8. The cyanide consumption increases more rapidly than the zinc consumption, and appears to be a

function of the original cyanide content, being greater the greater the amount of cyanide present. originally.

Discussion

In regards to conclusions 1, 2, 3 and 4 these can be accounted for by electrochemical action as already explained on pages 19 to 26, the solution pressure of the cyanide partly preventing the gold from being ionized and deposited on the zinc once the cyanide concentrations get above a certain value.

Conclusion 5 is a direct contradiction to a statement that has become almost axiomatic in the literature, "the alkalinity of the solution is always increased during precipitation." A possible explanation of this divergence may reside in the fact that titration methods for the determination of alkalinity due to lime in cyanide solution are far from accurate and unless the total alkalinity is determined by a pH measurement, accurate and comparable results are difficult to obtain. Also it should be noted that no lime was present in the solutions.

B Tests

These tests were identical with the A tests except that the zinc was conditioned with lead nitrate before being added to the solution. The quantity of lead salt added was 0.15 mmoles per liter or about 0.1 lb per ton. All other conditions were the same as in A.

The results are shown in Table B, and by Graph A - A.

Test	mm	"CN" ole/1	pl	Ŧ	Zn dissolved	Recoverv	
	bef.	aft.	bef.	aft.	mmole/1	per cent	
B -1	1.2	1.0	9.8	10.0	•453	93.4	
B-2	3.1	2.4	9.9	10.1	•5285	95.2	
B-3	4.1	3.0	10.0	10.0	.6795	91.3	
B-4	4.8	3.9	10.0	10.4	•6900	84.52	
B -5	11.4	10.0	10.2	10,4	•718	67.5	

TABLE B

Conclusions

- 1. The addition of a lead salt, within certain limits, improved precipitation.
- 2. The maximum recovery is attained, as in A, at a cyanide content of about 3.1 mmole NaCM per liter, or 0.31 lb per ton.

- 3. The recovery is decreased much more than when zinc alone is added if the cyanide content is increased beyond a certain concentration, 4.8 mmoles or about 0.47 lb NaCN per ton.
- 4. The amount of zinc dissolved is less when a zinclead couple is used than when zinc alone is added.
- 5. The pH or alkalinity of the solution is increased by precipitation.

Discussion

In regards to finding 3, it would seem that the zinclead couple is much more sensitive to cyanide concentration than is zinc alone. C Tests

In these tests the quantity of lead nitrate added was varied, all other factors being the same as in A and B tests.

The results are shown in Table C and Graph C.

Test No	"C mm c	N" le/l	рН		Zn dissolved	Recovery	Pb(N)3)2
	bef.	aft.	bef.	aft.	шпоте/т	per cent	mmore/1
A-5	3.15	2.0	10.0	10.5	.8305	89.3	0.0
C- 6	3.25	2.1	10.0	10.2	•5285	95 .1	0.075
B-2	3.1	2.4	9.9	10.1	•5285	95.2	0.15
C-2	3.2	2.5	9.9	10.3	•5285	95.2	0.30
C-3	3.2	2.4	9.9	10.1	• 302	64.2	0.60
C-4	3.2	2.5	9.9	9.8	.302	64.0	4.53

TABLE C

Note: Mmoles Pb(N)3 per liter x 0.6625 = 1b per ton.

Conclusions

- 1. Recovery is improved by the addition of a lead salt in small quantities.
- 2. Best results are obtained when the molecular ratio of zinc to lead is more than 7:1 (about 0.2 lb Pb(NO₃) per ton when 0.523 lb of zinc is used)

- 3. The presence of an excess of lead salts retards precipitation.
- 4. The zinc consumption is reduced when an excess of lead is present.
- 5. The pH of the solution is increased slightly by precipitation when small quantities of lead salt are present, but is decreased when lead is present in large amounts.

Discussion

Precipitation is very sensitive to the amount of lead salt added to the solution and once the quantity of lead added gets beyond a certain point, the recovery drops rapidly. The importance of accurate control over the amount of lead added is made manifest by these tests.

It should be noted, however, that the purpose of adding a lead salt may be twofold: first, to form a lead-zinc couple; and secondly, to precipitate as insoluble compounds certain impurities which may be present in working solutions: Evidently, when such conditions exist the quantity of lead salt added may be more then that indicated by these tests which were made on pure solutions. This point will be discussed further in reference to tests (H) and (U).

D Tests

The object of these tests was to determine the influence of the quantity of dissolved lime on recovery. Solutions containing different amounts of dissolved CaO were precipitated with the results shown in Table D and Graph D.

The quantity of lead salt added was 0.15 mmoles per liter.

Test No	"CN" mmole/1		"Ca O " mmole/l		pH		Zn	Recovery	
•	bef.	aft.	bef.	aft.	bef.	aft.	mmole/1	per cent	
D-0	3.1 5	2.4	0.0	0.0	10.0	10.1	•5285	95.2	
D-1	3.15	2.6	0.15	0.42	10.0	10.45	•5285	95.2	
D-2	3.2	2.8	0.48	0.32	10.6	10.6	•5285	95.7	
D-3	3.2	3.1	0.95	0.84	11.0	11.0	•5285	95.9	
D-4	3.2	3.1	4.95	3.7	11.6	11.6	•5363	98.85	
D - 5	3.15	3.1	9.85	8.85	11.85	11.90	•5663	98.70	
D 6	3.2	3.2	17.9	17.8	12.1	11.6	.612	98.55	

TABLE D

Note: Mmole CaO per liter x 0.1122 = 1b per ton

Conclusions from D tests

1. The presence of lime in the solution improves precipitation.

- 2. The recovery reaches a maximum at about 5.0 mmoles CaO per liter or 0.5610 lb per ton; the addition of more lime than this amount reduces the recovery slightly.
- 3. The presence of lime reduces the cyanide consumption, the latter being least when an excess of lime is present.
- 4. Lime stabilizes the pH of the solution, the alkalinity remaining about the same after precipitation as before, except if very little lime is present, when the pH will rise, or when an excess is present, the pH will drop.
- 5. The "protective" alkalinity is less after precipitation than before.
- 6. The amount of zinc dissolved is increased when lime is added.

Discussion

These tests show that an alkaline solution is favorable to precipitation. The discussion of these results will be taken up again in conjunction with the E and F tests.

E-F Tests

The (D) tests had shown that lime improved recovery but they did not disclose whether the improvement was due to the lime itself or to the increased pH of the solutions. The object of tests E and F, then, was to determine the influence of the pH of the solution on redovery.

Caustic soda was used to raise the pH and hydrocyanic acid was used to lower it, In this manner it was possible to vary the pH of the solution from 6.6 to 12.1 while maintaining the "free" cyanide content between 3.15 and 3.2 mmoles per liter. The only variable then, was the pH of the solution. Lead salt was added.

