


5-15-1934

Precipitation of Gold, Silver, and Copper from Cyanide Solutions on Activated Charcoal.

Rayworth Francis Howe

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Precipitation of Gold, Silver, and Copper from Cyanide
Solutions on Activated Charcoal.

by

Rayworth Francis Howe

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

MONTANA SCHOOL OF MINES

BUTTE, MONTANA

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Precipitation of Gold, Silver, and Copper from Cyanide Solutions on Activated Charcoal.

Introduction

Charcoal has been known for a considerable length of time to have the property of recovering gold, silver, and copper from cyanide solutions of these metals. Quantitative data that may shed light on the mechanism of the removal of these metals is very limited except that charcoal in a form known as activated has the power to abstract gold and silver in considerable quantities from the above solutions.

The aim of this research was to investigate the process of precipitation of gold, silver, and copper from cyanide solutions on activated charcoal. The problem has been divided into three aspects:

1. Determination of the conditions necessary for optimum extraction.
2. Study of the mechanism of precipitation.
3. Investigation of practical possibilities.

History

For a long time carbon has been advocated as a precipitant for gold from aurocyanide solutions. Late in the nineteenth century experimenters had obtained pre-

precipitates of gold and silver on charcoal from cyanide solutions of these metals, but due to erroneous ideas concerning the mechanism of this precipitation, no attempts were made to study the phenomena.

The first use of charcoal as a precipitant in metallurgy was made in connection with chlorination, chiefly in Australasia. As cyanidation gradually replaced the chlorination process, it was natural that charcoal should be tried as a precipitant for the precious metals from cyanide solutions, especially as the use of zinc for this purpose was still far from satisfactory. The first experiments in its use were made by W. Aitken at Reefton, New Zealand.¹⁾ The results obtained were not encouraging so the idea was temporarily abandoned, but in 1894, W. D. Johnston²⁾ of San Francisco applied for and was granted a patent on the developed process which was later used to some extent in Australia, although its use in the United States was confined almost entirely to a few isolated cases of precipitation from waste solutions. During the period from 1894 to 1913 little was learned regarding the precipitation on charcoal, and practically the only conclusions were that gold is precipitated more rapidly and in greater amounts than silver, and that free cyanide has a deleterious effect.

1) E. & M. J., Vol. 97, June 20, 1914, page 1233

2) Trans. Am. Inst. Min. Eng., 1896, Vol 26, p. 748

The methods used in the early investigations were inefficient, and the charcoal probably had a low adsorptive capacity. As precipitation with zinc improved and its theory became better understood, the use of charcoal and the interest in it gradually declined. This interest was again revived, however, about 1913 and as a result much experimental work was carried on and new theories were advanced.

The announcement in 1916 of the use of charcoal as a precipitant in place of zinc at the Yuanmi mine in Australia gave a new impetus to discussion and experiment. K. B. Moore and H. R. Edmands³⁾ developed and put into practice a method of precipitation on charcoal. They quenched the charcoal while red hot and pulverized it. The process then consisted in agitating the finely powdered material with the cyanide solution until the precipitating power of the charcoal had neared exhaustion. The charcoal was recovered by filtration, dried, burned, and the ash smelted.

The most recent practice in Australasia and South Africa involves wet grinding of the char and the formation of a cake of the ground material on the leaves of a leaf filter. The pregnant solution is drawn through several

³⁾ Engineering and Mining Journal, August 10, 1918, pages 256 - 7, "The Moore - Edmands Process of Precipitating Gold With Charcoal."

units in succession, the strongest solutions meeting the charcoal whose precipitating powers have been weakened through adsorption, and the weakest solutions meeting the fresh charcoal. After washing and drying, the cakes are burned to remove the carbon, and the ash is smelted.

Definition

Activated charcoal is a more or less pure amorphous carbon which has been defined in various ways, probably the simplest one being that given by H. H. Lowry⁴⁾ who says that active carbon is "that carbon which has a large adsorptive capacity per unit area of adsorbing surface." Considerable investigation has been made, but information is still very incomplete. The theory of its nature and formation, which satisfies known facts, is best expressed by Dr. N. K. Chaney.⁵⁾ According to his theory, active carbon exists as a distinctive physical modification which differs from the other known inactive forms of carbon by some characteristic peculiarity of molecular structure or arrangement. To this structure are attributed its special properties, namely its unique adsorptive power for gases, vapors, and certain substances in solution, its unusual chemical activity, and the limited tempera-

4) "On the Nature of 'Active' Carbon," by H. H. Lowry, Journal of Physical Chemistry, Vol. 34, Jan. 1930, p. 63.

5) Transactions of the American Electrochemical Society, Vol. 36, pages 91 - 111 (1918)

ture range of its formation.

There are numerous ways of preparing active carbon, but all of them increase the adsorptive capacity either by increasing the total surface per unit weight, or the degree of unsaturation of the surface atoms, or both. The general method is to subject the charcoal to an oxidizing atmosphere at elevated temperatures. It is important that a process be used which increases the hydrogen content of the charcoal, for the charcoal containing the most hydrogen has the largest sorptive capacity. The hydrogen content varies up to about 0.53 per cent⁶⁾ by weight.

