

AN ABSTRACT OF THE THESIS OF

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(Name) (Degree) (Major)

Date Thesis presented ~~May 10, 1937~~

Title ~~Determination of Gold and Silver in Cyanide Solutions~~

Abstract Approved: 
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The solutions obtained by leaching crushed gold and silver bearing ores with alkali cyanides are assayed for their precious metal content by one of several standard procedures. The largest volume of sample specified by any of these methods is 20 A.T. or about 600 c.c.

A method published by Mataichi Yasuda and extended by W.E. Caldwell and K.N. McLeod gave excellent recovery of gold and silver from solutions of salts other than their cyanides even when employing volumes up to forty liters.

Essentially the procedure consists of adding mercuric chloride, magnesium, and hydrochloric acid to the solution. Nascent hydrogen produced by the reaction of the acid on magnesium reduces gold and silver to the metallic state and mercuric chloride to the mixed precipitate mercury-mercurous chloride. This precipitate in falling through the solution collects gold and silver either by adsorption or amalgamation. The residue obtained is mixed with granular test lead, put in an electric furnace on a bone ash

cupel and treated as in ordinary assay practice.

A variation of the procedure just outlined depends upon the formation of the mixed precipitate mercury-mercuric amino nitrate by adding to the sample first ammonium hydroxide and then mercurous nitrate. The residue is collected and treated as just mentioned.

In the above determinative schemes the presence of cyanide was found to greatly inhibit gold and silver recovery. The purpose of this research project was to find some means of eliminating the cyanide ion in order that the accurate mercurial methods might be applied to the assay of large volumes of cyanide leach solutions.

It was found that quantitative recovery is had by the mercurial precipitate in acid solutions if the cyanide ion is first converted to ferrocyanide ion by treating the sample with an excess of ferrous sulfate.

By applying a correction factor to compensate for losses occurring in cupellation the gold content of 100 A.T. of solution is determined to within 0.01 or 0.02 milligrams and the silver to less than 2 milligrams. A procedure is hereby presented with which the value of gold and silver of a cyanide leach solution can be made to approximately one cent per ton.

DETERMINATION OF GOLD AND SILVER
IN CYANIDE SOLUTIONS

by

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A THESIS

submitted to the

OREGON STATE AGRICULTURAL COLLEGE

in partial fulfillment of
the requirements for the
degree of

MASTER OF SCIENCE

June 1937

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ACKNOWLEDGMENTS

I wish to express my appreciation to Dr. W.E. Caldwell for the encouragement and suggestions given while working on this problem.

Also, I wish to thank Prof. J.H. Batcheller for courteously extending the use of certain assaying equipment in the Mines Department.

L.E.S.

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DETERMINATION OF GOLD AND SILVER IN CYANIDE SOLUTIONS

Introduction

The use of alkali cyanide leach solutions in dissolving gold from its crushed ores has become a widely used process since its introduction in the early nineties. Routine control assays on the gold and silver content of the cyanide leach solutions, or the barren solutions after recovery of the precious metals, is made by one of many methods. The procedures most commonly employed are the copper sulfate method as used in South Africa (1), the evaporation (2)(3), and the zinc-lead acetate methods (4).

Assay Methods for Cyanide Solutions

In the copper sulfate method 20 assay tons of the sample (1 A.T. = 29.166 g. of liquid) are treated with solutions of the following reagents: potassium hydroxide, potassium cyanide, copper sulfate, sodium sulfite, sulfuric acid, and potassium ferrocyanide.

The reactions, then consist essentially of the formation of the reducing agent, sulfur dioxide, by the action of the sulfuric acid on the sodium sulfite, and the subsequent reduction of the noble metals to the finely divided metallic state. Copper sulfate, with potassium

ferrocyanide, and potassium hydroxide form a mixed precipitate of the copper ferrocyanide and copper hydroxide which in settling through the solution collects the metallic gold and silver by adsorption. The precipitate is collected by filtration and is treated as in an ordinary fire assay process for a dry ore by highly heating with a fusion mixture and cupelling the lead button obtained therefrom to obtain a noble metal bead. This bead is weighed, the silver parted from the gold with nitric acid, and the gold weighed. Silver is then determined by difference. This method requires considerable time and attention for an individual run.