The results obtained are shown in Table E-F, and in Graphs D and E-F.

Test No	"(mm(b eff .	N" pl/l aft.	"(mm bef.	3a0" 51/1 aft.	pI bef.	H aft.	Zn dissolved mmol/l	Recovery per cent	Reagent added ml.
E-2	6.5	5.4			6.45	6.7	0.1510	66.00	8 HCN
E-1	3.15	2.4		-	6.6	6.8	0.302	77.30	4 HCN
E-4	3.2	2.0	-	-	8.2	8.4	0.3775	95.00	3 HCN 8 NaCN
E-3	3.15	2.35	-	-	8.7	9.5	0,5285	95.00	2 HCN 16 NaCN
B -2	3.15	2.35	-	-	9.9	10.1	0.5285	95.2	only NaCN
F-1	3.15	2.3	0.21	0.42	10.1	10.45	0.5285	95.40	0.5 Na.OH
F-2	3.20	2.75	1.05	0.63	10.85	10.85	0.5285	95.40	5 Na OH
F3	3.2	3.1	1.05	1.42	11.1	10.9	0.5285	95.55	20 Na OH
F -4	3.2	3.15	6.05	4.84	11.62	11.95	0.4908	97.20	45 Na O H
F-5	3.2	3.25	7. 90	6.95	11.90	12.2	0.4530	97.25	65 Na OH
F-6	3.2	3.25	9.06	8.84	12.1	12.4	0.4530	96.80	75 Na OH

Note: Test E-2 is not strictly comparable with the others - It can, however, be compared with test A-6, page NaOH solution added was a 1 per cent solution. HCN solution added was a 8 per cent solution.

Conclusions

- 1. The pH of the solution has a marked influence on precipitation.
- 2. A pH of less than 8 is unfavorable to precipitation.
- 3. A pH of from 11.5 to 11.9 gives the maximum recovery.
- 4. Between pH 8 and 11, the recovery is practically constant.
- 5. A pH produced by lime is better for precipitation than one obtained by caustic soda.
- 6. Zinc consumption is low at a low pH, increases and remains constant from pH 8.7 to 11.1, and decreases for a higher pH than 11.1.
- 7. The cyanide consumption is less at a higher pH than at a low one.
- 8. The "protective" alkalinity changes erratically during precipitation when soda is used. At a higher pH, the alkalinity is reduced by precipitation.

Discussi on

These tests, in conjunction with the D series, demonstrate, that lime is an "activator" of precipitation, that not only does lime raise the pH of the solution to the required degree, but that the presence of the calcium ion enhances precipitation. Fortunately, lime is the caustic agent universally used in the cyanidation of gold ores so that some is always present in pregnant solutions, and recovery is thereby increased over that which would result if sodium hydroxide were used.

<u>G</u> Tests

In this series of tests the lime content was maintained constant at about 5 mmole per liter, or 0.516 lb per ton, and the NaCN content was varied. The object was to determine the influence of "free" cyanide when lime is present. Lead salt was added.

The results are shown in Table G and Graph G.

TABLE G

Test	"CN" mmole/1		"(mmole	"CaO" mmole/1		E	Zn dissolved	Recovery per cent	
14 0	bef.	aft.	bef.	aft.	bef.	aft.			
G-0	3.2	3.1	4.95	3.7	11.6	11.6	0.5363	98.85	
G-1	6.25	5.8	4.95	4.7	11.55	11.7	0.8305	97.20	
G-2	11.9	11.25	5.30	5.42	11.55	11.65	0.9360	92.20	
G-3	1.5	1.3	4.95	3.6	11.6	11.6	0.4530	98.2	

Conclusion

1. The NaCN concentration necessary to obtain maximum recovery is unchanged by the presence of lime. With or without lime it is about 3.2 mmoles per liter.

H Tests

The object of these tests was to determine the influence of sulphide ion on precipitation.

Merck sodium sulphide was added in increasing amounts to the solutions, all other factors remaining constant. The amount of lead nitrate was, as before, 0.15 mmole per liter.

The results are shown in Table H, and Graph H.

TABLE	H
-------	---

Test No	"C] mmo] bef.	y" Le/l aft.	"Ca mmo] bef.	eO" Le/1 aft.	pl bef.	I aft.	Zn dissolved mmole/1	Recovery per cent	Na2S mmole/l
H-1	3.3	3.25	5.26	4.53	11.2	11.3	0.302	98.5	0.021
H-2	3.3	3.2	5.3	4.95	11.7	11.35	0.340	97.25	0.062
н - 3	3.3	3.2	5.37	5.26	11.7	11.65	0.453	54.70	0.187
н 4	3.3	3.2	5.37	4.53	11.7	11.5	0.226	46.50	0.562
н 5	3.3	3.2	7.69	6.53	11.7	11.1	0.188	1.27	3.370
Н - 6	3.3	2.8	5.10	4.0	10.8	11.0	0.453	97.95	0.4163 (x)

Note: Mmole Na₂S per liter x 0.156 \pm 1b per ton.

(x) In regards to test H-6 the sulphide was precipitated by adding lead nitrate to the solution in such amounts as to combine with all the sulphite and leave a very slight excess of lead. The solution was filtered and the routine test was performed on the filtrate. The sulphide precipitate was well washed and assayed for gold. Traces were found showing that some gold had been adsorbed by the precipitate.

Conclusions

- 1. Sulphide has a marked influence on precipitation, even when present in small amounts.
- 2. The detrimental effect of sulphide can be somewhat obviate by the addition of a lead salt to precipitate the sulphide. The precipitate, however, adsorbs a small amount of gold.
- 3. The pH of the solution is somewhat lowered after precipitation.
- 4. The "protective" alkalinity is also lowered by precipitation.
- 5. The zinc consumption rises to a maximum and then falls off as the amount of sulphide in the solution increases.

Discussion

The presence of soluble sulphide in pregnant solutions has been reported by White (62) who states that it forms zinc sulphide with the shavings in extractor boxes, thereby affecting precipitation. The same occurs with zinc dust as is shown by these tests.

The addition of a lead salt precipitates the sulphide by the formation of insoluble lead sulphide, and in this way prevents the coating of the zinc particles.

The importance of carefully controlling the amount of lead salt added has been already discussed in reference to tests C. The amount added should be much as to precipitate the harmful impurities - in this case, sulphide - and leave a slight to form a couple with the zinc.