Theory

The proper explanation of precipitation from cyanide solutions on charcoal is that the alkaline cyanide is adsorbed without chemical change. In other words, it is not the free metal which deposits on the charcoal, but the cyanide radical carrying the metal. The mechanism⁷⁾ of adsorption is as follows: When organic polar compounds are placed in solution they will concentrate either at the surface of the solution or at the surface of certain solids and the molecules tend to become definitely oriented with radicals such as COOH, CO, CN, OH, or COHN₂, pointing into

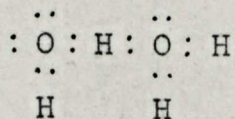
6) H. H. Lowry, Journal of Am. Chem. Soc., Vol. 49, p. 324 April 1924.

7) T. E. Bartell and E. J. Miller, Jour. Phys. Chem., Vol. 28, p. 992, (1924).

the water phase while the hydrocarbon groups are directly in contact with the solid carbon phase.

According to Langmuir,⁸⁾ attractive forces (residual forces) are present at the surface of all solids, and it is due to these forces that adsorption occurs. In water solutions both H^+ and OH^- ions are held on the surface of a solid, as for example carbon, in a more or less definite and regular arrangement. Adsorption occurs when the H^+ and OH^- ions are displaced by other ions. Lewis⁹⁾ indicates the structure of water as $H:\ddot{O}:H$. The water molecules are presumable adsorbed on the carbon and the apparent ion adsorption is dependent upon a change of intensity with which the different atoms are held together by electron pairs.

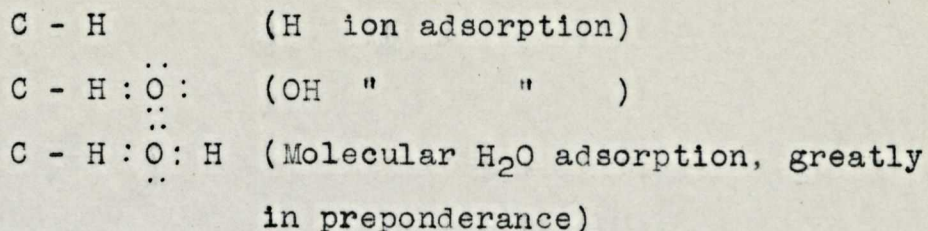
According to Lewis' theory, water molecules are held together as follows:



The orientation of the adsorbed water molecules as well as the H^+ and OH^- ions adsorbed is shown very simply in the following diagram:

⁸⁾ Outlines of Theoretical Chemistry, Getman and Daniels, page 241.

⁹⁾ "Valence and Structure of Atoms and Molecules" Chem. Cat. Co. (1923)



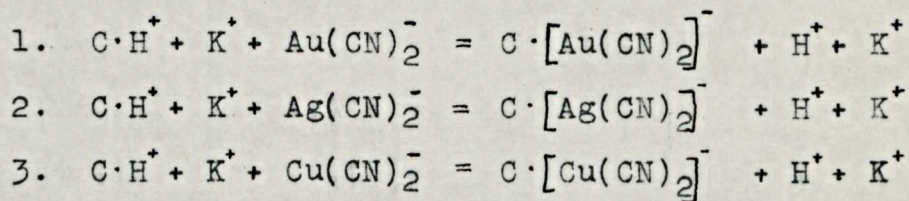
Recombination between adjacent hydrogen and hydroxyl ions is extremely rapid so that at any instant the number of hydrogen or hydroxyl ions actually remaining free will be a negligible fraction of the total number of water molecules. This, however, is not the case with active charcoal, which in the process of activation increases its hydrogen content due to its reaction with moisture or a hydrogen atmosphere. When the charcoal is placed in water there are a large number of hydrogen ions present on the surface of the charcoal, in excess of those recombining with hydroxyl ions to produce water, and these hydrogen ions are available for replacement by the metal bearing cyanide.

It is possible for other ions to displace both the hydrogen and hydroxyl ions thus held at the surface. It has been found that negative radicals with hydrocarbon groups displace OH more readily than do inorganic radicals, and ions of metals less noble than hydrogen do not displace it. Salts with hydrocarbon cations behave as noble metals in displacing hydrogen from carbon,¹⁰⁾ and

¹⁰⁾ Conclusions somewhat similar to this were reached by Tammann, Z. Anorg. Chem., Vol. 113, pp. 149-62 (1920).

the longer the hydrocarbon chain the greater the displacement, that is, the greater the adsorption.

