

The Solution and Precipitation of the Cyanide of Gold.

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THE fact that many millions of gold have been extracted by the cyanide process, during the last five or six years, from South African tailings which could not be profitably worked by any other method previously tried upon them, lends a peculiar practical interest to this branch of metallurgy.

Numerous writers have recently made valuable contributions on the process without exhausting the many complexities of the subject. Among the first American writers on the subject in its modern aspect were two former students of the University of California, Mr. Louis Janin, Jr., and Mr. Charles Butters. Young Janin was one of the first to enter this field, and performed much useful experimental work in the early stages of the history of the process.

At about the same time, Mr. Charles Butters, who had left California to erect chlorination works for the Robinson mine at Johannesburg, became interested in the cyanide process, and, after getting the chlorination plant in working order, put up, for working the tailings from the Robinson mine, a cyanide plant which achieved the first large-scale success ever made with this process.

The papers which Charles Butters, together with John E. Clennell and Edgar Smart, have contributed on the chemistry of the process, were among the first to give any adequate idea of its nature.*

Another important contribution to the literature of the subject is the paper of Dr. A. Scheidell, published in 1894 as a "Bulletin of the California State Mining Bureau." This contains an admirable summary of the state of the art at the time of its publication.

* *Eng. and Min. Journal*, Oct. 8, 22, 29, 1892; Nov. 2, 1895.

Many notable contributions have been made by others, some of which will be referred to in what follows, as called for by the context.

The rapid extension of this process in South Africa is evidenced by the value of the cyanide-product for the Witwatersrand district. In 1890 it was less than \$6000; in 1891 it had grown to over \$60,000; in 1892 to over \$3,000,000; in 1893 to over \$6,000,000; and it is still increasing.

Although, several years before 1891, I had obtained some very promising extractions from gold-ores by the use of cyanide of potassium solutions, I was prevented until that year, by the constant pressure of other duties, from any systematic study of the subject. In the experimental work then commenced I was aided by several of my students, more especially by Mr. Thomas E. Eichbaum, who at the time of his death, a couple of years later, was chemist for Mr. Almarin Paul at his cyanide-works in Shasta county, Cal.; Mr. C. W. Merrill, who has since erected cyanide-plants at Bodie, Cal., and at Harquahala in Arizona; Mr. Leslie Simpson, now in South Africa; Mr. H. C. Baldwin, now in Mexico; and Mr. F. Booth, now in Alaska.

The results of these studies, made on a large variety of ores, was to show in all cases a partial extraction of gold. This extraction varied from 20 per cent. to 95 per cent. While it was always easy to make a partial extraction of the gold, it proved difficult, and in many cases impossible, to get anything like a complete extraction. Another difficulty encountered in these experiments was that very dissimilar results were often obtained with ores of almost exactly the same composition.

A careful study of all this preliminary work soon convinced me that two equally important classes of causes were active in bringing about these variations in the result: the one of a chemical, the other of a mechanical, nature. It was equally clear that it was expedient to make a separate study of these two sets of causes; and as it was of course impossible to separate them in the treatment of samples of ores, a systematic investigation was laid out, involving the use of simple artificial products of known composition, so as to determine the various complicated elements of the problem.

In the long, involved and difficult investigation which followed, and which has occupied all my leisure time since 1892,

I have been greatly aided by my assistant, Mr. E. A. Hersam, for whose intelligent skill and faithful devotion to the work I wish to express my warm appreciation.

The great complexity of the chemistry of the cyanides, the lack of accurate information in the chemical text-books, and the consequent erroneous statements in many of the publications on the cyanide process, have greatly added to the difficulties of the study. It became necessary to test *de novo* almost every step of the ground, so that an investigation which I had hoped to finish in a couple of years has already taken twice that time, and is now only fairly begun. Nevertheless, some of the results already obtained are so important that I have decided to condense in this paper an outline of many closely-written pages of experimental notes on this subject. I hope to find time hereafter for a complete outline of the details.

In this discussion I propose to confine myself to two main points: How does gold dissolve in cyanide solutions? and How is it precipitated from them?

I.—THE SOLUTION OF GOLD IN CYANIDE SOLUTIONS.

1. *The Solution of Metallic Gold in Potassium Cyanide.*

The solubility of gold in cyanide of potassium solutions has been known for over 50 years. Soon after its discovery by Elkington, Faraday and Bagration it was investigated by Elsner,* who stated that he had found that while zinc would dissolve in a potassium cyanide solution with the evolution of hydrogen, gold and silver dissolved in such a solution only in the presence of oxygen. Although not enunciated by him in this form, the following reaction expressing these facts is usually known as the Elsner reaction:



The necessity for the presence of oxygen when gold dissolves in cyanide solution has been denied by Mr. J. S. MacArthur, who claims the honor of the invention of the cyanide process. In his article on "The MacArthur-Forrest Process of Gold Extraction," read before the Society of Chemical Industry, March

* *J. f. Prakt. Chemie*, xxxvii., p. 441, year 1846.

31, 1890, and reprinted and circulated by the "Gold and Silver Extraction Company of America," Mr. MacArthur says:

"Not having seen the original account of Elsner's researches, I am not in a position to criticize his experiments, but I never could find that the presence of oxygen was necessary either to dissolve gold by itself or from ores by cyanide."

He cites no proof of his opinion regarding the action on metallic gold, but confines himself to speculation, as follows:

"If a piece of gold be immersed in a cyanide solution, so that air, to act on it, would have to penetrate two or three inches of the solution, the gold will dissolve in its usual slow and steady fashion. The equation shows that either oxygen must be absorbed or hydrogen evolved. I have seen no evidence of the former, and can adduce no proof of the latter; but I think the latter more probable, because I cannot conceive oxygen penetrating even a film of cyanide solution without oxidizing the cyanide to cyanate, whereas, in the other case, as suggested to me by my friend, Mr. Ellis, the nascent hydrogen may be at once seized by the excess of cyanide present and ammoniacal compounds formed."

Unfortunately for this ingenious speculation, it does not seem to be borne out by the facts. Maclaurin* has shown by a very able research:

(1) That oxygen is necessary for the solution of gold in potassium cyanide solutions, and that it combines, quantitatively, according to Elsner's reaction.

(2) That the rate of the solubility of gold in potassium cyanide solutions passes through a maximum in passing from concentrated to dilute solutions.

(3) That this remarkable variation is explained by the fact, which he also proves, that the solubility of oxygen in cyanide solutions decreases with the concentration of the latter.