Another point of importance is the place in the circuit where the lead salt should be added. Test H-6 showed that some gold is absorbed by the lead sulphide precipitated. If the lead salt is added before the clarifying leaves, the occluded gold will be removed with the precipitated sulphide and will be lost, unless some means are taken to recover it. While only a small amount of gold may be occluded per ton of solution, yet when we consider the number of tons of solution going through the leaves a considerable amount of gold may be lost in this way. This may be one of the reasons why in some mills a "metallurgical" balance between the gold input and the gold output is so difficult to attain.

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I Tests

The object of these tests was to determine the influence of the sulphite ion on precipitation. Merck sodium sulphite was added in increasing amounts to the gold solutions.

The results are shown on Table I, and Graph I.

Test No	mmo: bef.	CN" le/l aft.	"(mmol bef.	CaO" le/l aft.	pj bef.	H aft.	Zn dissolved mmole/l	Recovery per cent	Na ₂ SO3 mmole/1
I-0	3.2	3.1	4.95	3.7	11.6	11.6	•5363	98.85	
I-1	3.3	3.3	4.63	4.63	11.4	11.35	•5285	98.45	0.040
I-2	3.3	3.3	5.00	4.84	11.4	11.35	•5285	98.45	0.159
I 3	3.3	3.3	4.53	4.63	11.3	11.2	•5285	97.6	0.635
I -4	3.3	3.3	4.84	4.84	11.3	11.15	•5285	97.6	2.538
1 - 5	3.3	3.3	5.26	4.60	11.3	11.4	•6 79 5	97.6	10.153

TABLE I

Note: Mmole per liter $Na_2SO_3 \ge 0.252 = 1b$ per ton

<u>Conclusions</u>

- 1. Sulphite has an adverse influence on precipitate.
- 2. After falling to a certain level, 97.6 per cent, the recovery is not influenced by the presence of greater amounts of sulphite.

- 3. The pH of the solution remains practically unchanged.
- 4. The "protectice" alkalinity varies erratically, being sometimes more and sometimes less than before precipitation.
- 5. The "free" cyanide remains unchanged.
- 6. The zinc consumption is increased when large amounts of sulphite are present.

Discussion

In connection with the influence of sodium sulphite it is interesting to note that the Merrill Company has patented a process in which sodium bisulphite is added to the solution in order to activate precipitation (see page 33). Bisulphite may be an activator in certain cases, but sulphite in alkaline gold cyanide solutions certainly is not.

J Tests

The object of these tests was to determine the influence of the sulphate ion on precipitation. Definite amounts of sodium sulphate were added to a pure gold solution, all other factors remaining constant.

The results are shown in Table J and in Graph J.

Test No	mmo: bef.	"CN" le/1 aft.	"(mm bef.	CaO" ble/l aft.	pH bef. a	aft.	Zn dissolved mmole/l	Recovery per cent	Na ₂ S O₄ mmole/1
J-0	3.15	3.1	4.95	3.7	11.6	11.6	0.5363	98.85	0
J-1	3.3	3.3	4.84	4.70	11.1	11.2	0.5363	98.10	0.035
j-2	3.3	3.3	4.95	4.40	11.25	11.0	0.5285	98.10	0.141
J- 3	3.3	3.2	4.95	4.90	11.3	11.3	0.5285	98.10	0.563
J - 4	3.2	3.15	4.90	3.90	11.3	11.4	0.5285	98.10	2.253
J - 5	3.25	3.3	4.95	4.48	11.3	11.3	0.5285	98.10	9.011
J-6	3.4	3.4	4.90	5.26	11.4	11.4	0.453	98.10	22,528
J-7	3.25	3.25	5.05	4.68	11.3	11.2	0.453	96.9	36.045
J - 8	3.4	3.3	5.47	5.20	11.4	11.3	0.453	95.4	72.090

TABLE J

Note: Mmoles Na₂SO₄ per liter x 0.284 = 1b per ton.

Conclusions

- 1. Sulphate has an adverse effect on precipitation, even in small amounts.
- 2. Within certain limits a larger quantity does not influence recovery more than small amounts.
- 3. The "free" cyanide content remains practically unchanged by precipitation.
- 4. The "protective" alkalinity is lowered by precipitation.
- 5. The pH of the solution is very little affected by precipitation.
- 6. The zinc consumed decreases with increased sulphate content.

Discussion

When sodium sulphate is added to a lime solution calcium sulphate is formed, the amount depending on the relative quantities of each present in the solution. If enough calcium sulphate results to approach the saturation point, about 4 lb per ton of solution, calcium sulphate will coat the zinc patricles and prevent contact with the solution: precipitation will be sluggish. This was especially noted when large amounts of sodium sulphate were added; a whitish precipitate formed in the solution and though it was filtered out the detrimental effect was not obviated. That the zinc becomes coated is shown by the fact that the amount of zinc dissolved decreases as the sulphate content of the solution is increased.

<u>k</u> Tests

The influence of the thiosulphate ion was studied by adding definite quantities of Na₂S₂O₃ to gold solutions, all other factors remaining constant.

The results are shown in Table K and Graph K.

Test	"CN" mmole/L		יי mm	"CaO" mmole/1		E	Zn dissolved	Recovery per cent	Na2S2Oz mmole/I
M O	bef.	aft.	bef.	aft.	bef.	aft.	шпоте/т	per cent	mmore/ T
K-0	3.15	3.1	4.95	3.7	11.6	11.6	.5363	98.85	0
K-l	3.3	3.2	4.84	4.84	11.4	11.05	•4 53	98.85	0.030
к - 2	3.3	3.2	5.37	4.63	11.4	11.5	.3775	98.85	0.121
K-3	3.3	3.2	4.53	4.74	11.4	11.5	•3775	98.85	0.483
K 4	3.3	3.2	4 .8 4	4.74	11.3	11.4	•3775	98 .8 5	1. 934
K-5	3.3	3.2	5.05	4.63	11.4	11.4	•3775	98.00	7•736
к - 6	3.3	3.2	4.84	4.63	11.3	11.4	•302	95.60	30.943

TABLE K

Note: Mmole Na₂S₂O3 per liter x 0.316 = 1b per ton

Conclusions

- 1. Thiosulphate, unless present in considerable quantities, has no influence on precipitation.
- 2. The "free" cyanide content of the solution remains constant.

- 3. The "protective" alkalinity is lowered by precipitation when sodium thiosulphate is present in the solution.
- 4. The pH is but slightly affected by precipitation.
- 5. The amount of zinc dissolved decreases as the thiosulphate content increases.

Discussion

Thiosulphates are often present in solutions due to the partial oxydation of sulphide ores, during the aeration of cyanide pulps, and a considerable amount may result when pyrrhotite is present in the ore. Fortunately, a certain quantity is necessary before precipitation is affected.