From the above discussion it is evident that the gold, silver, and copper are adsorbed on the surface of the charcoal due to the attractive forces between the carbon of the charcoal and the carbon atoms of the metallic cyanide. The equations expressing the adsorption of these respective cyanide radicals are:



Scope of Investigation

Due to the fact that all noble metals below hydrogen in the activity series can be removed from cyanide solutions by means of active charcoal, it was decided that the precipitation of gold, silver, and copper should be investigated. In order to develop the most favorable conditions for the use of charcoal, the following factors were tried and the corresponding recoveries determined:

1. Time of contact between charcoal and solution.
2. Ratio of quantity of charcoal to that of solution.
3. Concentration of free cyanide.
4. Metal concentration of the solution.
5. Effect of impurities.

Preparation of Solutions

A stock solution of $\text{KAg}(\text{CN})_2$ was prepared as follows. Pure silver was dissolved in dilute nitric acid and the solution evaporated to drive off the free HNO_3 . The silver nitrate was then dissolved in water and just enough KCN solution added to precipitate the major portion of the silver as AgCN . This precipitate was washed thoroughly by decantation and filtered. Most of the white precipitate of AgCN was dissolved in KCN solution, some being allowed to remain undissolved to insure absence of free cyanide. This stock solution was used in preparing other solutions of any desired strength for subsequent tests.

In the preparation of a stock solution of $\text{KAu}(\text{CN})_2$ a weighed amount of very finely divided gold was agitated with a solution of KCN of such strength that there would still remain a small amount of undissolved gold. This was to insure the absence of free cyanide.

The third solution, $\text{KCu}(\text{CN})_2 \cdot x\text{KCN}$, was prepared by dissolving $\text{Cu}_2(\text{CN})_2$ in a solution of KCN.

The stock solution strengths were:

$\text{KAu}(\text{CN})_2$	-----	0.48 mg. Au per cubic centimeter
$\text{KAg}(\text{CN})_2$	-----	4.49 " Ag " " "
$\text{KCu}(\text{CN})_2 \cdot x\text{KCN}$	---	2.4 " Cu " " "

Analyses for gold and silver were carried on by evaporating known volumes of solution in lead boats which were

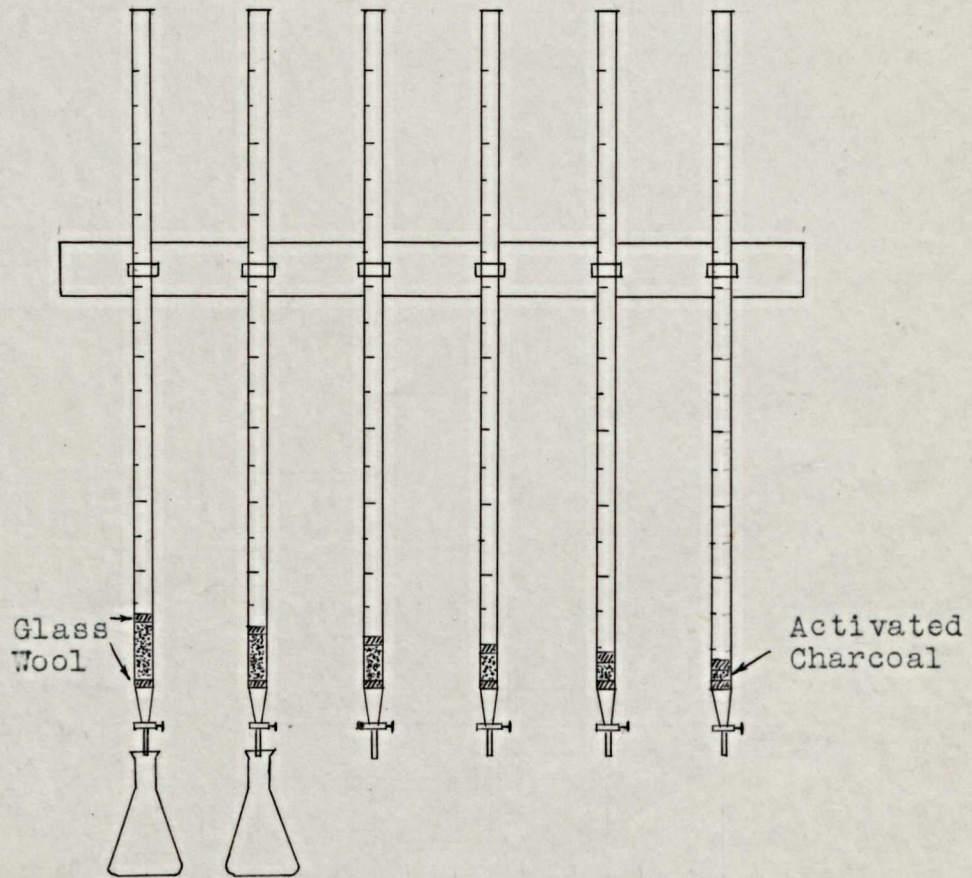
later cupelled. Copper was determined by means of the iodide method which is quite rapid and very sensitive. Of course there was very little metal left in the solutions after precipitation so that a great deal of care was necessary in analyzing them. This was especially true in the case of gold and silver because the buttons remaining after cupellation were, in many cases, extremely small, and, therefore, difficult to weigh with the proper degree of accuracy. The large number of tests which were required made it impossible to devote more than three or four hours to a single test, and as a result the amount of solution which could be run through was limited to from 50 to 75 cubic centimeters.

