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A Study of the Effect of Oxygen on the Rate of Dissolution of Gold in Cyanide Solutions.

John A. Cook

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A STUDY OF THE EFFECT OF OXYGEN ON THE RATE OF DISSOLUTION
OF GOLD IN CYANIDE SOLUTIONS.

by

John A. Cook

A Thesis
Submitted to the Department of Metallurgy
in Partial Fulfillment of the
Requirements for the Degree of
Bachelor of Science in Metallurgical Engineering.

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THE EFFECT OF OXYGEN ON THE RATE OF DISSOLUTION OF GOLD IN CYANIDE SOLUTIONS

The accepted chemical reactions in the dissolution of gold by cyanide solutions require the presence of gold, cyanide, water, and oxygen. The importance of dissolved oxygen in cyanide solutions as a factor is recognized by all the competent metallurgists familiar with cyanidation. However, this fact is often overlooked. That the manufacturers of cyanidation equipment realize the necessity of oxygen, is shown by the appliances they have developed which are attached to the agitators in order to saturate the cyanide solutions with air.

The Merrill-Crowe process is the classic example of taking advantage of the function of oxygen. When gold is precipitated from a pregnant solution, free cyanogen must be present or a complex zinc compound will form which precipitates and coats the zinc, thus preventing the displacement of gold from solution. The free cyanide redissolves some of the gold which has to be reprecipitated, hence causing an excessive consumption of zinc. If the oxygen is removed, the gold is not redissolved and only a slight amount of zinc above the theoretical amount is necessary.

As there are not much data in the literature concerning the rate of dissolution of gold in cyanide solutions containing varying amounts of dissolved oxygen, a knowledge of this property should have a practical as well as an academic value.

HISTORY

The history of cyanidation of precious metal ores, although interesting, will be confined in this article mainly to the effect of oxygen on the process.

Cyanogen compounds were first discovered, accidentally, by Diesbach¹⁾, a German dye chemist, in 1704. A little over one hundred years later, in 1805, Hagen,²⁾ another German announced that gold was soluble in potassium cyanide. In 1843, Bagration,³⁾ a Russian nobleman, conducted a research, the results of which were summarized by Argall⁴⁾ as follows:

- (1) That cyanide of potassium dissolves metallic gold.
- (2) That if the gold is fine it will pass rapidly into solution.
- (3) That the electric current does not assist solution.
- (4) That heat does assist solution.
- (5) That the dissolved gold can be precipitated on metallic surfaces without the aid of electricity.
- (6) That air has a marked quickening effect on the solution of gold in cyanide.

In 1846, L. Elsner,⁵⁾ in a paper titled "Observations on the Behavior of Reguline Metals in an Aqueous Solution of Potassium Cyanide",

1) Macquer, Dictionnaire de Chimie, I, 265.

2) Hagen, Untersuchungen, I, 665.

3) Bagration, Bull de l'Acad. Imple de St. Pet. (1843), II, 136.

4) Argall, Mining & Sci. Press, 95, 655.

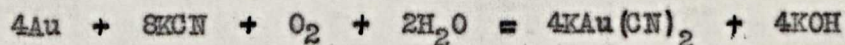
5) Elsner, Jnl. f. prak. Chem. (1846), 37, 441.

showed that the oxygen of the air played an important part in the solution of gold, silver, and some other metals. Although he did not put the reaction in equation form, to him is given the credit of the famous equation known as "Elsner's Equation."

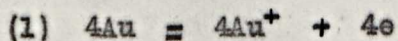
The researches of the MacArthur - Forrest⁶⁾ syndicate in 1886, were the first to put the extraction of gold and silver by cyanidation on a commercial basis. MacArthur stated that oxygen was not necessary for the dissolution of gold from their ores by cyanide solutions. However, the work of Elsner, 1846, MacLaurin,⁷⁾ 1893, Christy,⁸⁾ 1896, and Bodlaender,⁹⁾ 1896, have definitely proved that oxygen is necessary unless some other oxidizing agent is present.

THEORY

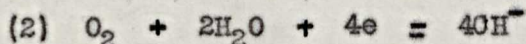
Elsner's equation for the dissolution of gold is:



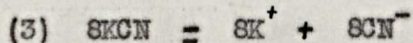
The reactions may be more clearly stated as follows:



The presence of oxygen is necessary to receive these electrons.



KCN ionizes in this manner:



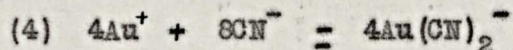
6) J. S. MacArthur, Jnl. Soc. Chem. Ind., 24, 311.

7) MacLaurin, Trans. Chem. Soc. London, (1893), 63, 724.

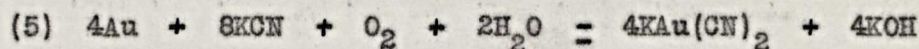
8) Christy, Trans. A.I.M.E. (1896), 26, 735.

9) Bodlaender, Ztsch. angew. Chem. (1896), 583.

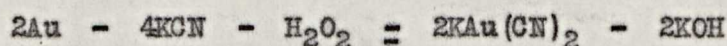
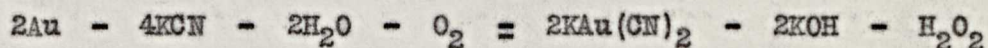
Then



Adding we obtain Elsner's equation.