L Tests

These tests were made to study the influence of the thiocyanate ion on precipitation. Definite quantities of sodium thiocyanate were added to pure gold cyanide solutions, all other factors remaining constant.

The results are shown in Table L and Graph L.

Test No	"CN" mmole/l		"CaO" mmole/l		рН		Zn dissolved	Recovery	NaCNS added
	bef.	aft.	bef.	aft.	bef.	aft.	mmore / T	per cent	mmore/T
L-0	3.2	3.1	4.95	3.7	11.6	11.6	0,5363	98.85	0
L-1	3.2	3.2	4.74	4.63	11.4	11.45	0.453	98,95	0•031
L-2	3 4 2	3.3	4.63	4.58	11.4	11.45	0.453	98.95	0.123
L-3	3.25	3.2	4.74	4.21	11.45	11.45	0.453	98.95	0.617
L-4	3.25	3.2	4.84	4.32	11.5	11.45	0.453	98,95	2.467
L-5	3.2	3.2	4.95	4.63	11.4	11.3	0.453	97.95	9,868
L ⊷6	3.3	3.2	5.47	5.16	11.4	11.1	0.3775	97.90	39 •4 72

TABLE L

Note: Mmole NaCNS per liter x 0.162 = 1b per ton.

Conclusions

1. In amounts not over 2.467 mmole per liter (about 0.4 lb per ton of solution) sodium thiocyanate favors precipitation.

- 2. Greater quantities of NaCNS than mentioned in 1 lowers the recovery.
- 3. The "free" cyanide content of the solution is unaffected by precipitation.
- 4. "Protective" alkalinity is lowered by precipitation.
- 5. The pH of the solution remains unchanged except when a large amount of thiocyanate is present; the pH is then lowered by precipitation.
- 6. The zinc consumption is lessened by the presence of NaCNS.

Discussion

The presence of thiocyanate in small amounts activates precipitation. This may possibly be due to the formation of thiocyanates of gold (73) which would react more energetically with the zinc than does gold cyanide this, however, is but an hypothesis and it would be rash to stress this possibility too far in view of the meagre data available.
M Tests

The object of these tests was to determine the influence of the ferrocyanide ion on precipitation. C.P. sodium ferrocyanide was added to pure gold cyanide solution in definite amounts, all other things remaining constant.

The results are listed in table M and shown on graph M.

Test	"CN" mmole/l		"Ca O" mmole/l		рH		Zn dissolved	Recovery	Na4Fe(CN)	
NO	bef. aft.		bef. aft.		bef. aft.		mmole/1	per œ nt	mmole/1 '	
M -O	3.2	3.1	4.95	3.7	11.6	11.6	.5363	98.85	0	
M-1	3.3	3.25	4.9 5	4.43	11.5	11.6	•453	98,60	0.0207	
M-2	3.3	3.2	4.95	4.98	11. 5	11.5	•4 53	98.50	0.0826	
м - З	3.3	3.3	5.26	4.95	11.5	11.5	•4 53	98.50	0.4132	
M -4	3.3	3.3	5.37	4.94	11.5	11.5	•453	96.90	2.0662	
M-5	3.3	3.1	5.42	5.00	11.5	11.4	•5285	96.60	10,3308	

TABLE M

Note: Mmole Na₄Fe(CN)₆ per liter x 0.608 = 1b per ton.

Conclusions

- 1. Ferrocyanide hinders precipitation although not very greatly unless present in notable amounts.
- 2. The "free" cyanide titration is little effected; only when relatively large amounts are present is it reduced.

- 3. The "protective" alkalinity is less after precipitation than before.
- 4. The pH of the solution remains unchanged during precipitation.
- 5. The amount of zinc dissolved is constant except when considerable Na₄Fe(CN)₆ is present; it then rises slightly.

Discussion

It is evident, from the results of these tests, that the use of unlined iron tanks for agitating pulps is not to be recommended. If iron is brought in contact with a cyanide solution, the iron will dissolve in the cyanide solution and will eventually be transformed into ferrocyanide.

Iron tanks, however, are not the only cause of ferrocyanides in mill solutions. Iron minerals contained in the ore may be decomposed and form ferrocyanides.

N Tests

In these tests an attempt was made to determine the influence of zinc-cyanide in gold solutions. Owing to the fact that zinc cyanide titrates at least partly as "free" cyanide, as explained on page 99 it was impossible to vary the zinc cyanide content independently of the "free" cyanide titration by, method used. Consequently, two factors varied during these tests: the zinc cyanide and the "free" cyanide, and the results obtained are that much less trustworthy. Some idea of the influence of minc cyanide alone can, nevertheless, be gained by comparing these results with the G tests where the "free" cyanide alone was varied. The results obtained are shown in Table N and Graph N.

TABLE N

Tes No	t " mm	CN" ole/l	"CaO" mmole/1	рH	Zn dissolved	Recovery	Zn(CN)2	
	bef.	aft.	bef. aft.	bef. aft.	mmore/ r	per cent	mmore/1	
N-0	3.2	3.1	4.95 3.7	11.6 11.6	•5363	98.85	0	
N-l	3.6	3.5	4.43 4.74	11.5 11.5	•453	98.60	0.0873	
N-2	4.2	3.9	4.53 3.90	11.5 11.45	•903	98. 50	0.4465	
N-3	6.9	6.7	4.63 5.10	11.5 11.35	3.030	98.45	3.0362	
N -4	16.6	14.5	5.26 5.69	11.4 11.3	6.191	98.00	6.0724	

Note: Mmole $Zn(CN)_2$ per liter x 0.235 = 1b per ton

Conclusions

- The presence of zinc cyanide in the solution is detrimental to precipitation, becoming considerable when the concentration of zinc cyanide increases.
- 2. The "free" cyanide reading is lowered by precipitation.
- 3. "Protective" alkalinity behaves erratically; it is sometimes lowered and sometimes raised by precipitation.
- 4. The pH of the solution is lowered slightly by precipitation.
- 5. The amount of zinc dissolved is influenced by the quantity of zinc cyanide in solution. When considerable amounts of zinc cyanide are present very little of the zinc added for precipitation is dissolved.

Discussi on

When zinc cyanide is added to an alkaline solution zinc hydroxide is precipitated, but is dissolved if cyanide is present in excess. This is discussed more thoroughly in Appendix II page 99 where the method of preparing zinc cyanide is given.

It will suffice here to say that contrary to the precipitate formed by the addition of a lead salt to a soluble sulphide, the precipitate formed by the addition of zinc cyanide to an alkaline solution does not occlude gold whatever.

O Tests

In these tests the effect of temperature was studied. The results are shown in Table O and Graph O.