Experimental

Precipitation tests were carried on in burettes as shown in Figure 1, with the charcoal held in place by means of glass wool. The level of solution was kept as nearly constant as possible to insure a uniform flow, and the number of cubic centimeters per minute was regulated by means of stopcocks. It was found necessary to check the rate of flow every few minutes. When a precipitation was complete the solutions of known volume were placed in lead boats for evaporation and were later cupelled. In the case of $\text{Cu}(\text{CN})_2 \cdot x\text{KCN}$ the cyanide was decomposed partly with HCl and HNO_3 and finally by fuming with H_2SO_4 . The Copper was then determined by the iodide method.

Figure No. 1

Precipitation Apparatus



Results

The first test conducted was the determination of the proportion of metal adsorbed for different rates of flow, with a constant amount of charcoal. All samples were 50 cubic centimeters in volume, and four grams of charcoal were used. The concentration of metal in the solutions was:

Gold ----- 0.121 mg. per cubic centimeter

Silver --- 0.424 " " " "

Copper --- 0.49 " " " "

The results of the test are given in Table I.

Table I

Relation between rate of flow and metal recovery with four grams of charcoal.

Rate of flow cc./min.	Per cent of metal recovered		
	Gold	Silver	Copper
0.25	99.66	97.06	91.3
0.5	99.60	96.6	91.1
1.0	99.53	96.4	91.06
2.0	99.3	95.3	89.81
4.0	98.8	91.6	88.6
9.0	78.5	69.5	65.1
12.0	56.4	51.3	41.2

It is evident that the highest recoveries are obtained with the lowest rates of flow, and that at about four cubic