There are several sources of error in the evaporation methods. The sample is limited to one or two assay tons which is put in a lead "boat" and taken to dryness on a steam bath. The boat is then rolled up with test lead and cupelled. This is tedious work and subject to loss of the highly concentrated residue by spitting upon nearing dryness.

A variation of the above scheme employs from five to ten assay tons of solution placed in a porcelain- or agate-ware evaporating dish with lead oxide and taken to dryness on a steam bath. The residue is removed, fused with a fluxing mixture, and treated as usual in fire assaying.

About the only other method which finds an important

use is the zinc-lead acetate, or "Chiddey" process. Lead-acetate is added to the gold bearing solution followed by the addition of the zinc dust. Zinc replaces gold and forms a spongy lead precipitate which collects the gold. The lead is collected and cupelled as usual.

Gold and Silver Determination in Non Cyanide Solutions

The work of Mataichi Yasuda (5), and as extended by Caldwell and McLeod (6) showed that minute quantities of gold may be obtained from large volumes of solution employing a semi-colloidal mercury and mercurous chloride collector.

To the solution bearing gold and silver, as salts other than their cyanides, mercuric chloride is added, followed by the addition of magnesium powder and hydrochloric acid. Nascent hydrogen produced by the action of the hydrochloric acid on the magnesium reduces the gold and silver to the metallic state and mercuric chloride to a mixture of mercury and mercurous chloride. This precipitate of mercury and mercurous chloride has the ability in falling through the solution of gathering gold and silver not only by adsorption but also by amalgamation. Also any noble metal not already reduced by the nascent hydrogen would be replaced by the metallic mercury and amalgamated in it. The residue is allowed to settle, most of the liquid is siphoned off, and the residue ob-

tained by filtration. This residue is then mixed with granular lead and cupelled in an electric furnace to get a noble metal bead.

A variation of the above method uses only mercurous nitrate and ammonium hydroxide from which is obtained the mixed precipitate mercury-mercuric amino nitrate. Collection and determination of gold and silver is carried out in the same manner as above.

Both of the above methods give excellent recovery of gold and silver even for minute quantities in volumes varying from two to forty liters.

Application of Mercurial Methods to Cyanide Solutions

It was desirable, therefore, to try to apply a method of this sort to cyanide solutions containing gold and silver for the following reasons: 1. But little attention is required for an individual determination. 2. A large volume of solution could be used conveniently, thus reducing errors in measuring and sampling. 3. Mercury replaces only those metals below it in the electromotive series, or in other words, the noble metals. This means that salts of copper and other base metals in the cyanide leach solution would not be reduced and give high silver results.

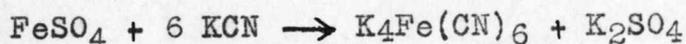
When the two above mentioned methods were applied to

gold and silver bearing cyanide solutions it was found that cyanide greatly inhibited quantitative recovery as is shown in Table I.

Development of Method

The problem, therefore, was to destroy or eliminate the cyanide ion in some manner so that it would not interfere.

A well known inorganic reaction is the formation of potassium ferrocyanide by the reaction of ferrous sulfate and potassium cyanide. Because of atmospheric oxygen some of the ferrous sulfate is converted to the ferric state, and as a result a precipitate of ferric ferrocyanide (Prussian blue) is produced. The two reactions involved are as follows:



The cyanide ions are, therefore, locked up in the complex negative ferrocyanide ion. It seemed feasible, then, that the use of ferrous sulfate might be the means of eliminating the deleterious cyanide ions from the solution, whence the colloidal mercury fall method should yield good results.