"CN" "Ca.O" Test pН Zn mmole/1 dissolved mmole/1 Recovery Temp No mmole/1 OC per cent bef. aft. bef. aft. bef. aft. 7 11.5 11.5 0.3775 3.2 5.00 4.797.80 0-1 3.2 98.85 3.2 4.95 3.7 11.6 11.6 0.5285 20 0-2 3.2 11.5 11.6 0.5285 98.90 5.00 3.8 37 3.2 3.2 0-3

TABLE O

Conclusions

- 1. Precipitation is influenced by temperature.
- 2. Beyond a certain temperature, about 20°C, the influence of temperature is less marked than it is below.
- 3. Within the limits of the tests neither the "free" cyanide nor the pH is influenced by temperature.
- 4. The amount of zinc dissolved is less at lower temperature, but is not increased perceptibly by a rise of temperature.

Discussion

We see by these tests that the influence of temperature on precipitation is more marked at temperatures lower than 20°C than at higher. The importance of this statement is evident in countries where seasonal variations in temperature are marked: recovery would decrease during the winter while it would not increase materially during warm weather.

P Tests

These tests were run to determine the influence of the gold content of the solution on recovery. The zinc content was varied in proportion to the gold content, i.e. the zincgold ratio was kept constant.

The results obtained are shown in Table P and Graph P.

Test No	mm o :	CN" le/l	"CaO" mmole/1	рH	Zn dissolved	Recovery	Au	
	bef.	aft.	bef. aft.	bef. aft.	mmole/1	per cent	mmole/1	
P-1	3.3	3.3	4.84 4.60) 11.5 11.5	•4530	95.90	0.02615	
P-2	3.2	3.1	4.95 3.7	11.6 11.6	.5 363	98.85	0.040	
P-3	3.3	2.3	4.95 3.69	11.5 11. 2	•679 5	99.50	0.0678	

:

TABLE P

Note: Mmole Au per liter x 6.31 = 0z per ton.

Conclusions

The recovery increases with the concentration of the gold in the solution.

Discussion

At first sight it might be believed that the increased recovery is due to the fact that in calculating the recovery the denominator is greater, thus: <u>(Heads - Tails)</u> x 100 = per cent Heads recovery. Actually, however, the barren solution resulting from the precipitation of the high gold solution, had lower values than the others, showing that the precipitation is really enhanced by the presence of more gold. R Tests

In these tests the molecular zinc-gold ratio was changed and the effect on precipitation was observed.

The results are shown in Table R and Graph R.

Test No	"(mm bef.	CN" ole/1 aft.	"Ca mmo: bef.	a 0" le/1 aft.	pH bef. aft.	Zn dissolved mmole/l	Recovery per cent	Mmole Zn-Au Ratio
R-1	3.3	3.2	5.00	1.79	11.5 11.4	•3775	94.50	50 :1
R-2	3.2	3.1	4.95	3.7	11.6 11.6	•5363	98.85	100:1
R-3	3.3	3.0	5.00	5.10	11.5 11.6	•6 0 40	98 .7 5	200:1

TABLE R

Conclusions

- 1. Recovery is influenced by the molecular zinc-gold ratio. If the ratio is less than 100:1 recovery will be less, while a ratio greater than 100:1 does not have a marked influence.
- 2. The "free" cyanide titration after precipitation is decreased as the ratio is increased.
- 3. The "protective" alkalinity is decreased by precipitation with a low ginc-gold ratio, and it is increased for a high ratio.

- 4. The pH during precipitation is unchanged whether a high or a low ratio is used.
- 5. The zinc consumption increases with the ratio employed.

Discussion

The conclusions reached by these tests do not mean that it requires 260 g. of zinc to precipitate 8 of gold. It means that the amount of zinc in contact with the gold solution at any given time should be in the molecular ratio of 100 to 1 if good precipitation is to result. This contact with a large excess of zinc is obtained by the use of pressure filters where the solution is forced through a thickness of zinc dust.

S and T Tests

The S tests were made to determine what results would be obtained by treating a lime-free solution containing the "impurities" present in tests (H), (I), (J), (K), (L), (M) and (N).

The procedure followed was to add the same amount of impurity to a lime-free solution as had been added to a solution containing lime. Thus, for S-3 say, the same quantity of sodium thiosulphate was added as had been used for K-4, and so on.

The same procedure was followed for the (T) tests except that the pH of the solution was brought up by mean of caustic soda to the value it had when lime was present. The (T) tests are therefore strictly comparable with the (H), (I), (J), (K), (L), (M) and (N) tests since the only variable obtaining is the substitution of NaOH for CaO.

The recoveries obtained under these various conditions are shown in Table S-T.

Test	"Impurity"	Corresponds	Recovery - per cent				
100			with lime	no lime	with NaOH		
S-1 T-1	Sulphide	н-3	54.70	20.10	7.92		
S-2 T-2	Sulphite	I -4	97.60	96.20	98.3		
5-3 T-3	Thicsulphate	K -4	98.85	94.35	98.3		
S-4 T-4	Sulphate	J 4	98 .10	94.3 5	95.10		
S-5 T-5	Thiocyanate	L-4	98.95	93.20	95.00		
5-6 T-6	Ferrocyanide	M 4	96.90	90.25	95.70		
S−7 T−7	Zinc cyanide	N-3	98.45	93.15	98,30		

TABLE S-T

Conclusions

•

- 1. Lime is a better activator of precipitation than caustic soda, except in the case where sulphite is present.
- 2. In all cases recovery is improved by the presence of an alkali, whether the alkali is lime or sodium hydroxide.

- 3. In the case of sulphide the presence of sodium hydroxide lowers the recovery, while lime tends to diminish the injurious effects of the sulphide.
- 4. When zinc cyanide is present there is only a slight difference in the recoveries obtained with lime or with caustic soda present in the solution.

U Tests

The solution used for these tests was a cyanide solution which had been used to dissolve gold from a rich gold ore. The solution had been kept in an iron tank for some years. so that some iron had been introduced into the solution, possibly in the form of ferrocyanide. The solution also contained copper to the extent of 0.005 per cent, titrated 1.0 mmole per liter free cyanide (0.1 lb per ton), 2 mmole CaO per liter (0.22 lb per ton) and had a pH of 10.7. The gold content was 0.887 oz per ton of solution.

Three tests were made on this solution; the first with the solution as shown above; the second, after increasing the cyanide and the lime content of the solution to 0.32 and 0.56 lb per ton respectively; and the third by precipitating out some of the impurities by lead nitrate, filtering, and correcting the cyanide and lime concentrations to the same amounts mentioned previously. Zinc in sufficient amount produce a Zn-Au ratio of 100:1 was added. The solutions were descrated by the vacuum method.

The results obtained are shown in Table U.