But, to continue with our quotation from Mr. MacArthur, he says:

"However, we do not concern ourselves much with the reactions of pure gold, but as a matter of fact we cannot find that oxygen plays any part in the cyanide-extraction of gold from ores. We have treated an ore with cyanide with free access of air, and then a parallel experiment was done with boiled water, the bottle filled to the stopper with solution and ore, and the stopper sealed. The extraction was the same in both cases."

It will be seen that nothing is said as to the composition of the ore, so that the experiment is not decisive.

* *Jour. Chem. Soc.*, xliii., 724, May, 1893.

While Maclaurin's experiments seemed conclusive, still the difference of opinion between Elsner and Maclaurin on the one hand, and the reputed discoverer of the cyanide process on the other, was so fundamental that it seemed worthy of further investigation. The importance of this fundamental reaction is not merely scientific, it is of the greatest practical importance in the application of the process.

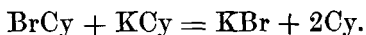
Hence, this was one of the first points to which I turned my attention. The result of my investigation was an entire confirmation of the accuracy of the Elsner reaction. That is, repeated experiments indicated that a solution of pure cyanide of potassium in pure water, from which all other substances are excluded, is entirely without action on metallic gold. Under favorable circumstances, such a solution absorbs oxygen from the air (without, as MacArthur assumed, immediately oxidizing the cyanide to cyanate), and the affinity of the potassium for oxygen and water, combined with the affinity of the cyanogen for gold and cyanide of potassium, leads to the formation of caustic potash and potassium aurocyanide, as per Elsner's reaction. When the air present is limited, the reaction stops when the oxygen of the air is exhausted, and begins again when it is supplied.

2. *The Effect of Oxidizing Agents.*

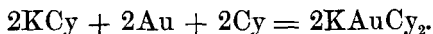
This point being clearly proved, the question next arose: Would not other oxidizing agents, capable of liberating nascent cyanogen in a cyanide solution in the presence of gold, also cause its solution? Several hundred experiments showed that this assumption was likewise correct. Nearly all the oxidizing agents were found to be effective. Among those used were: Potassium chlorate, nitrate, permanganate, bichromate, and ferricyanide, and the peroxides of barium, manganese, lead, and sodium. Each of these, and other oxidizing agents, when added to a potassium cyanide solution, increased the solubility of the gold over that shown in a similar solution without such addition. Among the most convenient and efficient of these agents were peroxide of sodium, peroxide of manganese, and ferricyanide of potassium. These experiments were made in 1892-3. It now became apparent that there were many analogies between the cyanide process and the chlorination process. In

the chlorination process the gold requires only free chlorine and water for its solution, as the chloride of gold is soluble in water, but in the cyanide process there are required, first, free cyanogen to form the cyanide of gold, and then free cyanide of potassium to form the soluble double cyanide.

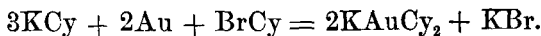
As these facts became clear, other means of producing nascent cyanogen in the presence of metallic gold and a solution of potassium cyanide suggested themselves. Cyanogen bromide was the first of these agents that proved effective, in experiments made January 19, 1894. When cyanogen bromide is added to a solution of potassium cyanide the following reaction ensues :



In the presence of metallic gold and an excess of potassium cyanide, the further reaction ensues :



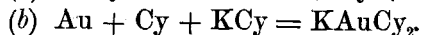
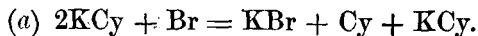
Or, as the two reactions are in reality simultaneous, this may be expressed, as has already been done by Mr. Sulman* as follows :



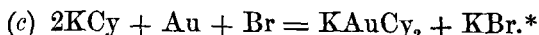
The success of the above experiment was so great that ten days later, January 29, 1894, a simpler process was tried. This was, to add a small amount of dilute bromine water to a dilute stock-solution of potassium cyanide, the latter in chemical excess, in the presence of metallic gold.

* Messrs. Sulman and Teed claim (in the *Eng. and Mining Journal*, February 23, March 30 and April 10, 1895) to have made the first discovery of this reagent, and they received an English patent September 14, 1895. Whether their work antedates mine or not, I do not know. A. W. Warwick, in a valuable paper in the *Eng. and Min. Journal*, June 29, 1895, claims to have made the same discovery independently, but does not give the date, and seems to misunderstand the real nature of the reaction that takes place, assuming that oxygen must be present when cyanogen bromide acts in a solution of potassium cyanide in the presence of gold. The *Mining and Scientific Press* of March 2, 1895, says that some months previous to that date a letter had been received from an assayer in northeastern Washington claiming that bromine could be substituted in the cyanide process. E. A. Schneider, *Eng. and Min. Journal*, March 23, 1895, makes a similar claim. It would, therefore, appear doubtful whether Messrs. Sulman and Teed are the original discoverers of the bromo-cyanogen process.

The reactions that take place may be analyzed as follows :

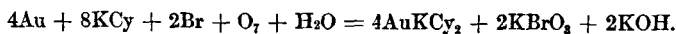


Or, as the reactions under favorable circumstances may be simultaneous :



Of the two reagents, bromo-cyanogen and dilute bromine-water, I distinctly prefer to add the latter to the potassium cyanide solution, in spite of the opinion of Mr. Teed† to the contrary. The use of the dilute bromine-water is much the simpler method, as the reagent is easily made of any desired strength and may be added as needed, care being taken always to have the potassium cyanide in excess, and not to add the bromine-water faster than the cyanogen set free can be absorbed by the gold. To do this correctly requires experience and skill; and unless the work is in the hands of a competent metallurgist, a great loss of cyanide and poor results will follow, whether bromo-cyanogen or bromine-water alone is added to the stock-solution of potassium cyanide. The reason of this appears to be the great tendency of free cyanogen to form paracyanogen, to oxidize into certain obscure compounds of a dark color, and to "run down" generally. Hence, if the cyanogen is set free faster than the gold can absorb it (owing to lack of contact at the time that the cyanogen is set free), a loss of cyanogen takes place to no useful purpose. Strong solutions of bromine and cyanide of potassium should be avoided for like reasons.