Two liter bottles holding about 70 A.T. of the solution were chosen as a convenient size to handle. These were over three fourths filled with tap water. Particles

TABLE I

Mercurial Methods Applied to Cyanide Solutions

NH₄OH-Hg₂(NO₃)₂ Method

Milligrams Used		Milligrams Recovered		Percent Recovery	
Au	Ag	Au	Ag	Au	Ag
2.85	-----	1.10	-----	30	--
2.85	-----	1.54	-----	54	--
1.87	10.48	.87	8.82	47	84

HgCl₂-MgHCl Method

2.85	20.96	.90	16.40	32	78
2.85	20.96	.91	15.61	32	74

of pure gold which had been weighed to within 0.01 milligram were dissolved in a minimum of aqua regia in small porcelain crucibles, and transferred to the two liter bottles. A measured volume of a standard silver nitrate solution was introduced. Since the cyanide concentration of leach solutions employed in various metallurgical plants varies considerably, a solution of .025% was chosen as a representative strength. To obtain this concentration in the two liters, .5 grams of potassium cyanide was used. Thus was prepared a gold and silver bearing cyanide solution simulating an ore leach solution.

The stoichometric weight of ferrous sulfate required to react with the potassium cyanide varies from 0.7 to 1. gram, depending upon which one of the complex iron cyanides is produced. Amounts of ferrous sulfate in a fresh solution varying from 0.2 to 5 grams were, therefore added to the two liter samples. From this point some of the runs were finished by the ammonium hydroxide-mercurous nitrate method and the rest by the magnesium-mercuric chloride-hydrochloric acid procedure. In the first method 40 c.c. of 28% ammonium hydroxide was added and then 20 c.c. of mercurous nitrate, that volume being equivalent to 4 grams of mercury. In the second, 50 c.c. of saturated mercuric chloride solution, 5 grams of magnesium powder, and 60 c.c. of concentrated hydrochloric acid were used. The results are given in Table II A and B.

TABLE II -A & B

Mercurial Methods with Ferrous Sulfate

-A-
 NH₄OH-Hg₂(NO₃)₂ Method

Grams FeSO ₄	Milligrams Used		Milligrams Recovered		% Recovery	
	Au	Ag	Au	Ag	Au	Ag
0.2	.85	10.48	.15	8.63	17.7	82
0.2	1.14	10.48	.13	8.90	11.4	85
1.	.85	10.48	.09	8.96	10.6	82
3.5	1.72		.33		19.2	
5.	.22	10.48	.03	5.92	13.6	56
5.	6.42		.53		8.3	

-B-
 HgCl₂-Mg-HCl Method

0.2	1.14	10.48	.81	10.09	71	96
1.	1.14	10.48	.95	10.04	83	96
1.	.81	10.48	.47	9.53	58	91
1.	2.55	20.96	.98	19.48	38	93
1.	1.51	10.48	1.23	9.53	82	91
2.	1.02	10.48	.94	9.71	92	93

Results show that the use of ferrous sulfate was not applicable to the ammonium hydroxide-mercurous nitrate method. Even when used in excess the recovery of gold did not exceed 20%. Silver recovery was somewhat higher but not satisfactory. In the basic medium the iron salts are converted to their insoluble hydroxides and the excess is not sufficient to react with all the cyanide. Possibly there is some slight reversal of the ferrocyanide ion formation giving some free cyanide. Cupellation of the large residue was exceedingly difficult. Scorification was then tried as a means of removing iron oxide in a slag, but results were not satisfactory.

Somewhat encouraged by the recovery in Table II B in which the percentage yield increased with an increase in the amount of ferrous sulfate used, several runs were set as before but employing 5 grams of ferrous sulfate. Table III shows that a quantitative yield is obtained for both gold and silver when using the excess of ferrous sulfate.

Discussion of Results

In examining the results of numerous runs it was noticed that the gold recovery was between 94 and 96%. If 95%, the average of recovery, is applied as a correction factor to the weight of gold obtained, it was found (Table IV) that in most cases the corrected value of gold was within 0.01 of a milligram of the theoretical yield. This

TABLE III

Ferrous Sulfate-Mercurial Method

Vol. of Sample	Amount Used		Amount Recovered		% Recovery	
	Au	Ag	Au	Ag	Au	Ag
	4.56	10.48	4.38	10.37	96.2	98.8
	6.80	31.44	6.39	29.21	93.9	93
	.65	10.48	.62	9.96	95.4	95
	1.87	20.96	1.80	20.69	96.2	98.8
	1.84	31.44	1.77	31.40	96.2	99.6
	13.85		13.13		94.8	
	2.08	20.96	1.99	18.49	95.5	84
2,000	.52	10.48	.49	8.17	94.3	78
c.c.	.80	20.96	.77	16.88	96.3	77
	.11	11.84	.10	9.70	90.9	82
	.05	8.78	.047	6.77	94	77
	22.93	123.00	21.36	115.00	93.2	93.5
	60.22	262.0	57.04	251.0	94.8	96
	.76	22.7	.70	18.5	92.2	81
	2.91		2.80		96.2	
	6.65		6.39		96	
	.37		.36		97	
	1.70		1.60		94	