Some authorities think that Bodlaender's equation expresses more correctly the reaction. The equation is as follows:

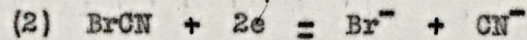
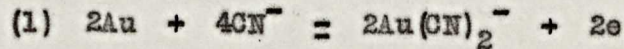


In fact, Bodlaender states that he found hydrogen peroxide present and was able to account for 70% of the theoretical amount. However, the overall results of the two equations are the same and the oxygen is the receiver of electrons in both cases. Whether the oxygen, after accepting the electrons, forms the OH radical or hydrogen peroxide is really of no importance in this article.

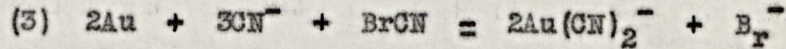
It is interesting to note that Barsky, Swainson, and Hedley¹⁰⁾ found the equilibrium constant of Elsner's equation, calculated from the free energies of formation, to be 10^{66} which shows that, in the presence of oxygen, the reactions will proceed practically to completion. They also calculated the equilibrium constant of Bodlaender's first equation to be 10^{16} and K for the second equation to be $10^{49.8}$. The sum of the latter equilibrium constants equals the first, therefore the reactions proposed by Bodlaender are possible.

In the presence of oxidizing agents, such as cyanogen bromide, oxygen is not necessary because the reaction can proceed as follows:

10) Barsky, Swainson, and Hedley, Trans. A.I.M.E. (1934), 112.



Adding the above two equations, we obtain:



While oxidizing agents will take the place of the oxygen of the air, it is not economical to use them since they are expensive, and also from the fact that they will liberate cyanogen even in the absence of gold, thus causing a waste of cyanide.

Christy explains the function of oxygen very aptly, "One cannot avoid noting a certain analogy between the action of oxygen of the air on the blood and on the cyanide solution. In the former the oxygen is held by the red corpuscles in a state of readiness for combination, but it is not actually used for combustion except under the nervous stimulus which determines combustion at the point where energy is to be produced. In the cyanide solution, the oxygen and the cyanide of potassium may exist side by side in solution (as experiment shows) without sensible action on each other, unless the presence of gold determines the Elsner reaction at the point where oxygen, water, gold, and cyanide of potassium meet."

METHOD

The work was conducted with pure gold and with oxidized gold ores. The solutions had a cyanide concentration approximately the same as that used in mill practice, and the oxygen content varied from hill to saturated.

To saturate water with air, a Winchester bottle fitted with a two-hole stopper was nearly filled with water. Through the stopper were

passed two glass tubes of different lengths. The short tube was connected to the suction pump which caused air to be drawn through the water. In order to break up the air so that it would not come to the surface in large bubbles, a bulb was blown on the end of the long glass tube and in the bulb small holes were pierced by means of a blow pipe. This dispersed the air by the formation of small bubbles, thus giving the water better aeration. The water was allowed to aerate for an hour and then allowed to stand for an hour at a constant temperature to insure the complete elimination of the finely disseminated undissolved air bubbles which would otherwise interfere.

The saturation of oxygen in solution was taken as that maximum quantity of oxygen which dissolves from free air which is very much less than the quantity of oxygen that dissolves in water from an atmosphere of pure oxygen. The amount of oxygen that dissolves depends on its concentration in the atmosphere from which it is derived. Dalton¹¹⁾ showed that the solubility of the individual gases in a mixture of gases is directly proportional to their partial pressures, the solubility of each gas being nearly independent of the presence of the others. The oxygen content of the air saturated water is a function of the temperature and pressure.

The solubility of gases in water is appreciably diminished in the presence of dissolved solids and liquids, especially electrolytes¹¹⁾. However, the experimental work of Barsky, Swainson, & Hedley showed that the solubility of oxygen in cyanide solutions was practically unaffected by concentrations up to 2%.

11) Getman and Daniels, Outlines of Theoretical Chemistry, 142.

The chart of Weinig and Bowen¹²⁾ showing the altitude-pressure and standard saturation curves of oxygen is very convenient. For any particular plant a solubility curve for that elevation may be plotted. The solubility curve for the elevation of Butte is plotted on page 8, figure I. The chart, however, was not used in this work; the barometer was read directly, the temperature of the water taken, and its oxygen content calculated. The solubility of oxygen in water was attained from the tables of Hodgman and Lange¹³⁾.

For example, the solubility of oxygen in 100 grams of water at 20° C. when the total pressure (i.e. the sum of the partial pressure of the gas plus the aqueous tension) is 760 mm. is 0.004339 grams. Take the percent of oxygen in the air at 20.9. The barometric pressure at Butte, 5755 ft. elevation, is 618 mm. of mercury. At 20° C. the aqueous tension of the water is 17.363 mm. of mercury.

An oxygen saturated solution of water contains

$$0.209 \times \frac{(618 - 17.363)}{(760 - 17.363)} \times 0.004339 \times 10,000 \\ = 7.335 \text{ mg. of oxygen per liter.}$$

Oxygen free water was obtained by connecting five Florence flasks in a train. To the glass tube at each end of the train a rubber tube and pinchcock were attached. The flasks were filled with water, placed on a hot plate, the exhaust end pinchcock opened, and allowed to boil which removes all the dissolved gases. After boiling an hour, the pinchcock was closed and the train removed immediately from the hot plate

12) Weinig and Bowen, Transactions A.I.M.E., (1925), 71, 1018.