Test No	"CN" lb/t	V	"CaO" 1b/t	рH	Recovery per cent
U-1	0.1	<u></u>	0.22	10.7	35.2
U-2	0.32		0.56	11.5	98.7
U-3	0.32		0.56	11.5	98 .9

TABLE U

These results show in a convincing manner the importance of having a sufficient amount of free cyanide and lime in the solution if good precipitation is to be attained.

An interesting fact was brought forth by test U-3. The precipitate resulting from the lead nitrate treatment adsorbed an appreciable quantity of gold, about 0.001 oz per ton of solution treated by lead salt. This means that should such conditions be met with in practice and if the lead salt is added ahead of the clarifying filters, for every 1000 tons of solution treated one ounce of gold is lost. V Tests

In these tests, the influence of the time of contact was studied. The Merrill method. of chemical deoxydation as described on page 41 was used because it gave a better control over the time of contact than did the evacuation method.

The results are shown in Table V and Graph V.

TABLE V

Test No	ıı mm	CN" ole/l	"C mmo	a0" le/1	Нą	Zn dissolve d	Recovery	Time min.	
```	bef.	aft.	bef.	aft.	bef. aft.	mmole/1	per cent		
V-1	3.3	3.3	4.74	3.9	11.5 11.5	0.227	98.0	5	
<b>V-</b> 2	3.3	3.05	4.74	4.6	11.5 11.7	0.3775	98 <b>.65</b>	15	
V-3	3.3	3.0	4.74	4.65	11.5 11.6	0.453	98.85	30	
V-4	<b>3</b> •3	2.8	4.74	4.85	11.5 11.6	0.903	98.85	60	

### Conclusions

- 1. A certain time of contact between the zinc and the solution is essential to good precipitation.
- 2. The maximum is attained in about 30 minutes and any longer period only results in greater zinc consumption, without any increase of recovery.

### Discussion

In practise, where filter presses are used, conclusion 2 would not be applicable. With filter presses the solution is forced into intimate contact with the zinc so that less time is required to precipitate the gold. When the zinc dust is added loosely in the solution - as was the case for all these tests - about half an hour is necessary before complete precipitation takes place.

#### General Conclusions

- 1. With pure gold cyanide solutions the best recovery is attained when the "free" cyanide content is 3.2 mmoles per liter (0.31 lb per ton) whether or not lime is dissolved in the solution.
- 2. The pH, or total alkalinity, of the solution has a marked influence on precipitation, a pH of about 11.6 giving the maximum recovery.
- 3. Alkalinity produced with lime gives, generally, a higher recovery than that produced by sodium hydroxide, and the quantity of lime giving the best recovery is about 5 mmoles per liter (0.56 lb per ton).
- 4. When sulphite is present better precipitation is obtained with sodium hydroxide dissolved in the solution than with lime.
- 5. Sulphide, sulphite, sulphate, thiosulphate, ferrocyanide and zinc cyanide, when present in the solution, lower the recovery. Of these, the sulphide is the most detrimental. On the other hand, thiocyanate, in small amounts improves recovery.
- 6. A lead salt, in small amounts, improves precipitation; when an excess is present, however, precipitation is retarded.
- 7. The concentration of gold in a solution influences the extent of precipitation; the higher the gold content of

solution the better the recovery, all other things being equal.

- 8. The amount of zinc added to the solution is important. A molecular ratio of zinc to gold if less than 100 to 1 lowers the recovery.
- 9. The recovery is lowered if the temperature of the solution falls below 20°C.
- 10. When foreign substances are removed from a solution by precipitation with a lead salt, the precipitate so formed may occlude or adsorb gold. When such conditions obtain it is bad practise to add the lead salt before the clarifying leaves.
- 11. The alkalinity is not always increased by precipitation.
- 12. Leibig's method of determining "free" cyanide is unreliable when zinc is present in the solution.
- 13. Clennell's method of determining "protective" alkalinity, with or without Green's modification, is unreliable in the presence of zinc.
- 14. "Protective" alkalinity does not give a good picture of the conditions obtaining during precipitation; a much more reliable measurement is the pH.

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### APPENDIX I - PREPARATION OF SOLUTIONS

## 1. The Preparation of Pure NaCN Solution

A stock solution was prepared by bubbling HCN gas through distilled water in which a definite quantity of Merck C.P. NaOH (98 per cent) was dissolved, the HCN being produced by the action of 1:1 H₂SO₄ on Merck NaCN balls 96 per cent pure. The gas was water washed before passing to the distilled water. From time to time samples were removed and titrated for cyanide by silver nitrate until the quantity of NaCN shown by the titration increased when caustic soda was added to the sample. This showed that an excess of HCN was dissolved in the solution. The bubbling of HCN was stopped.

Small pellets of NaOH were added one at a time to the solution, a sample being tested after each addition, until the addition of more caustic soda to the sample did not change the titration. This indicated that all the excess HCN had been changed to NaCN.

The solution was not alkaline to phenolphtalein thereby indicating that an extremely slight excess, if any, of caustic was present in the solution.

About four liters of solution titrating 82.04 lb per ton or 41.02 g. per liter were prepared. From this stock solution dilute solution containing 0.1 millimoles NaCN per ml. and 0.04 millimoles of gold per liter were prepared by adding distilled water to 119.5 ml. of stock NaCN solution and 14.22 ml. of stock gold solution to form a liter of NaCN-Au solution. A solution made up in this manner permitted to vary the cyanide content at will without changing the gold content of the working solution.

Each new lot of solution prepared was assayed for gold and any variations noted were taken into account.

#### 2. The Preparation of Pure AuNa(CN)2 Solution:

Pure gold was dissolved in a pure solution of sodium cyanide, by passing lime-washed air through the solution, a slight excess of cyanide over that theoretically required being present.

Highly purified gold was prepared by a modification of the Krüss process as follows (46): A gold bead weighing approximately 3 grams was inquarted with about 12 grams of silver and parted with nitric acid after being rolled out into a thin sheet in a manner similar to that employed for bullion assaying. The resulting cornet gold was then dissolved in about 7 parts of warm aqua regia made up in the following proportions (47): 200 ml. of concentrated hydrochloric acid, 45 ml. of concentrated nitric acid and 245 ml. of water. The gold dissolved

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readily in this mixture, the whole going into solution in about five minutes. According to E.Priwazuick the reaction which takes place is as follows:

Au +  $HNO_3$  +  $4HCl = HAuCl_4$  +  $NO + 2H_2O$ 

The gold solution was then transferred to a porcelain evaporating dish and the solution evaporated down slowly with repeated addition of HCl to a thick syrupy consistency. The traces of silver left in the gold gradually dropped down in the form of the chloride as evaporation proceeded and the solution assumed a deep red color as the concentration of HAuCl4 increased.