* In the *Eng. and Min. Journal*, June 1, 1895, in an article on "A Bromo-Cyanide Process for Gold Extraction," Mr. C. A. Mulholland offers the following provisional explanation of the reaction which takes place when bromine is added to cyanide-solutions in the presence of gold :



This very involved reaction appears to have been imagined because it was supposed that gold could not dissolve unless oxygen was present, the author having lost sight of the fact that the bromine is capable of doing the same work as oxygen.

† *Eng. and Min. Journal*, April 20, 1895.

The ideal requirement seems to be to secure that intimate molecular contact which is assumed in equation (c), above. In this case the cyanogen reacts in the nascent state. This is a condition hard to realize in the treatment of ores.

In the treatment of gold strips in cyanide-solutions, I found that with a given cyanide solution and a given bromine-water solution, the amount of gold dissolved by the combined treatment with cyanide and bromine-water was, in one case, four times as great as the sum of the amounts of gold dissolved by the same amounts of cyanide and bromine-water solutions, each acting separately, all the other conditions being the same.

Chlorine-water may be used instead of bromine-water. According to the reaction in equation (c), 1 ounce of bromine as such will cause the solution of 2.45 ounces of gold, while 1 ounce of chlorine will cause the solution of 5.52 ounces of gold, and, as per Elsner's reaction, 1 ounce of oxygen will dissolve 24.5 ounces of gold. Weight for weight, the oxygen is more effective than either chlorine or bromine. I have also found that, properly applied, the oxygen of the air gives as good and even better results than either chlorine or bromine. But the latter, being more soluble in water, are more conveniently used.*

It may be concluded from these experiments, that cyanide of potassium solutions, acting alone, are absolutely without action on metallic gold; that the addition of some substance capable of taking the potassium away from a part of the cyanogen, thus setting the latter free in the nascent state, is an essential condition to the solution of metallic gold in potassium cyanide;

* A possible application to the chlorination-process suggests itself. Owing to insufficient roasting or imperfect gassing, the tails from the chlorination-vats often run high. At present these must either be thrown away or else dried, re-roasted and regassed and leached. It might be feasible to have a set of large tailing-vats into which such lots might be thrown wet and leached with a dilute solution of cyanide until they were sufficiently low in gold to throw away. The small amount of chlorine remaining in such tails would act to set free cyanogen enough to fix the gold. Care should, of course, be taken to wash out soluble metallic salts and to neutralize the free acid before adding the cyanide. Such a method is likely to fail in the hands of Mr. Stetefeldt's old enemy, "the muscular amalgamator." And it is doubtful whether sintered clots, formed in roasting, and coarse gold which has escaped the amalgamator, would yield to this treatment.

and that this agent may be either the oxygen dissolved from the air, or supplied artificially, or a suitable oxidizing agent, such as some of those already mentioned, or an equivalent addition of chlorine, bromine, or iodine, or the compounds of these with cyanogen.

Which of these should be used will depend on many conditions, hard to specify briefly. There is danger in using too strong an oxidizer or too much of it. In such a case, not only are other secondary reactions likely to ensue with ores containing metallic sulphides, arsenides and antimonides, which lead to the destruction of the cyanide, but, as already pointed out, the free cyanogen itself, if set free faster than it can be taken up by the gold, simply runs down into oxidized products without doing any good. This is the great difficulty in the treatment of low-grade ores. Nothing but experience and intelligent and trained supervision can meet this difficulty.

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. If a thorough utilization of the cyanide is desired, the action of the oxidizer should be such that the cyanide will be decomposed only under the stimulus of the presence of the gold. Under these circumstances, the cyanogen will be utilized to the utmost. If, however, the oxidizer is a powerful one, capable of attacking the cyanide on its own account in the absence of gold, the inevitable consequence will be a rapid destruction of the cyanide, just as would be the destructive effect of such oxidizers on the blood.

It cannot be too much emphasized that it seems to be nascent cyanogen only that acts on the gold. I have tried saturating a cyanide of potassium solution with free cyanogen, but have usually obtained only very unsatisfactory results. The ten-

dency to form paracyanogen probably explains why the cyanogen in this case has so little effect on the gold. The further tendency of the paracyanogen to absorb oxygen and run down explains also why its presence in quantity is not only of no use but is a positive detriment, as it prevents the oxygen from setting free nascent cyanogen which can attack the gold.

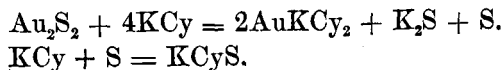
On the whole, with low-grade ores and dilute solutions, the cyanide-solution itself will, if properly aerated, carry oxygen enough to dissolve the gold; so that artificial oxidizers are seldom needed, unless there is some reducing agent present in the water or the ore, which absorbs the oxygen. In such a case, and with richer ores and stronger solutions, there is sometimes a distinct advantage in the use of oxidizing agents. But, unless used with the nicest discrimination, they do more harm than good.

3. *The Solubility of Gold Sulphide in Potassium Cyanide.*

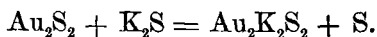
There still remains a great difference of opinion as to the condition in which gold occurs in its ores. There is no doubt that the greater part of it occurs in the metallic state. Many contend that it is always metallic. It cannot be denied, however, that it occurs combined with tellurium, and there is some evidence that it occurs combined with other sulphides, antimonides, arsenides, and, perhaps, with bismuth, to form compounds little understood, but of great practical importance in the treatment of sulphide ores containing gold.

It seems to be impossible to combine gold with sulphur alone in the dry way. I have, therefore, tried the sulphide of gold, Au_2S_2 , thrown down from the acid chloride by sulphydric acid gas. In a 5 per cent. solution of potassium cyanide this sulphide dissolved completely in four minutes; in a 1 per cent. solution, in ten minutes; in a one-fifth per cent. solution, in one hour. In all cases there were found in solution sulphide of potassium (K_2S) and sulphocyanate of potassium ($KCyS$), and, in most cases, suspended sulphur. The latter was most apparent with the dilute solutions of cyanide.

The reactions which occur seem to be expressed most simply by the following formulas:



A third reaction seems indicated by some of the quantitative results, viz. :



The exact relation of these three reactions seems to depend on the strength of the cyanide-solution used. The remarkable solubility of the sulphide of gold is no doubt partly due to the greatly increased surface of the sulphide exposed to the attack of the solvent, but it is also due, no doubt, to the double affinities set up between the gold and the cyanogen on the one hand, and the potassium and the sulphur on the other. There is evidently no call here for oxygen or an oxidizing agent to increase the solubility of the gold.