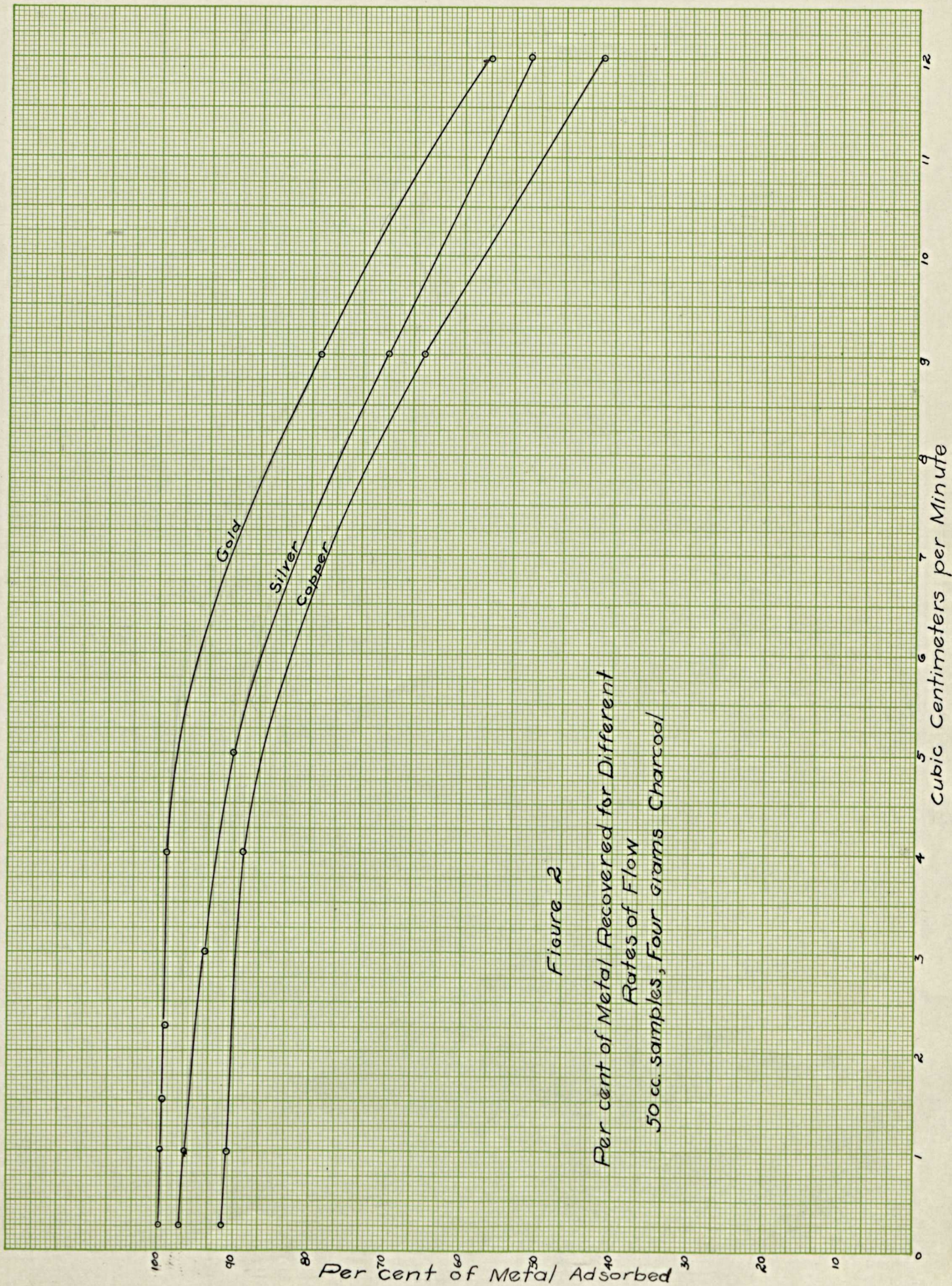


Figure 2

Per cent of Metal Recovered for Different Rates of Flow
50 cc. samples, Four grams Charcoal

centimeters per minute the recovery begins to decrease quite rapidly as shown in Figure 2. This decrease is fairly constant up to 12 cubic centimeters per minute, above which the flow is too rapid to gauge accurately.

It is significant that, in this test and the ones following, the gold recovery is the highest and that of the copper is the lowest.

The purpose of the second test was to determine the relation between the quantity of charcoal and metal recovery. In this test the weight of charcoal was varied from 0.25 grams to five grams for a 50 cubic centimeter sample. The rate of flow was 0.25 cubic centimeters per minute, and the metal concentration was the same as in the previous test.

Table II

Relation between quantity of charcoal and metal recovery with a constant flow of 0.25 cc. of solution per minute.

Weight of Charcoal	Per cent of metal recovered		
	Gold	Silver	Copper
0.25 g.	59.58	29.09	34.8
0.75 "	93.72	65.38	50.8
1.25 "	96.4	83.26	62.32
2.0 "	97.2	91.8	74.6
4.0 "	99.3	96.7	91.3
5.0 "	99.83	99.67	94.6