Copper Sulfate Method

	.90	11.52	.86	10.99	95.6	95.4
600	3.12	15.75	3.00	14.7	96	93.4
c.c.	12.54	62.9	12.17	59.88	96.8	95.2

Chiddey Method

600	.12	5.24	.115	4.68	89.5	95.6
c.c.	4.96	20.96	4.79	19.46	93	96.5

TABLE IV

Correction Factor Applied to Gold Recovery

Milligrams Used	Milligrams Recovered	Corrected Recovery
4.56	4.38	4.62
6.80	6.39	6.73
.65	.62	.65
1.87	1.80	1.89
1.84	1.77	1.86
13.85	13.13	13.83
2.08	1.99	2.10
.52	.49	.52
.80	.77	.81
.11	.10	.105
.05	.047	.0495
22.93	21.36	22.48
60.22	57.04	60.20
.76	.70	.74
2.91	2.80	2.94
6.65	6.39	6.73
.37	.36	.38
1.70	1.60	1.69

percent held in runs employing a higher cyanide concentration, when the same ratio of cyanide to ferrous sulfate was maintained.

Just why this constant percentage loss is found in amounts of gold varying from a few hundredths of a milligram up to as high as 60 milligrams is not readily apparent. An exceedingly slight reversal of the ferrocyanide ion formation as an equilibrium reaction might produce some cyanide. However, in these runs carried out under identical conditions the amount of cyanide produced should have been the same. This then should give rise to an equal amount of gold loss in each run. Instead a constant percentage loss was experienced.

The discrepancy seems better explained as due to some mechanical loss of gold during the volatilization of mercury in the cupellation process. Analogous to the cupellation of these residues is the recovery of gold from amalgams by distillation of the mercury. The mercury distilled off contains minute quantities of gold.

To test this explanation 12.06 milligrams of gold and 62.02 milligrams of silver as very thin gold and silver foil were placed on a cupel with forty grams of test lead, and four grams of mercury. The mercury readily amalgamated with the wadded up foil and some of the granular lead. The cupel was put in the furnace and treated as usual. From the 12.06 mg. of gold there was recovered

11.14 mg., or 92.5%. From the 62.02 mg. of silver there was obtained 57.87 mg., or 93%. The conditions of this test were not quite the same as in a regular run since the amount of mercury was a little greater and there was no mercurous chloride present. However, it serves to show where the 5% loss of gold is encountered. Silver itself is somewhat volatile from the molten state and is subject to greater variations due to individual differences in cupellation. Since the market price of silver is much less than that of gold, its tendency toward a greater loss is more permissible.

Table III also gives results on simulated cyanide leach solutions for the copper sulfate and Chiddey methods employing the specified maximum 20 A.T. of solution. The percentage recovery on both is practically the same as for the mercurial method. The chief advantage of the latter method is, therefore, its application to larger volumes of solution. When calculating the content per ton of solution this method using 100 A.T. should give results approximately five times more accurate.

Procedure for Unknown

The method for analyzing an unknown cyanide leach solution would be as follows: Measure into any suitable container (bottles are convenient) 100 A.T. more or less of the unknown. To this add a solution containing a

weight of ferrous sulfate approximately ten times the weight of the cyanide contained in the sample. Add 50 c.c. of a saturated mercuric chloride solution and put in five grams of magnesium powder. Add 60 c.c. of concentrated hydrochloric acid. Pour in by portions to prevent bubbling over. If the volume of sample taken is much greater than the 100 A.T., (i.e., about 10 liters) double the amount of mercuric chloride, magnesium, and acid used. Allow to stand six to eight hours, or over night. Siphon off the clear liquid and transfer the residue from the bottle into a beaker, rinsing out any residue remaining in the bottle with small portions of water. Let it settle for a few minutes, and then filter using a rough quantitative filter paper. As the bulk of the residue is being washed onto the filter paper sprinkle in about 20 grams of granular test lead so that the two will become intimately mixed. Allow to drain and dry.