4. *The Solubility of Gold Telluride in Potassium Cyanide.*

It being very difficult to prepare the telluride of gold in a wet way similar to that in which the sulphide of gold was produced, I have experimented with telluride of gold prepared by fusing pure gold with tellurium, as well as with natural minerals containing tellurium and gold and silver.*

The result of the experiments so far made has been to show that the tellurides of gold and silver experimented on both dissolve in the cyanide solution with the greatest difficulty. This is probably due to the fact that the affinity of potassium for tellurium is much smaller than for sulphur; but tellurium, tending to absorb oxygen and forming tellurous acid, also tends to retard the oxidation of the potassium and the solution of the gold.

5. *The Solubility of Antimonide of Gold in Potassium Cyanide.*

An antimonide of gold produced by fusion of the pure metals acted very much as did the telluride of gold. A copious white powder of antimony oxide formed in the solution and the action was retarded, probably for the same reasons as operated with the telluride of gold.

* I have had great difficulty in obtaining material of this kind of sufficient quantity and purity for the work, and would be greatly obliged to members of the Institute who will supply me with adequate material. What I particularly desire is the pure tellurides of gold and silver existing separately in such quantity that it will pay for the outlay of time and labor necessary for analyses and experiments.

II.—THE PRECIPITATION OF GOLD FROM CYANIDE SOLUTIONS.

Those who are familiar with the instability of most of the salts of gold, and the ease with which all reducing agents, and even light, precipitate metallic gold, will be surprised at the tenacity with which gold is held in solution as aurocyanide of potassium. None of the usual agents can be relied on to precipitate it; sulphydric acid, oxalic acid, sulphurous acid, ferrous sulphate, etc., which are usually so prompt in precipitating gold, are of no avail here. So long as the cyanide of potassium is in excess, they give either not the least trace of a precipitate or only a very imperfect one. In order to have these agents act with certainty, it is necessary to destroy all the cyanogen present. This is a long and difficult process. My attention was early directed to the need of a certain method of recovery, for precipitation by zinc-shavings was exceedingly inconvenient in laboratory tests. For a long time the only certain method that could be relied upon was either to evaporate the whole solution to dryness in a dish made of test-lead, and to scorify the residue, or else to acidify the solution with sulphuric acid, and boil till copious fumes of sulphuric acid appeared and the gold separated out in the metallic state. The solution was then diluted, filtered and the residue scorified. The results were satisfactory, provided the evaporation was pushed far enough to destroy all the cyanide, and no chlorides were left in the solution. Otherwise the results were liable to be low. The extreme tedium of this method, even on a laboratory scale, led very early in the study of the solubility of gold to a parallel study of the causes that contributed to the opposite effect, viz., the precipitation of gold from its solutions. In reality, these are the two opposite aspects of the same question.

According to most of the authorities, when a solution of potassium aurocyanide is acidified with sulphuric acid the cyanide of gold promptly separates as a yellow precipitate. From the solution obtained in treating gold-ore with a 1 per cent. cyanide-solution, even when it contains several hundred dollars' worth of gold per ton, nothing of the sort takes place. The solution remains perfectly clear and colorless. It is only when the solution has been evaporated down and the acid gets concentrated and hot that the canary-yellow aurocyanide separates out. If the acid gets stronger, this salt is gradually decom-

posed, and finally metallic gold remains. The cyanide of gold is more difficult to decompose than the telluride. For it is only the strongest hot sulphuric acid which will convert the canary-yellow crystals of AuCy into metallic gold.

The remarkable fact that the gold remains in solution after being acidified with a strong mineral acid, and that a precipitate forms only on the long-continued application of heat, seems to show that a compound HAuCy_2 , which I shall call aurocyanhydric acid, is formed, similar to the ferrocyanhydric and the ferricyanhydric acids; in short, that we have to deal with an acid radical of the same class as the two just named, and not with an ordinary double cyanide, AuCy, KCy, as is usually supposed. There are many converging indications pointing to this conclusion which it would take too long to enter into here.

1. *Regeneration of Potassium-Cyanide from Dilute Solution by Acidification.*

Before this fact was understood, it was thought that the gold was kept in solution by the free HCy left in the solution after acidification by sulphuric acid. If this free acid could be removed, it was hoped that the gold cyanide would be precipitated. At the same time it was hoped that the free HCy could be regenerated by absorption in caustic potash. This subject was exhaustibly investigated in February to May, 1893.

It was found that although, when acidified with sulphuric acid, a 1 per cent. solution of potassic-cyanide gave not the least apparent trace of escape of HCy, yet, if the solution thus acidified was left for several weeks near an open vessel containing caustic potash, nearly all the HCy would be absorbed by the alkali. As this operation was too slow to be of practical use, air was pumped first through the acidified solution and then through the solution of caustic. The same air was used over again to avoid the presence of carbonic acid. By using steam with the air, the contents of the stock-solution in cyanide were reduced in three hours from 1 per cent. to 0.07 per cent. of free HCy. By using absorption-towers (the usual means of increasing surface-exposure) such results might be reached in practice without the use of steam. Similar results were reached, without the use either of absorption-towers or of steam, in from eight to ten hours.

At the same time it was found possible to regenerate from a 1 per cent. stock-solution of cyanide, a concentrated solution of any desired strength of potassium- or calcium-cyanide, with a total of cyanide actually recovered, up to 80 or 90 per cent. The avidity with which caustic potash or lime absorbs the HCy reduces the loss to a minimum. In case the solution contains alkaline sulphides, these would have to be removed previously by treatment with lead carbonate or sulphate.

A method was thus found which, with a little engineering skill, can be used for regenerating solutions of cyanide of potassium.

2. *The Precipitation of Gold from Aurocyanhydric Acid.*

Although it was thus found possible to remove, down to 0.01 per cent., the free HCy from such a solution acidified with sulphuric acid, still the gold, even to the amount of \$603 per ton, or 0.1 per cent., would remain in the perfectly clear, colorless solution. As already stated, the only explanation found for this was the presence of aurocyanhydric acid (HAuCy_2) in solution. It was found that, even under these circumstances (absence of all free KCy, and only a trace of free HCy), all the usual reagents, such as oxalic, sulphurous, sulphydric acids, etc., failed to precipitate the gold, either giving no precipitate or else only a very imperfect one.