The syrup was then poured in a thin stream into a large glass vessel of distilled water and a solution of about l gram of gold per 20 ml. of water was made in this way. The solution was left to settle for five days, and was then filtered. The filtrate was then diluted with distilled water to about 500 ml. The gold chloride solution was heated to a moderate temperature and oxalic acid was added to precipitate the gold. The gold precipitated slowly in the form of a scum which floated on top of the liquid. After three days the scum had settled to the bottom of the vessel. The acid solution was then decanted off and the gold was washed repeatedly with cold and then warm distilled water.

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The gold was again dissolved in aqua regia and submitted to the same treatment as before except that, instead of adding oxalic acid, zinc dust was used as precipitant. The gold precipitated in the form of small spongy granules which quickly settled. The solution was decanted off and the gold was washed in warm dilute then strong HCl to remove the excess zinc. Finally it was washed thoroughly with warm distilled water.

Four liters of gold cyanide solution assaying 17.49 oz. per ton or 0.5546 g. per liter and titrating 0.3 g. NaCN per liter were made up and were used as stock solution.

From this stock solution working solutions of a gold content of 0.04 mmol per liter or 0.2524 oz. per ton were made up in lots of 16 liters.

After dilution the free cyanide was, theoretically, 0.0085 lb NaCN per ton, an amount impossible to titrate by Leibig's method, and the working solutions were considered as being exempt of free cyanids from this source.

Each new lot hf 16 liters prepared was sampled and assayed for gold as a check and any variation was taken into account in the calculations.

It may be said that the variations were very small. All told, eight lots were prepared and assayed with the following results, 17 1/2 A.T. of solution being the size of the sample in every case:

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Lot	NO	Au
		oz/T
l		0.2520
2		0.2522
3		0.2530
4		0.2524
5		0.2528
6		0.2524
7		0.2526
8		0.2526

#### 3. Preparation of Lime Solution.

A saturated solution of Shawinigan slacked lime at 60 per cent available CaO was prepared and allowed to settle. Clean solution in lots of four liters were taken from this stock solution and filtered.

Stock gold solution in the proportion of 14.22 ml. per 985.78 ml. of lime water was then added and the solution was titrated for lime by oxalic acid.

By making up the lime solution in the manner indicated - adding 14.22 ml. of stock solution to a volumetric flask and diluting to the 1 liter mark with lime water - it was possible to vary the CaO content as desired by adding definite amounts of lime solution to the working solutions without producing any change in the gold concentration. Obviously, since the gold contact of the lime solution is the same as that of the working solution, any volume of the former can be added to the latter without changing the gold content of the working solution. This method was adhered to in the preparation of all the solutions used.

As with all the solutions a gold assay was run on a sample of each batch prepared and any divergence from the calculated value was duly taken into account in the computations.

#### 4. Preparation of Zinc Cyanide Solution

Zinc cyanide was prepared by adding drop by drop a strong solution of sodium cyanide to a saturated solution of zinc sulphate until no more precipitation took place. The white **powdery precipitate formed was allowed to settle and was washed thoroughly with distilled water.** Dilute cyanide was then added but not enough to dissolve all the precipitate. The solution was then filtered and the clear solution was assayed for zinc. The  $Zn(CN)_2$  content was calculated on this basis.

#### 5. Other Solutions:

All other: solutions, that is, those containing the "impurities" which were added to the pure gold solution, were propared from Merck's C.P. reagents. A definite amount was dissolved per volume of solution and on this basis the amount of "impurity" added to the pure gold cyanide solutions was calculated. As before, the reagents were dissolved in distilled water containing the required amount of stock gold solution to bring the gold content of the solution to that obtaining in the working solution i.e., any amount of "impurity" could be added without changing the amount of gold per liter of working solution.

Solutions of the following reagents were prepared as indicated above:  $Na_2S$ ,  $Na_2SO_3$ ,  $Na_2SO_4$ ,  $Na_2S2O_3$ , NaCNS, and  $Na_4Fe(CN)_6$ .

It should be noted that all these compounds are sodium compounds so that in each case only one factor was changed since the gold solvent used was itself a sodium salt, NaCN. Thus, when Na₂SO₄ is added the only new factor introduced is the presence of  $SO_4^{--}$  ions in the solution, and so on.

### APPENDIX II - METHODS OF A NALYSIS EMPLOYED.

#### 1. Assaying of Gold Solutions

Two methods were used: (a) evaporation in a lead boat; (b) a modification of the Chiddey method.

(a) The Evaporation Method.

The method consists of evaporating a definite volume of solution in a lead boat, scorifying when necessary, and coupelling.

This method, which is undoubtedly the most accurate, was used for high gold solutions.

(b) Modified Chiddey Method

This method was used for barren solutions. The procedure is as follows:

The solution is added to a beaker of convenient size and heated to near the boiling point.

Add 5 ml. concentrated HCl (For 20 A.T. or more add 10 ml. concentrated HCl).

Add 20 ml. of a 20-percent solution of lead acetate made with sufficient acetic acid to prevent hydrolysis. Heat to simmering. Place in the mixture a strip of aluminium (1/8 in. by 1/2 in. by 6 to 8 in. long).

Digest for 30 minutes, keeping solution at simmering heat.

Add 25 ml. of HCl.

Form ball with lead sponge. Let digest 15 minutes more.

With clean solutions the lead sponge will form in one mass while with foul solutions the lead sponge will be more granular.

Decant through a cone filter using a fast filter paper. With the fingers press the lead sponge into the bottom of the paper cone. Add silver for parting.

Remove the filter paper and cut off the cone just above the mass of lead.

Place the lead and paper on a piece of lead foil and dry thoroughly.

Wrap the foil about the sponge and cupel.

The sponge can be cupelled directly if care is taken to remove as much of the filter paper as possible.

The method is fairly rapid and very convenient in that little attention is required. Unlike the original Chiddey method the sponge does not break up if left too long in the hot solution, and there is no danger of "spitting" during coupellation due to undissolved zinc. It is very accurate for dilute or barren solutions but a little low for high gold solutions.

In the latter case, however, the solution can be submitted to two successive treatments when a fairly high degree of accuracy can be attained, as shown by the following test:

200 ml. of a high gold solution gave, by evaporation, a parted bead of 5.97 mg. The same quantity of the solution was assayed twice by the method described above. The results obtained were:

Parted	bead	from	first	treatment	=	5.960	mg.	
Parted	bead	from	second	treatment	=	0.005	mg.	
				Total		5.965	mg∙	
				Error		0.085	pe r	cent