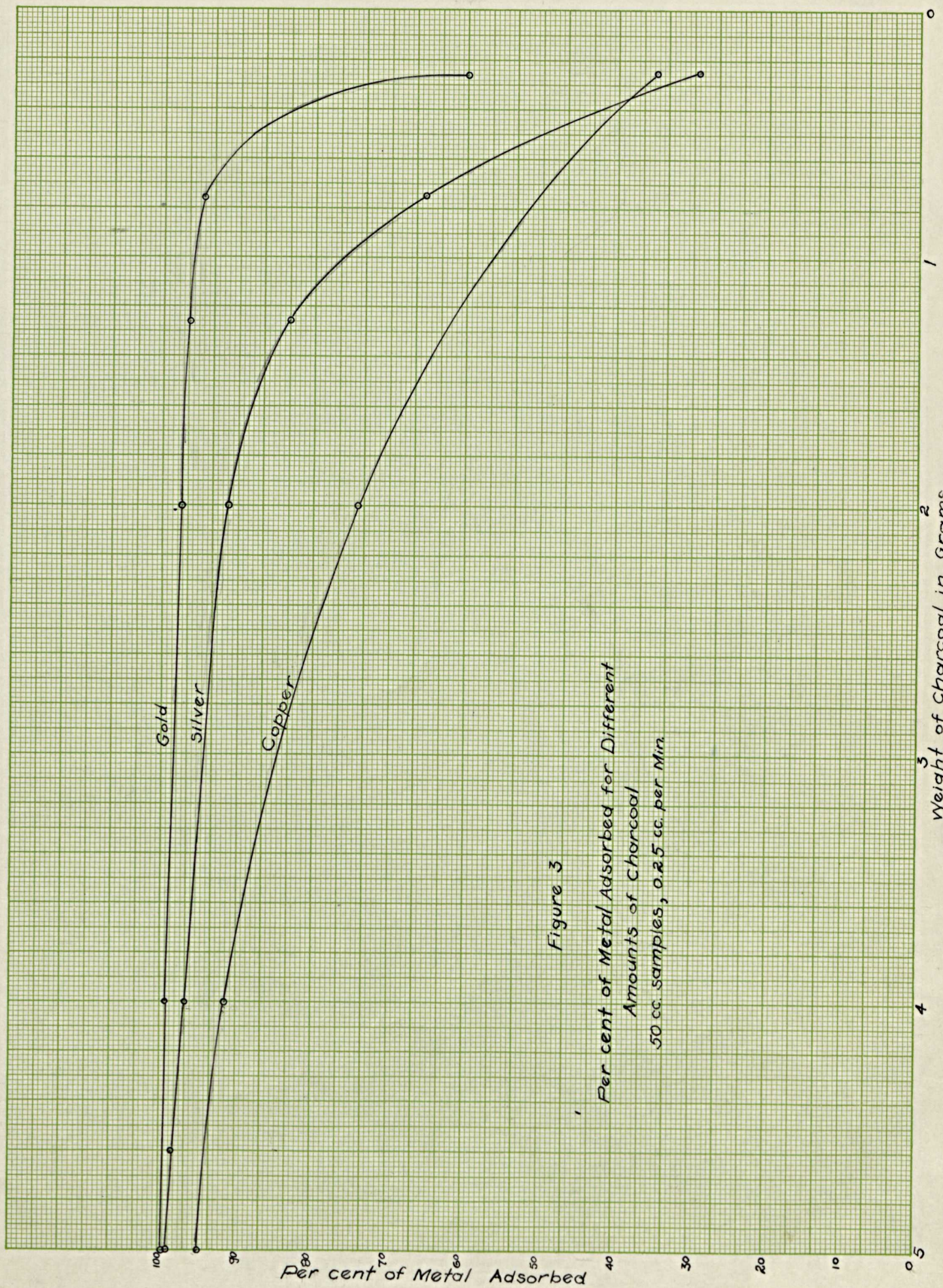


Figure 3
Per cent of Metal Adsorbed for Different
Amounts of Charcoal
50 cc. samples, 0.25 cc. per Min.

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MILLIMETERS, 10th lines heavy.

When small amounts of charcoal are used, gold is much more completely removed than either silver or copper. However, the recoveries with small amounts of charcoal are much lower than with large amounts because of the relatively small surface area upon which adsorption can take place. As the weight of charcoal was increased the amount of metal adsorbed, that is, the recovery increased very noticeably until with five grams the recoveries reached 99.83 per cent for gold, 99.67 per cent for silver and 94.4 per cent for copper as shown in Figure 3. Due to these high values, five grams of charcoal were used in all subsequent tests.

The relation of the loss of cyanide to different concentrations of free cyanide in solution is shown in Figure 4, which gives the results of a series of tests with five grams of charcoal and 50 cubic centimeters of solution, run through at the rate of 0.25 cubic centimeters per minute. Samples were prepared by adding to portions of the stock solutions sufficient KCN to produce the required solution strengths which varied from zero pounds per ton of free cyanide to eight pounds per ton. Results of this test are listed in Table III.

Table III

Relation between concentration of free cyanide and amount of cyanide adsorbed, using five grams of charcoal for 50 cc. of solution and a flow of 0.25 cc. per minute.

Conc. of CN in pounds/ton	CN adsorbed in pounds/ton	Per cent of CN adsorbed
0.7	0.4	57.2
1.3	0.8	61.5
2.2	1.25	56.8
3.2	1.8	56.2
6.4	2.6	40.6
8.0	2.8	35.0

A brief study of Figure 4 reveals that the amount of cyanide adsorbed by the active charcoal increases very rapidly with an increase of free cyanide.

When the solutions from the above test were analyzed for metal content it was found that the recovery was not affected by any amount of free cyanide. However, the total quantity of metal which the charcoal would normally adsorb, has been reduced by the presence of the cyanide radicals, which are attracted to the surface of the charcoal in the same manner as the ions of the metallic cyanide.

The fourth test was conducted with the object of determining the relationship between the concentration of

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Millimeters, 10th lines heavy.