Experiments were made as early as March, 1893, with nitrate of silver, nitrate of lead, and mercurous nitrate. A complete precipitation of the gold resulted when an excess of nitrate of silver was added, either to the above aurocyanhydric acid or to the corresponding potash salt. This would be a neat and practicable method on the large scale, if it were not for the cost of the silver. The nitrates of lead and mercury gave partial precipitation in most cases.

Oxidizing agents, such as permanganate of potassium and peroxides of manganese and lead in acid solutions, also facilitate the precipitation. The filtration of the solution through red lead or massicot has been covered by an English patent granted to P. de Wilde, December 22, 1894.

3. *Precipitation of Gold from Potassium-Aurocyanide by Means of Charcoal.*

On July 3, 1894, an American patent was granted to the late

William D. Johnson, at that time chemist of the California State Mining Bureau, for a method of extracting gold from a cyanide-solution by passing the solution through a series of charcoal filters, and subsequently burning the charcoal and smelting the ashes with suitable fluxes.

The use of charcoal for this purpose had already been tried for extracting gold from the chloride solutions produced in the Plattner process. For this purpose it is certainly a very efficient method of precipitating gold; but the subsequent extraction of the gold from the charcoal is almost as troublesome as the extraction of the gold from the original ore.

Dr. Johnson claimed that a single filtration would remove 25 per cent. of the gold, and that, by repeated filtrations, 95 per cent. of the gold could be recovered. It is evident that if only 25 per cent. of the gold present could be recovered by a single filter, it would take a very large number of filters to remove all the gold, and consequently a large volume of charcoal would have to be burned to recover it.

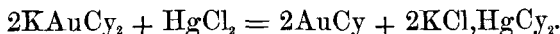
In order to test the method, the following experiments were tried: Two cyanide-solutions containing each 100 c.c. with about 0.1 per cent. of gold (\$603 per ton solution), were each filtered through separate filters, and the process was repeated four times. Each filter contained seven grammes of charcoal. One of the solutions was alkaline, the other had been made acid with sulphuric acid. From the acid one 15 per cent., in the other case 6.5 per cent., of the gold present was precipitated by the charcoal. These experiments, made under much more favorable conditions than could occur on the large scale, show that this method can hardly prove of service with rich solutions in practical work.*

* Since this paper was presented at the Denver meeting, I have been paying more attention to the action of dilute cyanide solutions, and I have thought it well to investigate the action of charcoal on such solutions.

For this purpose the following experiments were outlined: Two solutions of 2000 c.cms. each were prepared. The one (a) contained 0.001 per cent. of gold as potassium aurocyanide, or \$6.03 per ton solution, but no free cyanide of potassium. The other (b) contained the same amount of gold, but also 0.2 per cent. of cyanide of potassium. Each solution was contained in a Mariotte bottle 11.4 cms. in diameter, so arranged that the solutions were discharged upon charcoal filters so that the charcoal was kept constantly submerged, and under a constant head. The charcoal was crushed so that it passed a 20-mesh sieve, but was mostly

4. *Precipitation of Potassium-Aurous Cyanides by Mercuric Chloride.*

Fremy (*Encyclopédie Chimique*, t. 2, *Métalloïdes*, Sec. 2, Fasc. 2, p. 463) states that potassium-aurocyanide is precipitated by mercuric chloride according to the following reaction:



This reaction I have also tested. A solution assaying several hundred dollars per ton, and carrying only a trace of free cyan-

fine dust. It was contained in a cylindrical glass tube, 10 cms. long by 2 cms. in diameter; it weighed in each case dry 10 grammes.

It took nearly two days for the first 800 c.cms. of solution to filter through each filter. The filtrate from (a) contained no gold. That from (b) contained a trace (less than 0.01 mg.). The next 1200 c.cms. took nearly five days to filter. Filtrate (a) contained 0.01 mg. of gold, while (b) contained 1.40 mgs. The charcoal from (a) contained 20.03 mgs. gold, while that from (b) contained 18.70 mgs.

The actual recovery of the gold by the charcoal was in (a), in the absence of free cyanide, 99.95 per cent.; in (b), in the presence of 0.2 per cent. free cyanide, it was 93.03 per cent. The free cyanide, in the latter case, was reduced from 0.2 per cent. to 0.118 per cent.

These results are of great importance, for they show that, under certain conditions, all the gold can be precipitated from potassium aurocyanide by means of charcoal, and that even in the presence of free cyanide of potassium 93.03 per cent. can be precipitated.

Further study of the data given above shows that the charcoal in (a) contained 0.2 per cent. gold, or \$1206 per ton, while (b) contained 0.187 per cent., or \$1182 per ton. These figures would seem to represent the limit of enrichment at which the charcoal ceased to act in either case, the limit being lower in the presence of the free cyanide. In the case of the stronger solutions previously tested (which were 100 times richer in gold), the content of the charcoal in the acidified test was 0.21 per cent. gold, or \$1266 per ton; and in the alkaline one, containing a certain amount of free cyanide, it was 0.091 per cent., or \$548 per ton.

These results would seem to show that Dr. Johnson's view that the charcoal can be depended on to precipitate 25 per cent. of the gold present at each filtration is erroneous. It would rather seem that a given amount of a certain charcoal has a definite capacity of precipitation; that within this limit it acts completely and promptly; beyond this limit it acts less completely and quickly; and that finally it ceases to act at all. The presence of free cyanide of potassium seems to lower its precipitating capacity, and perhaps at a certain point stops it altogether; acidification seems to increase the capacity. These views are, of course, provisional, as the subject is still under investigation.

It must be evident that in its present form the method gives a much less concentrated precipitate of gold (only 0.2 per cent.) than either the zinc, the electric or the cuprous method of precipitation. The precipitate obtained in the latter method often contains 40 to 60 per cent. of its weight in gold, or it assays from \$240,000 to \$360,000 per ton.

ide of potassium, remained perfectly clear for several hours after the addition of mercuric chloride. The next day, however, I found a yellow precipitate of cyanide of gold, so fine that it filtered clear with great difficulty. When, finally, a clear filtrate was obtained, the gold continued to precipitate for several days; it also had a tendency to adhere strongly to the walls of the tube. These indications seemed to point to the need of heat to hasten the reaction. Consequently I tried heating the solution. I found that this greatly aided the reaction. On boiling the solution for a few minutes the gold was almost entirely thrown down as the yellow cyanide, and could be easily filtered out, leaving a perfectly clear filtrate.