13) Hodgman and Lange, Handbook of Chemistry and Physics, 570.

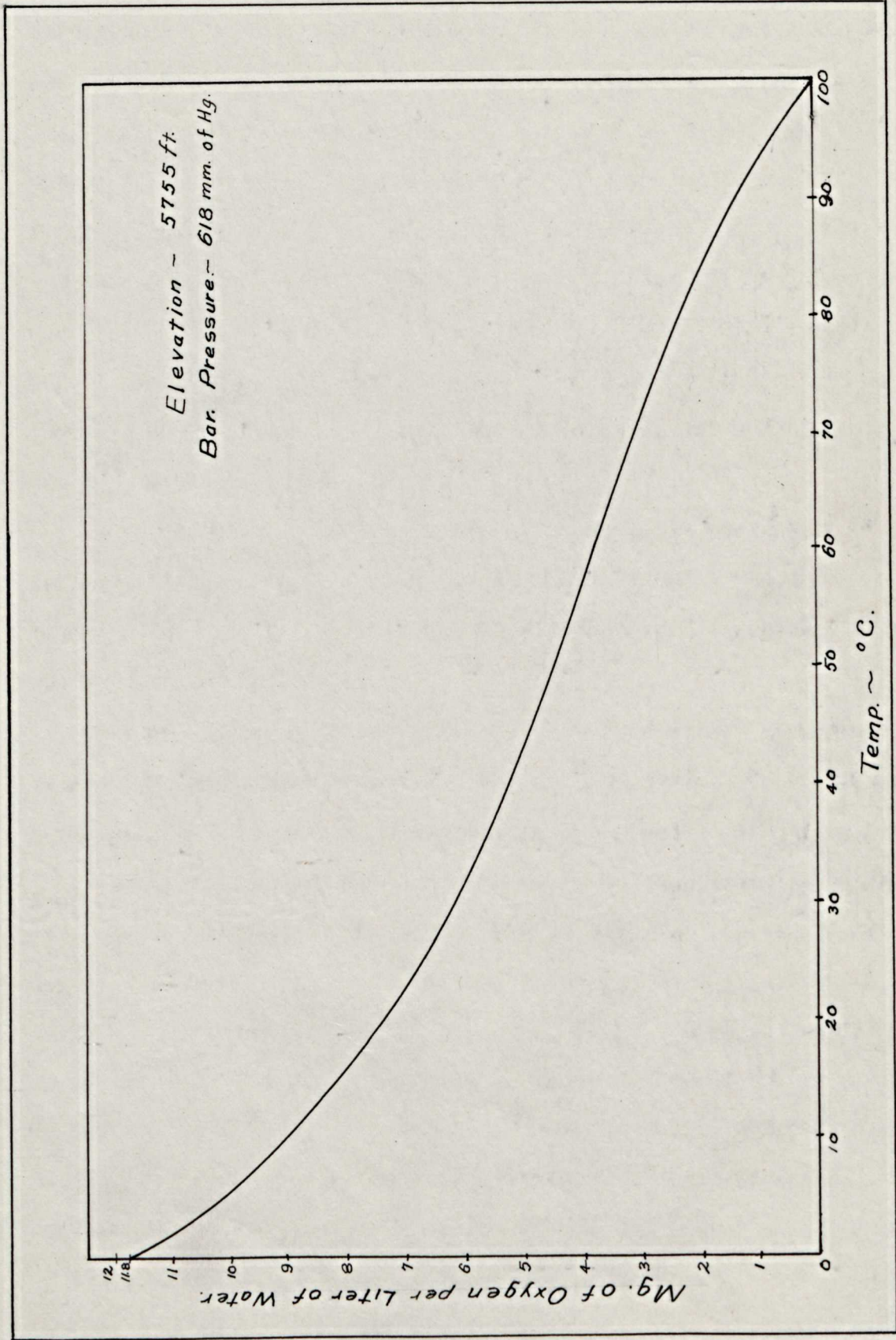


Fig. 1 - Oxygen Saturation Curve.

and connected to a hydrogen generator, or to a natural gas connection, and the pinchcock opened. (The composition of Montana natural gas is: CH_4 , 84.18%; C_2H_6 , 9.64%; CO_2 , 3.40%; N_2 , 2.78%). If the flasks are placed in a cold water bath, considerable time may be saved as the flasks cool very slowly in air. As the flasks cool, a vacuum forms and the water is drawn back from each preceding flask. When cold all the flasks with the exception of the one on the exhaust end is full of oxygen free water. Any contamination of the water by the gas is restricted to the second flask from the exhaust end. This flask of water was only used as a buffer.

The reagents were added to 500 cc. bottles, the proportion of saturated water added, and then the bottle filled with oxygen free water by opening the second pinchcock and allowing the pressure of the gas to force the water out.

The proportion of oxygen saturated water and oxygen free water to be added is calculated as follows: If the saturated contains 7.5 mg. of oxygen per liter and it is desired to obtain water containing 3 mg. of oxygen per liter and the bottles contain 500 cc., then the oxygen saturated water required is $\frac{3}{7.5} \times 500 = 200$ cc. The amount of oxygen free water required is 300 cc. Adding a drop of kerosene to the water before adding the oxygen free water helps to prevent absorption of oxygen while filling the bottle. Kerosene has no effect on the rate of dissolution of gold in cyanide solutions, although, added in small amounts it counteracts the harmful effects of graphite if present. The filling tube should be kept below the surface of the water.