On a bone ash cupel weighing about sixty grams spread a layer of test lead following the general concave shape of the cupel. Remove as much of the dried residue from the filter paper as is convenient, mash the lumps, and place in the center of the cupel. Put a ring of granular lead around the outside of the residue but not covering it. With a little lead cover the residue remaining on the filter paper, wad it up and place on top of the cupel. The total weight of lead used should not greatly exceed

45 grams.

Introduce the cupel slowly into the muffle so that the filter paper will be burned and mercury and its salts volatilized. This last mentioned step must be executed cautiously and requires the close attention of the analyst. Otherwise, a too rapid volatilization of the mercurial residue will cause spitting and serious losses of value, or perhaps salting of an adjacent cupellation. When the cupel has been placed in the hottest part of the muffle, increase the temperature to nearly 1000 C. and create a reducing atmosphere by putting near the cupel bits of wood, cork, or like material. When the lead has "uncovered", as shown by its bright red appearance, cool the muffle to normal cupellation temperatures. Upon completing the cupellation, determine gold and silver as usual in assaying. The weight of the gold obtained is then divided by 0.95 as a correction for losses in cupellation.

Discussion of Procedure

Several texts are available which give detailed discussion of the theory and technique of fire assay methods (7)(8)(9). These may be consulted as references.

In routine mill procedure, the cyanide content of the leach solutions is periodically determined by a simple titration with silver nitrate. Knowing this concentration it is then but a simple matter to calculate the weight of

ferrous sulfate necessary to give the required excess.

If the silver content is known to be low, salting silver may be added as standard silver nitrate solution, or a weighed quantity of silver may be put on the cupel.

Insoluble ferric ferrocyanide which is formed from the solution collects in the mercurial residue. Upon heating it is converted to iron oxide. The high temperature is necessary for the cupel's absorption of the iron oxide or the formation of a slight scoria with lead oxide.

In case the amount of ferrous sulfate added was large a preliminary scorification may be necessary before cupellation to dispose of iron oxide in the slag. If so, arrange the residue and filter paper in the same manner as on the cupel.

The purpose of the seemingly large amount of lead used is to reduce losses of silver during the initial high heating by having a large proportion of lead to silver.

The use of the hood when adding hydrochloric acid to the solution is unnecessary. The cyanide has been converted to ferrocyanide and only a faint odor of hydrocyanic acid is noticed.

Application of the Method

As already indicated this method is applicable to the assay of a cyanide leach solution when accuracy is desired. The corrected recovery to 0.01 of a milligram in a

hundred assay tons means the estimation of the gold value to 0.35 cents per ton at the present price of gold (\$35.00 per ounce).

The recovery of silver is subject to errors due to cupellation procedure. If, however, silver is determined within but two milligrams in a hundred assay tons, the estimation of its value is made to within one cent per ton at the present variable market quotation of \$0.50 per ounce.

The efficiency with which an unworked body of ore may be treated by the cyanide process could be easily determined. As a laboratory test, a relatively large sample of ore could be leached with cyanide and the precious metal content of the solution determined. This means less errors in sampling, either of the ore, or the solution obtained if its volume is excessive.

As has already been indicated, the method is applicable either to a pregnant cyanide leach solution or more especially to the barren solution from which gold and silver have been removed to test completeness of extraction.

Summary

(1) It has been shown that a semi colloidal mercury-mercuric amino chloride precipitate is not applicable to quantitative collection of gold and silver from cyanide

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solutions even when ferrous sulfate is used as a means of removing the cyanide ion.

(2) Quantitative recovery is had from cyanide solutions by a semi colloidal mercury-mercurous chloride precipitate in an acid medium if the cyanide ion is first converted to ferrocyanide ion by treatment with ferrous sulfate.

(3) A determinative method for gold and silver in cyanide solutions has been presented. A recovery within 0.01 to .02 milligrams for gold and within 2 milligrams for silver is obtained from 100 A.T. of solution.

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