In the filtrate from the aurous cyanide the mercury could be saved and the cyanide recovered by adding, very exactly, the amount of sulphide of potassium to throw down the mercury as sulphide. Cyanide of potassium would thus be regenerated in the solution. The latter would then be ready for another leaching; and even should a little gold be left in the solution from imperfect precipitation it would not be lost. The precipitated cyanide of gold, gently ignited at a low red heat in the air, turns to pure gold.

This method of precipitating may be useful under certain circumstances, but the necessity of heating the solution adds so many complications and so much expense to a leaching-process, that it is robbed of many of its advantages. In the presence of free cyanide of potassium this precipitation does not take place.

5. *On the Precipitation of Potassium Auocyanides by Copper and its Compounds.*

It was early noted in the study of the cyanide-process that copper, with its compounds, was destined to play a very important rôle in the development of the process. In fact, it is well known that certain copper-minerals are active obstacles to the successful extraction of gold from its ores.

The thought naturally suggested itself: May not this difficulty in the solution of gold be utilized to aid in its precipitation? In March, 1893, a sheet of metallic copper was immersed in a solution of cyanide of potassium containing a third of a gramme of gold in solution. Instead of the precipitation of metallic gold on the copper, a light yellow precipitate began to

form throughout the liquid. Very little of this formed on the copper itself; it was found as a sediment throughout the liquid. After three days three-fourths of the gold had been precipitated. The copper was then removed; but the gold-containing sediment continued to separate from the solution for over a week, until all but 11 mgs. of the gold had been precipitated. This very important experiment did not at the time seem to lead to anything practicable, for the action seemed too slow and uncertain to be of any value.

Recalling the fact that the sulphide of copper had been suggested by C. H. Aaron and L. D. Godshall (*Eng. and Min. J.*, Nov. 29, 1890) for the precipitation of gold from the chloride-solution produced in the Plattner chlorination-process, it occurred to me that a similar precipitation might take place from the cyanide-solution. Hence, on May 4, 1893, three lots of potassium aurocyanide, with 0.02 per cent. of KCy and a quarter of a gramme of gold, were treated by agitation for four hours with CuS precipitated from CuSO_4 by H_2S . The still moist precipitate was washed and then stirred into the solution. One of the solutions was left neutral, the other made strongly alkaline with caustic potash, and the third made acid with sulphuric acid. In the alkaline and neutral solutions two-thirds of the gold were thrown down by the copper sulphide; in the acid one, all of it was precipitated. Numerous experiments with the sulphide of copper produced by fusion showed that the form originally used gave the best results, probably on account of its greater surface. Since the date of its first discovery, in May, 1893, this method of recovery of gold from cyanide-solutions has been repeatedly used in my laboratory, and has stood the most rigid tests. It is necessary to acidify the solution with a mineral acid like sulphuric acid, and it is best to remove as far as possible the free HCy by one of the methods already explained. In case there is less than 0.1 per cent. of free HCy present this may be omitted. The CuS, Aq produced by the action of H_2S on a solution of CuSO_4 is then added to the solution; the whole is stirred thoroughly at intervals for several hours and then filtered out. The gold will be contained in the residue.

In one case, CuS, weighing, when dried, 5 grammes, was added to 1000 c.c. of an acidified solution of aurocyanhydric

acid containing 1 gramme of gold in solution. All the gold was precipitated. The copper sulphide precipitated one-fifth of its dry weight of gold. The gold was readily recovered from the residue, after making it alkaline by digesting it with sodium sulphide, in which the gold is readily soluble. The copper sulphide may then be used over again. From the sulphide-solution the gold is readily precipitated by electrolysis, the more readily as the solution is small in bulk and concentrated. Other methods of extracting the gold from the copper are also available.

The gold may also be removed from the cyanide-solution, after acidification, by filtering it through CuS without agitation. I prefer, however, to agitate first and filter afterwards. Another method that was used was to add copper sulphate and then sulphydric acid to the acidified solution. Provided the excess of free HCy be first removed, one atom of copper will thus precipitate one atom of gold, or one pound of metallic copper as sulphate will precipitate 3.11 pounds of gold.

Both of these methods were used with complete success on the solutions obtained by treating gold-ores with cyanide solution at various intervals from May, 1893, to 1896.

A careful study of the solutions used in the above experiments showed that the gold was precipitated without more than a trace of copper going into the solution. The unusual occurrence of one metal precipitating another without itself going into the solution, led to a careful study of the reaction involved. This was also viewed in the light of the experiment with the strip of metallic copper already mentioned. Also, in an experiment made in 1894, where Cu_2S was used to precipitate the gold from an acid solution of aurocyanide, a white precipitate, containing cuprous cyanide, was formed, which gave to the entire solution the appearance of milk. It was also noticed that when copper sulphate was added to a strong solution of aurocyanide, a white precipitate formed which contained gold and copper. Also, when H_2S was added to a gold-cyanide solution containing copper, it was noticed that, at the first instant when the gas came in contact with the solution, a white precipitate was formed, which gradually changed to the black color of copper sulphide as more H_2S was added. All these considerations pointed to the conclusion that the gold-containing

precipitate was in all cases mainly a salt of aurocyanhydric acid, either cuprous aurocyanide or the corresponding sulpho-salt.

This explanation of the reaction was made early in 1894. As soon as this was settled, another method suggested itself, and proved to be a success. A solution of cuprous chloride was prepared by adding sodium chloride to a solution of cupric sulphate, and saturating the mixture with sulphurous acid. When this was added to the potassium aurocyanide, a white precipitate was formed at once, which contained all the gold. In the first experiment tried the metallic copper, present as cuprous chloride, precipitated over twice its weight of gold. All the cuprous salts were found effective for this purpose. Even the cuprous cyanide formed by adding copper sulphate to a potassium cyanide solution, and then acidifying with sulphuric acid and filtering out the white, curdy cuprous cyanide, was thus effective. As this salt is much more permanent than the cuprous chloride, it may prove of service in practice, though it is more expensive than the latter. I have also found that cuprous hyposulphite precipitates aurocyanides. The precipitate, however, is soluble in excess of either potassium cyanide or sodium hyposulphite. Hence a complete precipitation of the gold can only be expected after the solution has been made acid.