The bottles were filled to within one-quarter of an inch from the top and the stopper inserted at a slight angle, thus removing all small

air bubbles. Melted paraffin was poured over the cork, filling all cracks and making an air tight seal. The bottles were then placed on rolls for a definite length of time. After agitation the solution was removed, filtered if necessary, and the gold content of the solution determined on an adequate portion.

DETERMINATIONS OF THE SOLUBILITY OF GOLD METAL.

The first test was made on pure gold in the form of "cornets" prepared according to the method explained by Rose¹⁴⁾. These cornets, 70 grams each, were then placed in the 500 cc. bottles and the correct proportions of saturated and oxygen free water along with one-half gram of potassium cyanide. The bottles were corked and sealed and allowed to stand for sixty hours.

Data:

Barometer 608 mm. of Hg.

Temp. of water . . 17° C.

Cyanide conc. . . 0.1% or 2 lb. per ton of solution.

pH of solution . . 10.4

Vapor pressure of water at 17°C. . . . 14.4 mm. of Hg.

Weight of oxygen dissolved in 100 g. of water as 0.004606 g. at 20°C. when the total pressure is 760 mm. of Hg.

Time of contact of gold with the cyanide solutions 48 hours.

Water saturated with air contains 7.66 mg. of O₂ per liter.

14) Rose, Metallurgy of Gold, 479.

Table I.

Oxygen Content of Water.	Wt. of Au Dissolved in mg.
0 mg.p.l.	trace
1 mg.p.l.	0.55
2 mg.p.l.	1.09
3 mg.p.l.	1.64
4 mg.p.l.	2.05
5 mg.p.l.	2.12
6 mg.p.l.	2.40
7 mg.p.l.	2.74
7.66 mg.p.l.	3.56

The above data are shown on a graph, Figure 2, page 13.

The experiment was repeated using the same method as the last one with the exception that gold discs 6 mm. in diameter and approximately 0.01 mm. in thickness, were used. The reason gold discs were used in place of cornets was that while the cornets weighed exactly the same, there was a chance that the exposed surface might vary somewhat, thereby causing a source of error.

Data:

Barometer 612 mm. of Hg.

Temp. of water . . . 20°C.

Cyanide conc. . . . 0.1% or 2 lb. per ton solution

pH of solution . . . 10.4

Vapor pressure of water at 20°C. . . . 17.36 mm. of Hg.

Weight of oxygen dissolved in 100 g. of water is 0.004339 g. at 20°C. when the total pressure is 760 mm. of Hg.

Time of contact of gold with the cyanide solutions 96 hours.

Water saturated with air contains 7.26 mg. of O₂ per liter.

Table II.

Oxygen Content of Water	Mg. of Au Dissolves in mg.
0 mg.p.l.	Trace
1 mg.p.l.	0.38
2 mg.p.l.	1.85
3 mg.p.l.	3.15
4 mg.p.l.	4.37
5 mg.p.l.	5.75
6 mg.p.l.	6.78
7 mg.p.l.	8.76

Data shown on graph, Figure 3, page 14.

DETERMINATIONS OF THE SOLUBILITY OF GOLD IN ORES.

After the above results were obtained some attempts were made to determine the effect of the oxygen content of cyanide solution on the extraction of gold from their ores.

The first ore on which tests were made was from the Argenta district, Montana. It was an oxidized ore containing chiefly silica, limonite, and a small amount of carbonates. The ore assayed 0.32 oz. in gold and 1.4 oz. in silver per ton. The acidity of the ore was equivalent to 2.5 lbs. of available lime per ton of ore.

Four assay tons of ore were weighed and put in the 500 cc. bottles along with one-half gram of potassium cyanide and one-half gram of lime which contained 71.8% available lime. The oxygen content of the water was obtained in the same way as before only instead of having 500 cc. of solution there were 457 cc. The density of the ore was found to be 2.7, therefore, four assay tons occupied a space of 43 cc. After sealing, the bottles were placed on rolls for 24 hours, removed, the pulp allowed to settle, and the supernatant liquid poured through a filter. The amount of gold dissolved when filtering in this manner in contact with the air was not considered, as it would be negligible.