à

The presence of foreign compounds, even in rather large quantities, does not seem to offset the results so long as sufficient hydrochloric acid is added to attack the aluminium.

A 500 ml. volumetric flask was remarked to hold 17.5 A.T. and this was the amount used for all barren solution determinations.

2. Zinc Analysis

The zinc in solution was determined in the following manner:

200 ml. of the filtered barren solution were placed in a Low "copper" flask, about 10 ml. of concentrated sulphuric acid were added and the whole was taken to dryness.

The residue was dissolved in warm water, three grams of ammonium chloride and about two ml. of ammonia being added. The solution was warmed, filtered and the precipitate, if any, was washed with weak ammonia solution.

The filtrate was acidified with strong HCl, 3 ml. being added in excess.

The zinc was then titrated with a standard solution of potassium ferrocyanide using uranium nitrate as exterior indicator.

# 3. "Free" Cyanide Determination

The "free" cyanide was determined by Liebig's method using silver nitrate and potassium iodide as indicators.

The reactions are as follows:

 $AgNO_3 + KI = AgI + KNO_3 \qquad (1)$  $AgI + 2NaCN = KI + NaAg(CN)_2 \qquad (2)$ 

A standard solution containing 0.85 g. of pure silver nitrate per liter was prepared. Therefore, on a 10 ml. sample, each ml. of standard solution used was equal to 1 mmole NaCN per liter.

The method is far from ideal or accurate when zinc is present in the solution.

An attempt was made to titrate the "free" cyanide content of the zinc cyanide solution prepared for the (N) tests by the Liebig's method, but the results obtained are unreliable.

On the basis of the zinc content the solution contained 10.25 g.  $Zn(CN)_2$  per liter or 0.09 moles per liter. On the basis of Liebig's cyanide titration the "free" cyanide content was 4.615 g. NaCN per liter or 0.094 moles per liter. According to these determinations, then, the proportion of Zn to CN in the solution is almost exactly 1:1, that is the formula of the zinc-cyanide compound would be ZnCN and not  $Zn(CN)_2$ .

We can explain these peculiar results by assuring that the Zn(CN)₂ is partly ionized thus:

# $Zn(CN)_2 = Zn^+ 2CN^-$

and that the silver nitrate titration indicates only the ionized or "free" CN.

The above theory is given some credence by the fact that the "free" cyanide content increases with increased dilution of the zinc cyanide solution as shown by the following series of tests.

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Diluti on	mmoles/l "free"CN
5:1	51.1
10:1	56.5
50:1	74.8
100:1	91.0

It is also possible, that other compounds are formed between zinc and cyanide such as  $2h(CN)_3$ ,  $Zn(CN)_4$ , etc., each of which may be totally or slightly dissociated according to the dilution. Furthermore, in an alkaline solution zinc hydroxide is formed, and this will, obviously, influence the results.

Woolf (49) noted that when zinc is present in alkaline cyanide solution the amount of free alkali in solution will influence the "free" cyanide titration: the higher the free alkali the more nearly the "free" cyanide titration will approach the total cyanide, until, if free alkali is high enough, the two titrations will coincide.

This is undoubtedly due to the decomposition of Zn(CN) 2 or similar compounds, by NaOH.

Smith (51) also mentions that lime decomposes  $Zn(CN)_2$ , resulting from precipitation, with liberation of "free" cyanide, and according to Robertson (14) alkaline  $Na_2Zn(CN)_4$  (( $Zn(CN)_2$ dissolved in NaOH) is "a ready and practicable solvent for gold".

When zinc is present in the solution conductometric methods of analysis should be used if accurate results are desired.

### 4. "Protective" Alkalinity Determination

The method used was Clennell's (53) as modified by Green (54) when zinc is present in the solution.

The standard solution used was prepared by dissolving pure oxalic acid in distilled water in such proportion that each cubic centimeter of solution used corresponded to 1 mmol CaO per liter when a 10 ml. sample was taken.

5 ml. of a 5 per cent solution of potassium ferrocyanide was added to the sample before titration when zinc was present.

An alcoholic solution of phenolphthalein was used as indicator.

### 5. Determination of pH

This was determined by a Beckman pH meter; the readings were corrected for sodium ion effect.

### 6. Determination of Oxygen

It has been shown by Tromp and Schilz (55) that cyanide alone does not interfere with oxygen determination by Winkler's method (56) although the presence of common impurities found in mill solutions render the method worthless. As the oxygen determination made during this investigation were on pure cyanide solution, Winkler's method was used. It is much more convenient and less tedious than the hydrosulphite method put forward by Weinig and Bowen (57).

Winkler's method is based on the fact that oxygen reacts with manganese hydroxide to form manganous acid:

 $Mn(OH)_2 + 0 = H_2MnO_3$ 

The amount of oxygen taken up is determined idiometrically by adding hydrochloric acid and potassium iodide to the manganous acid, the following reactions taking place:

> $H_2MnO_3 + 4HCl = MnCl_2 + 2H_2O + Cl_2$ 2KI + Cl_2 = 2KCl + I₂

The liberated iodine is titrated with standard sodium thiosulphate solution, using starch indicator.

The thiosulphate solution, made up approximately one tenth normal, was standardized against air-saturated solution made by bubbling air through water for about half an hour, and the amount of oxygen dissolved was determined by means of a pressure-temperature chart (57) or by the use of tables set up for the purpose (58).

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The reagents required are: an approximately 4N. MnCl₂ solution, a 35 per cent NaOH solution containing 10 per cent KI, a standard Na₂S₂O₃ solution; and starch solution.

The procedure used was as follows:

A narrow-necked flask of over 250 ml. capacity a Low "copper" flask is convenient - was marked on the lower part of the neck to hold exactly 250 ml. when a few light glass beads are placed in the flask. The glass beads permit easy stirring of the solution.

A portion of the solution to be tested was poured with care into the flask, stirred gently in the flask and was rejected. The flask was then filled to the mark with a second portion of the solution and corked with a punctured rubber stopper.

By means of a long thin pipette passed through the small hole in the cork and reaching to the bottom of the flask, 1 ml. of alkaline potassium iodide solution was introduced into the solution, and immediately afterwards 1 ml. manganese chloride. The flask was shaken and allowed to stand till the precipitate settled. Then, again by means of a long pipette, about 3 ml. of concentrated hydrochloric acid were introduced and the contents of the flask once more shaken.

The precipitate dissolved readily with the liberation of iodine which is titrated in the usual way.

The use of a long necked flask reduces to a minimum the absorbtion of oxygen from the atmosphere and obviates the the necessity of an oil or parafine cover over the solution. Tests made by the writer showed that an evacuated solution could stand in the flask at least fifteen minutes without appreciable adsorbtion of oxygen.
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