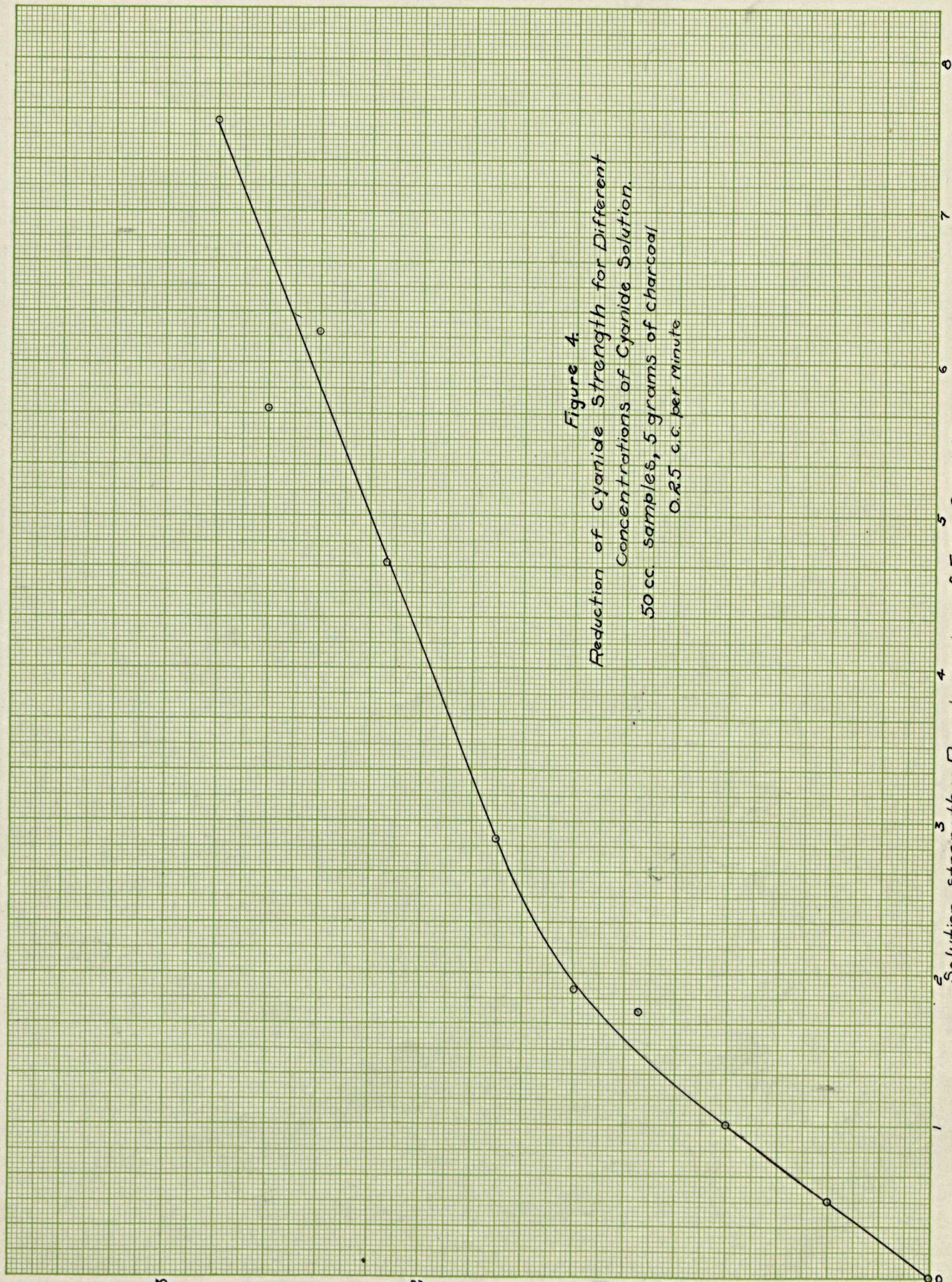


Figure 4.
Reduction of Cyanide Strength for Different
Concentrations of Cyanide Solution.
50 cc. samples, 5 grams of charcoal
0.25 c.c. per Minute

Reduction in Cyanide Strength - Pounds per Ton

Solution strength in Pounds per ton of Free Cyanide

metal in the solution and the metal recovery. The results of this test are given in Table IV.

Table IV

Relation between metal concentration and recovery, using five grams of charcoal for 100 cc. of solution, flowing at 0.25 cc. per min.

Metal conc. Mg./cc.	Per cent of metal recovered		
	Gold	Silver	Copper
0.02	99.99	99.33	94.9
0.2	99.80	99.30	94.8
0.4	99.72	99.1	94.6
0.6	99.4	98.9	94.4
1.0		98.45	92.85
1.2		98.1	91.75

In order to obtain comparable results, solutions of silver and copper cyanides were prepared which varied in strength from 0.06 mg. per cubic centimeter to 1.2 mg. per cubic centimeter. The highest concentration of gold was 0.6 mg. per cubic centimeter. The other conditions employed were 100 cubic centimeter samples, five grams of charcoal, and a rate of flow of 0.25 cubic centimeters per minute. The results are shown in Figure 5.