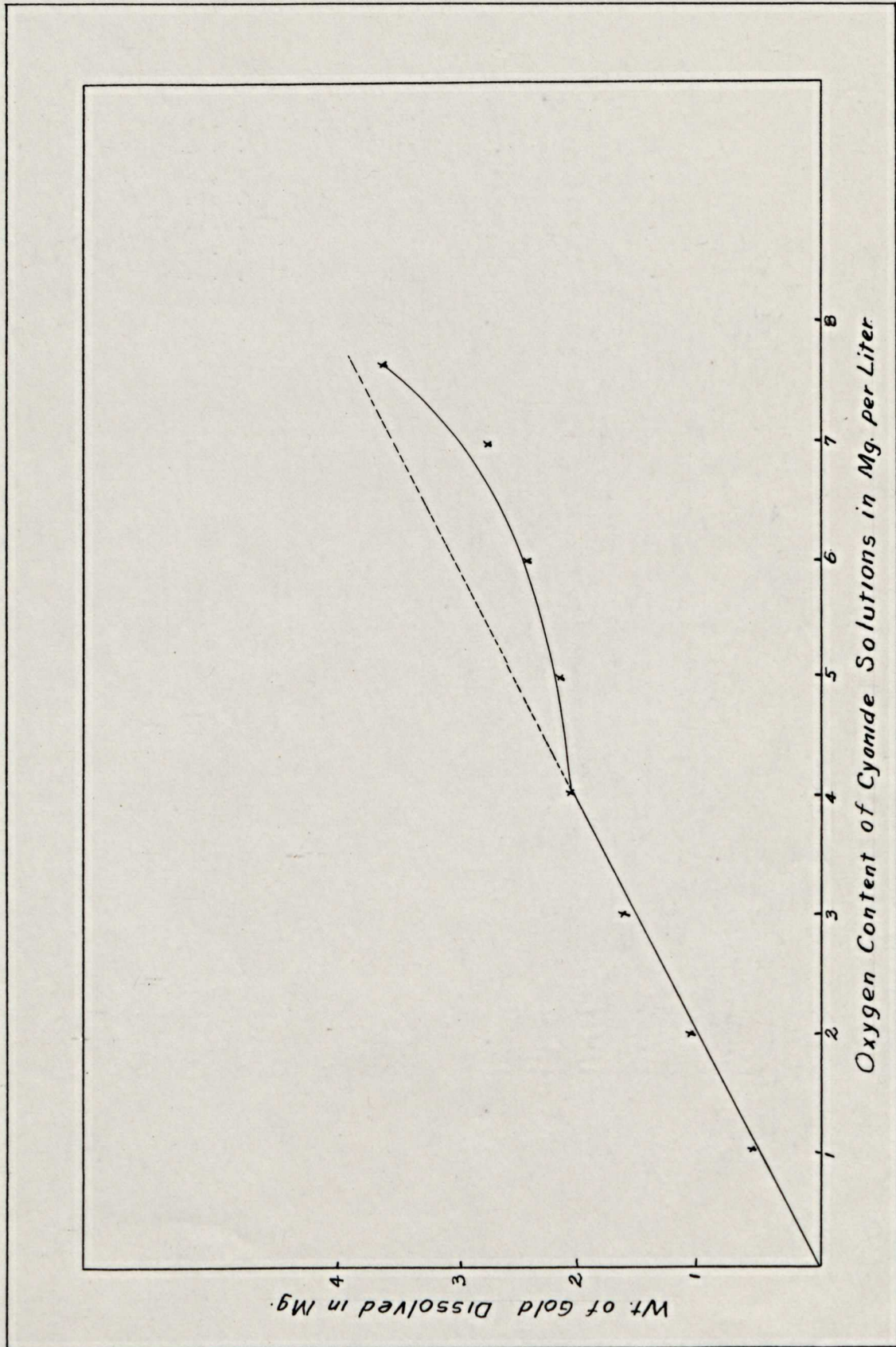


Fig. 2 - Solubility of Gold Metal.