The method that I have used most constantly since April, 1895, is to add sulphuric acid to gold-cyanide solution till it reacts acid to litmus. If the solution is strong in HCy, it is usually best to remove this first, either by the aeration method already described, or else to remove it, previous to the acidification, by means of the zinc-sulphate method, to be mentioned later. To the acidified solution I add cuprous chloride, as above described. When this solution is added, the gold and excess of HCy come down at once as a white precipitate, generally turning slightly yellow. The cuprous chloride should be added till a drop of the filtrate gives a red precipitate with ferrocyanide of potassium. The gold is thus rendered insoluble, and may be filtered out as cuprous aurocyanide (CuAuCy_2). This compound is insoluble in dilute acids, but readily soluble in cyanide of potassium. The gold is easily extracted from it in several ways.

In October, 1895, Prof. P. de Wilde, of the University of Brussels, published a method of precipitating gold from cyanide solutions in the *Revue Universelle des Mines, de la Métallurgie, etc.*, in an article entitled "Note on a New Method for the Extraction of Gold from Tailings, Slimes and Concentrates."

His method consists in three steps:

a. The leaching of the ore, etc. This he does, as in the Siemens and Halske process, with an 0.05 per cent. KCy solution, containing about the same amount of free caustic soda or lime, as may be necessary.

b. The recovery of the excess of alkaline cyanide. This he attempts, as had already been proposed by MacArthur, by adding ferrous sulphate and precipitating ferrous cyanide until potassium ferricyanide gives with a drop of the filtrate a precipitate of Prussian blue. In order to avoid the precipitation of the gold it is necessary that the free alkali should be nearly neutralized before adding the ferrous sulphate. This method will work, as I have proved by experiment, but I regard it as thoroughly unpractical. The bulk of the precipitate is something enormous; it takes a week to filter and remove the gold-solution; it is constantly changing composition, running finally into Prussian blue; and it is no simple matter to extract the cyanide from it when once it has been obtained. The author himself evidently does not put much faith in it. He concludes by remarking that with dilute cyanide-solutions this step of recovery may be omitted.

c. The precipitation of the gold. Here he describes a method the same in principle, and almost the same in detail, as the one I have described as used in my laboratory since April, 1895. I translate from his article:

"My third operation is based on the following principle: In a solution containing the double cyanide of gold and potassium (AuKC_2) (or sodium) one precipitates all the cyanogen in the form of aurous cyanide (AuCy) and cuprous cyanide (CuCy), on acidifying first the solution with sulphurous acid (SO_2) and then adding a solution of sulphate of copper (CuSO_4).

"The reaction is extremely sharp, and the least excess of sulphate of copper suffices to produce an absolutely complete precipitation of the gold. In operating under the most varied conditions and with solutions containing only five or six milligrammes of gold to the 1000 c.c., I have never been able to find the least loss of gold.

"If the liquid contains alkaline cyanide in excess (which is the case in my method), this is transformed completely into cuprous cyanide.

"The acidification can be made by the injection of sulphurous anhydride (SO_2) by means of a solution of sulphurous acid, or of an alkaline bi-sulphite (meta-sulphite of potassium or of sodium $\text{Na}_2\text{S}_2\text{O}_5$)."

It will be seen that Prof. de Wilde makes his cuprous salt in the solution itself, also acidifying the solution at the same time with sulphurous instead of sulphuric acid. This may appear an advantage; I think, however, that the mechanical difficulty of treating a large volume of solution with gas will more than offset the slightly greater cost of the sulphuric acid for the same purpose. However this may be, I prefer my method of making the cuprous salt outside of the stock-solution and from strong solutions, so that the application of the sulphurous acid may be more readily controlled and the production of the cuprous salt more complete. With these slight differences of detail, the methods are the same. Whether the method was first discovered in Belgium or California is a mere matter of dates.

I have tried the method suggested by Prof. de Wilde, as well as my own, with solutions containing from only \$3 to over \$600 per ton of gold (from $\frac{1}{20000}$ of 1 per cent. gold up to $\frac{1}{10}$ per cent. gold), and I have found them both to remove the gold with a sharpness and completeness that is a great relief, after trying the other methods in use.

I find, however, that with Prof. de Wilde's method it is necessary to let the solution stand at least twelve hours before filtering, otherwise all the gold may not be precipitated. In fact, in some cases not the slightest trace of a precipitate will form for several hours, the liquor remaining clear as crystal. At last, however, it never fails to come down. Gently heating the solution hastens the reaction; cold retards it. At the ordinary temperature of the air (60°F.) heating is not necessary for the completion of the reaction, but more time must be then allowed. It is best, however, to allow the filtrate to stand for several hours, another twelve hours if possible, to be sure that no further precipitate comes down. This is where my method has the advantage; being formed in concentrated solutions, my cuprous salt is already reduced and the precipitate forms sooner. I think the reason for the delay in his method is the greater dilution of the copper salt and the sulphurous acid, which retards the formation of the cuprous salt.

I feel sure that this method in either of its forms will prove a valuable addition to our present means of recovering gold from cyanide-solutions.

But before the advantages of this method can be duly appreciated, it will be necessary to briefly consider the methods for precipitating gold at present in use. There are only two which have made any headway on a working-scale, namely, the use of zinc-shavings, as recommended by the MacArthur-Forrest people, and the use of electricity, as in the Siemen and Halske process. I shall consider them in inverse order.

6. *The Use of Electricity for Precipitating Gold from Cyanide Solutions.*

The use of electricity for depositing gold and silver for electroplating has been practiced successfully for so many years that it would seem that this method would also be a simple, expeditious and practical method of precipitating gold from the cyanide-solutions obtained by leaching gold-ores. But a little reflection will make it clear why so many processes for this purpose which have been patented have never been heard of since.

In electroplating, it is possible and practicable to use: 1, soluble gold anodes, by which the counter-electromotive force of the precipitated metal is entirely neutralized; 2, concentrated solutions of the double cyanide of gold and potassium, so that the specific resistance of the solution is low; 3, an electrolyte of constant composition, whereby the proper working-conditions may be constantly maintained after they have once been reached.

None of these conditions can be secured in precipitating the gold from a cyanide ore-extraction solution.