The most significant fact to be noted from the table

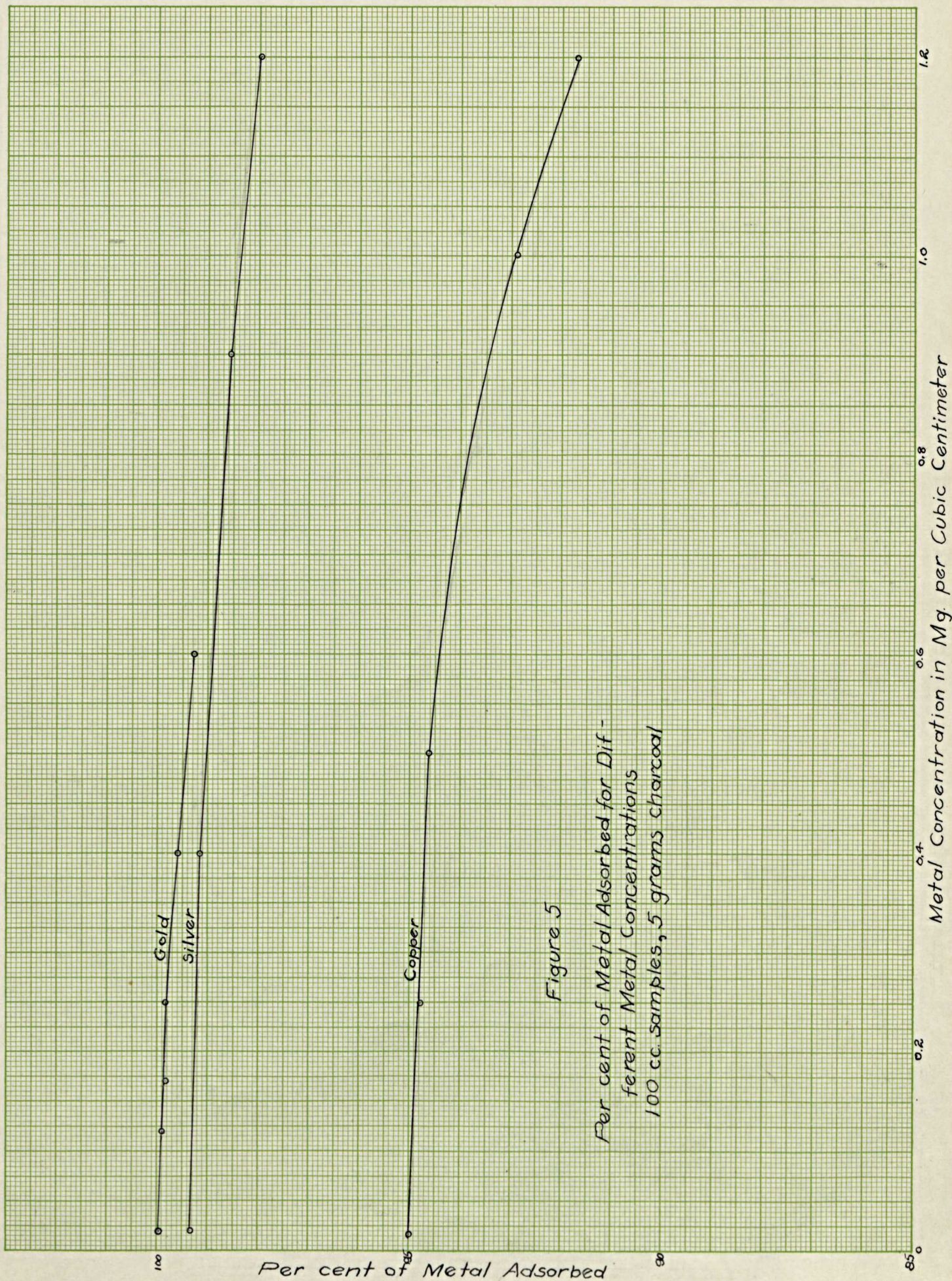


Figure 5
Per cent of Metal Adsorbed for Dif-
ferent Metal Concentrations
100 cc. samples, 5 grams charcoal

is that the highest recovery is obtained with the solutions of lowest metal concentration, and that, as the amount of metal in solution is increased, the recovery decreases noticeably.

By means of this series of tests the conditions were developed for obtaining optimum extraction with synthetic solutions containing a single metal and no impurities. It was now possible to try the same conditions on a mill solution which contained gold, silver, free cyanide, protective alkalinity, and impurities. Analysis of the solution showed a value of 0.0031 mg. of gold per cubic centimeter, 0.0093 mg. of silver per cubic centimeter, three pounds of free cyanide per ton, and one pound per ton of protective alkalinity. Conditions used in the test were: 100 cubic centimeter samples, five grams of charcoal, and a rate of flow of 0.25 cubic centimeters per minute. Two tests were run in parallel in order to obtain a check on the results.

Precipitation of gold from mill solutions was found to be very complete, the extraction being 99.37 per cent. This is only slightly lower than the recovery obtained under similar conditions using a synthetic solution of $\text{KAu}(\text{CN})_2$.

The removal of silver, although not quite as complete as for gold, was nevertheless very high. In this

case the extraction was 98.64 per cent as compared to 99.67 per cent for the synthetic solution of $KAg(CN)_2$. It is evident, then, that active charcoal is almost as powerful in abstracting these metals from complex mill solutions as from pure synthetic ones.

Conclusions

Factors which have an important bearing upon the precipitation of gold, silver, and copper from cyanide solutions upon activated charcoal are:

1. Time of contact between charcoal and solution.
2. Quantity of charcoal in relation to that of solution.
3. Concentration of free cyanide.
4. Metal concentration in the solution.

The time of contact between charcoal and solution is one of the most important factors to be considered in the removal of metal from solution. The maximum recovery is obtained with the longest time of contact, and conversely, the lowest recovery with the shortest time.

When the capacity of charcoal for metal is approached the recovery falls off very rapidly, but when there is a large excess of charcoal, recoveries are high. Data indicate that charcoal has different capacities for gold, silver, and copper, that of gold being the highest, silver next, and copper last.

Cyanide losses through adsorption on charcoal are much

higher for high concentrations of free cyanide than for low ones. This presence of free cyanide has no effect upon the recovery of metal except that it lowers the total amount which the charcoal would normally adsorb.

The metal concentration of the solution is a very important factor. Although less metal is adsorbed per unit volume of solution of low metal concentration, the extraction is much higher.

Little can be said definitely in the light of increased knowledge brought out by this investigation concerning the cyanidation of gold or silver ores. There may be many possibilities, but further research will be necessary in order to bring these to light.

I wish to acknowledge the help and guidance of Dr. C. L. Wilson, Professor of Metallurgy, and Mr. J. U. MacEwan, Instructor in Metallurgy at the Montana School of Mines, under whose direction this work was performed.