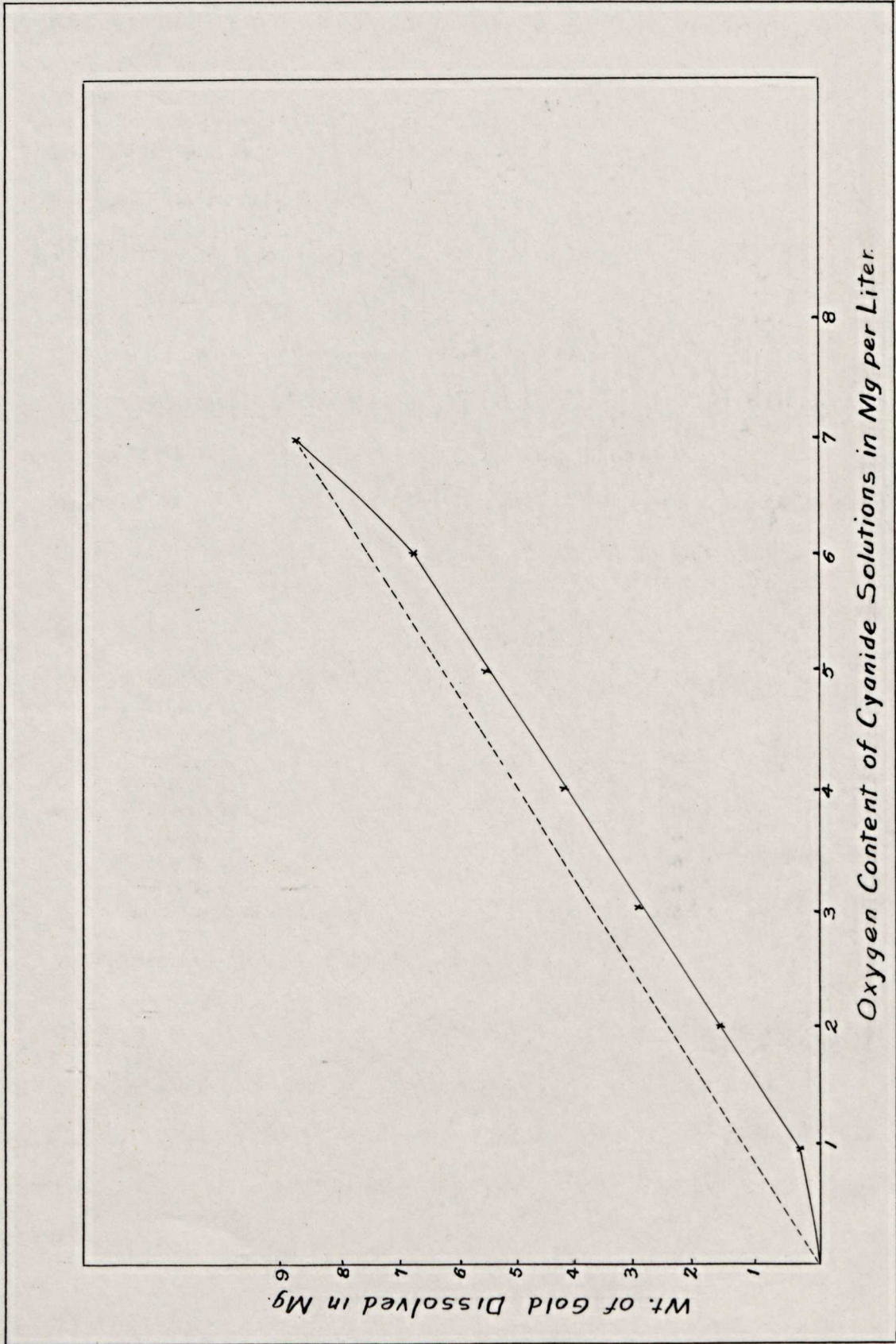


Fig. 3 - Solubility of Gold Metal.

The gold content of the solutions were determined in the usual manner.

Data:

Barometer 615 mm. of Hg.

Temp. of water . . 20°C.

Cyanide conc. . . 0.119% or 2.38 lbs. per ton of solution

pH of solution . . 11.4

Vapor pressure at 20°C. . . . 17.36 mm. of Hg.

Weight of oxygen dissolved in 100 g. of water is 0.004339 g. at 20°C. when the total pressure is 760 mm. of Hg.

Time of contact of ore with the cyanide solutions 24 hours.

Water saturated with air contains 7.3 mg. of O₂ per liter.

Table III.

Oxygen content of Water	Mg. of Au Dissolved
0 mg.p.l.	0.62
1 mg.p.l.	0.75
2 mg.p.l.	0.44
3 mg.p.l.	0.50
4 mg.p.l.	0.56
5 mg.p.l.	0.69
6 mg.p.l.	1.19
7 mg.p.l.	1.69
7.3 mg.p.l.	1.94

Data shown on graph, Figure 4, page 17.

The second ore on which tests were made came from Bannack, Montana. The ore was similar to the ore from Argenta, with the exception that it had a higher gold content. This ore assayed 0.74 oz. of gold and 2.1 oz. of silver per ton. The procedure was exactly the same as in the last determination.

Data:

Barometer 605 mm. of Hg.

Temp. of water . . 18°C.

Cyanide conc. . . 0.119 or 2.38 lbs. per ton of solution.

pH of solution . . 11.5

Vapor pressure of water at 18°C. . . . 15.3 mm. of Hg.

Weight of oxygen dissolved in 100 g. of water is 0.004515 g. at 18°C. when the total pressure is 760 mm. of Hg.

Time of contact of ore with the cyanide solutions 24 hours.

Water saturated with air contains 7.47 mg. of O₂ per liter.

Table IV.

Oxygen content of Water	Mg. of Au Dissolved
0 mg.p.l.	0.87
1 mg.p.l.	0.94
2 mg.p.l.	1.13
3 mg.p.l.	1.50
4 mg.p.l.	1.88
5 mg.p.l.	2.07
6 mg.p.l.	2.07
7 mg.p.l.	2.13
7.47 mg.p.l.	2.64

Data shown on graph, Figure 5, page 18.

CYANIDE CONSUMPTION

In the case of the ores, tests were made to determine the cyanide consumption to see if any appreciable difference between the oxygen free solutions and the oxygen saturated solutions existed. According to Elsner's equation one mg. of gold requires 0.0827 mg. or 8.27×10^{-5} g. of KCN. With the small quantities of gold dissolved no difference in cyanide consumption could be noted by titrating with standard silver nitrate solution and using KI as an indicator. The cyanide consumption of the Bannack ore was 0.30 lbs. per ton of solution, or 0.75 lbs. per

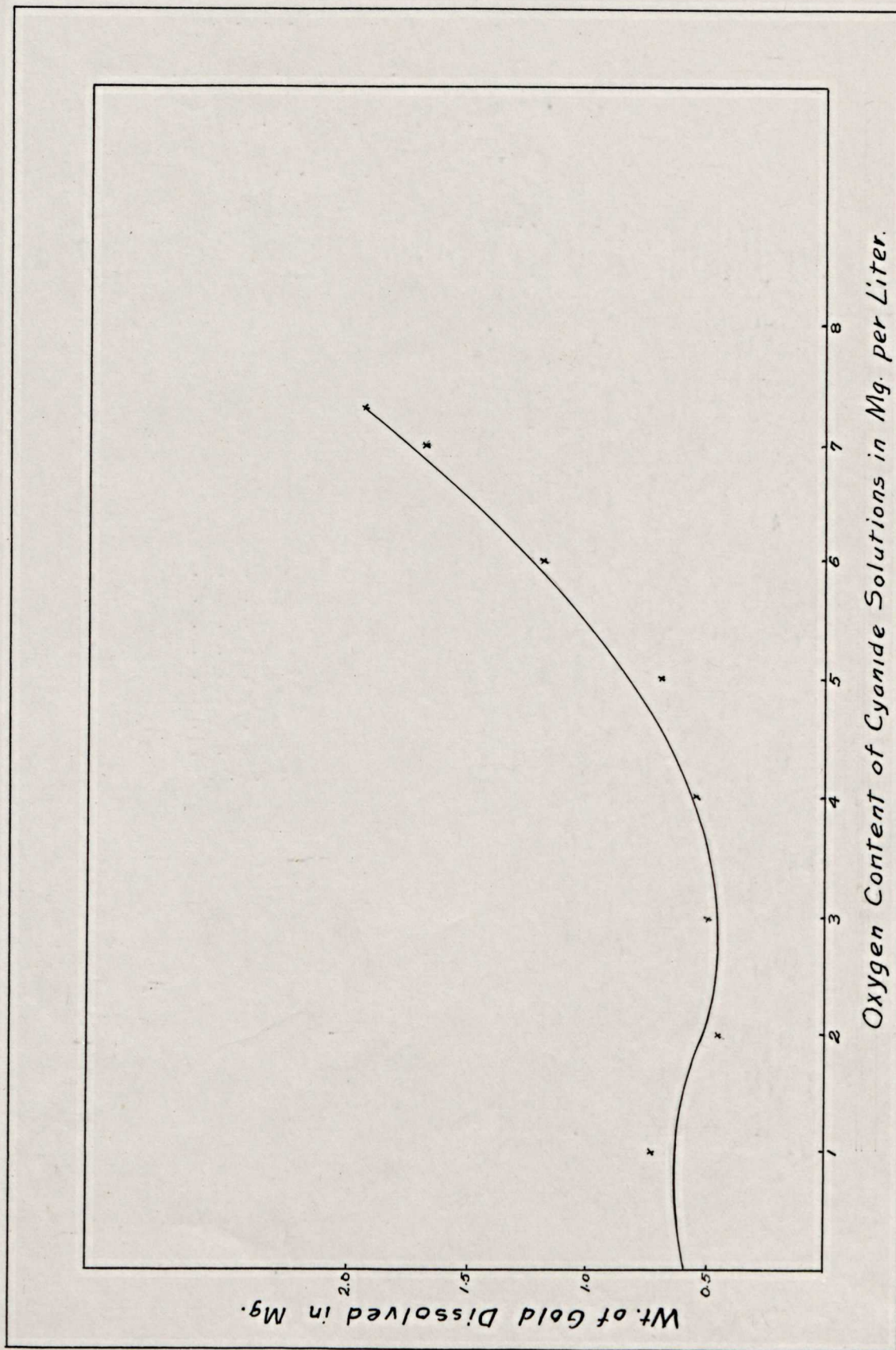
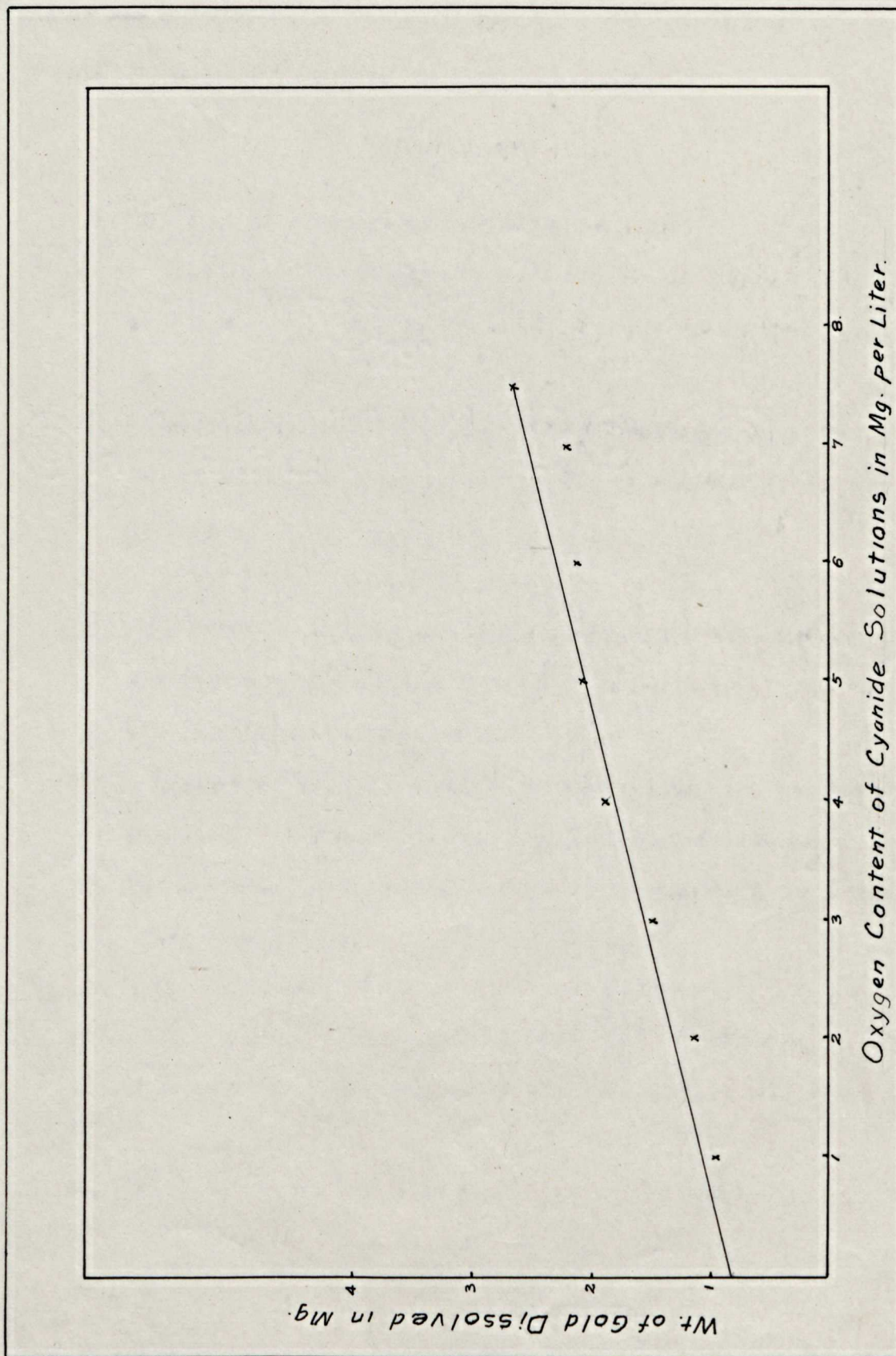


Fig. 4 ~ Solubility of Gold in Ore.



Oxygen Content of Cyanide Solutions in Mg. per Liter.

Fig. 5 - Solubility of Gold in Ore.

ton of ore and the Argenta ore consumed 0.25 lbs. per ton of solution or 0.625 lbs. per ton of ore.

OXYGEN CONSUMPTION

The chief methods of oxygen determination are:

- 1) Gasometric¹⁵⁾ determination, in which the oxygen is actually measured. This is the most accurate method but takes a long time to complete a determination.
- 2) Schutzenberger's¹⁶⁾ method which depends on the reducing action of sodium hyposulphate on a blue solution of indigo carmen.
- 3) Winkler's¹⁷⁾ iodometric method.
- 4) White's¹⁸⁾ method, a colorimetric method that depends on the degree of coloration imparted to a solution of pyrogallie acid in the presence of caustic soda.
- 5) Method of Weinig & Bowen¹²⁾ which depends upon the reducing action of a standard hydrosulphite solution upon a solution of indigo blue. This method is accurate to one-tenth of a mg. per liter of solution.

The above three methods are suitable for a laboratory while the latter two are readily adaptable to the requirements of a mill man.

An attempt was made to determine the oxygen content of the cyanide

15) Augustus H. Gill, Gas and Fuel Analysis for Engineers, 39.

16) Jnl. Soc. of Chem. Ind., London, (1889), 8, 729.

17) Jnl. Soc. of Chem. Ind., London, (1889), 8, 727.

18) Jnl. of Chem. & Met. & Min. Soc. of S.A., (1918).

solutions from the ores for their oxygen content by White's method. While the method is rapid, the results are not dependable on account of grading colors of different solutions, which nearly always contain various kinds of salts. In some cases it is almost impossible to make a determination due to the formation of a precipitate. White's method as modified by Hamilton¹⁹⁾ will give better results. Although variations of one mg. per liter can be distinguished, the method of Weinig & Bowen is to be preferred. The apparatus, while simple in design, is both rapid and accurate. After becoming accustomed to the operations to be made, a determination may easily be made in two minutes by this method.

A determination of the oxygen content of the solutions was made by Winkler's method. The amount of oxygen consumed by the small amounts of gold dissolved was so minute that the data were not considered dependable and were discarded. Oxygen determinations were not made on the pregnant solutions when using gold only. Calculating from the equation, 0.04 mg. of oxygen is all that is required to dissolve one mg. of gold.

CONCLUSIONS.

The cyanidation of precious metal ores is a complex chemical process, affected by many variables one of which is the oxygen content of the solution.

Referring to graphs 2 and 3, it will seem that the amount of gold dissolved in equal units of time varies directly with the oxygen content of the cyanide solution, and that gold will not dissolve in the

19) E. M. Hamilton, E. & M. J. 110, 116.

absence of oxygen or some oxidizing agent. In other words, the rate of dissolution of gold in cyanide solutions is directly proportional to the partial pressure of the oxygen.

Although the results, as obtained when using gold only, were not obtained in experiments with ores, the importance of oxygen in solution when extracting gold from their ores is clearly indicated. Since gold dissolved when no oxygen was present in solution, there probably was an oxidizing agent in the ore. Due to inadequate data no definite statement can be made on this point.

The solubility of gold increases slowly with an increase in temperature but solutions are rarely heated in cyanide plants. Since the solubility of oxygen in water decreases with an increase in temperature and the solubility of gold is directly proportional to the amount of dissolved oxygen in solution, it would appear that the increase in solubility due to a rise in temperature would be offset by smaller amounts of dissolved oxygen.

ACKNOWLEDGEMENTS.

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