It is true that in the Siemens and Halske method a soluble anode of iron plate is used; but all the cyanogen that combines with the iron is lost, ferrous cyanide and finally Prussian-blue being formed to no useful purpose. The principal difficulty, however, is one that cannot be obviated, viz., the high specific resistance of the dilute solutions that must be used. With solutions always containing less than 1 per cent., and sometimes less than 0.05 per cent., of free cyanide, and perhaps 0.001 per cent. of gold, or less, the resistances are something enormous, and with any other metal than gold no one would think of pre-

cipitating such a solution with electricity. The high specific resistance of the solution may be met by using an increased surface of anode and cathode and by artificial circulation, but this can only be done at an outlay and with a complication which robs the method of its cheapness, simplicity and convenience.* It is true that electrolytic methods of precipitation are used in the analytical laboratory as convenient methods of analysis. But a long experience with these methods on the small scale has convinced me of the great difficulties which will always stand in the way of their application on the large scale. It is one thing to electroplate an article with gold in a strong solution of aurocyanide of potassium with a gold anode which constantly adds as much gold to a solution as is precipitated, and it is quite another to precipitate all the gold from a solution with an insoluble, or even an iron, anode when the solution contains perhaps 0.05 per cent. of cyanide of potassium and perhaps 0.001 per cent. of gold. Here the problem is to reduce the gold-content to 0.00001 per cent. (or from \$6 to 6 cents per ton solution). Any one who has attempted this recovery (which is 99 per cent. of the gold contained in solution), without at the same time destroying most of the cyanide present, will agree with me that it is no easy task.

There is another difficulty that I have met with. Under certain circumstances the gold is precipitated not only on the cathode, but also on the anode; and, in addition, in many cases of the treatment of the solutions produced from ores a precipitate settles out from the electrolyte which also contains gold. The reason for the first difficulty seems to be that when the current decomposes the salt KAuCy_2 , it decomposes it not into $\text{K,Au} + 2\text{Cy}$, but the K alone goes to the cathode, while the acid radical, AuCy_2 , goes to the anode. The deposition of gold which appears on the cathode is due to the metallic potassium attacking and reducing gold as a secondary reaction from the solution there adjacent. Great density of current and long treatment will finally throw out all the gold on the cathode, but

* Since writing the above my attention has been called to a corroboration of these views in an article entitled: "Zinc vs. Electricity," by Mr. John Yates, *South African Mining Journal*, September 26 and October 3, 1896. In this article an interesting comparison of these two methods of precipitation is given.

there is enough force in this tendency to greatly retard the electro-deposition of the gold.*

I have been able, by acidifying the solution with dilute sulphuric acid, to get fairly complete precipitation in a reasonable time, say 12 to 24 hours, on a small scale, both with insoluble anodes (carbon, platinum or lead) and with soluble ones (zinc, iron or copper). Of course, in this case the cyanide is destroyed, unless special steps are taken to recover it. The precipitation is much more rapid and complete from these dilute gold-solutions when the reaction is acid than when it is alkaline or neutral.

The difficulties which I have pointed out in the electrolytic method may be met by great technical skill, as has been the case in the Siemens and Halske process, and in that way, when they are reduced to a minimum, the method may be crowned with success. But in the absence of such skill it is bound to be a failure, and the difficulties are of such a serious and fundamental nature as to lead to the desire for another and simpler plan.

7. *The Precipitation of Gold from Cyanide Solutions by Means of Metallic Zinc.*

The precipitation of gold from cyanide-solutions by means of zinc-shavings has been more generally used on the large scale than any other. It appears on the face of it the simplest method that could be devised, and in proper hands and under intelligent supervision it has given, on the whole, better results than any other method in general use. Nevertheless, those who have used it most are the most anxious to find some other method.

Some of the principal objections urged against it are the following:

* A similar state of affairs has been shown to be the case by Professor Hittorf (Ostwald's *Chemische Energie*, 2te Auf., ii., 880) in the electro-deposition of potassium-silver cyanide. I have also noticed a similar state of affairs with copper. When a solution of potassium cuprous cyanide is electrolyzed with a platinum anode at a voltage below that at which metallic copper is deposited on the cathode, yellowish-brown crusts of cupric cyanide separate out on the anode. These dissolve in the electrolyte when stirred. Fragments of the crusts that drop from the anode on the cathode are reduced to metallic copper. At a higher voltage metallic copper comes down on the cathode from the solution generally. I have also noticed a similar thing in electrolyzing potassium aurocyanide with platinum electrodes. In order to see this action clearly it is necessary to avoid an excess of free KCy.

1. The great consumption of zinc compared with the amount of gold precipitated.

2. The great destruction of potassium cyanide to no useful purpose.

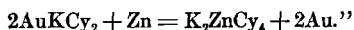
3. The great difficulty of removing zinc and cyanogen residues from the gold, thus causing loss in melting and the production of an unclean bullion.

4. The failure, in certain cases, to precipitate the gold.

I do not need to dwell on the first three of these difficulties. They have been sufficiently emphasized by every one who has described the practical application of the cyanide process; but the incomplete precipitation of the gold has not been sufficiently recognized.

One reason for this appears to be that the reaction which takes place when gold is precipitated from the potassium-aurocyanide is not as simple as it is generally supposed to be. Thus Dr. Scheidell, in the *Bulletin* of the California State Mining Bureau, on the "Cyanide Process," 1894, p. 34, states the usually accepted view. He says:

"The action of zinc on gold-solution is theoretically very simple, a simple substitution of the gold by the zinc according to the equation:



This reaction had also been given in almost the same words by Butters and Clennell (*Eng. and Min. Journal*, Oct. 29, 1892). Wilson ("Cyanide Process," p. 34) and Rose ("Metallurgy of Gold," p. 323) adopt the same reaction.

My attention was first called to this subject by a remark of Mr. W. R. Feldtmann (*Eng. and Min. Journal*, August 11, 1894), who, speaking of the precipitation of gold by zinc, says:

"Its completeness appears to depend, in a measure, on a slight excess of cyanide of potassium being present in the solution."

The same fact was recognized by one of my students, Mr. B. E. Janes, when acting as assayer at the Mercur Mine, Utah (*Mining and Scientific Press*, May 23, 1896).

This led me to investigate the reaction which occurs. I had prepared a solution of potassium aurocyanide with about 1.3 per cent. metallic gold and no free cyanide. A solution made from this by dilution, so as to contain 0.1 per cent., or \$603

per ton, gold, was then treated with strips of sheet zinc for twenty-four hours. The strips were carefully burnished with emery-paper, or with a sharp knife, to avoid any film being left on the surface of the zinc. Commercial sheet-zinc was used as is done in practice. The solution was contained in glass tubes sometimes at rest, sometimes rotated mechanically for the whole period of twenty-four hours.

In no case was more than a trace of gold precipitated. In many cases, where the zinc was brightly burnished, not a trace of gold came down, and the strips weighed exactly the same to a hundredth of a milligramme before and after the test, and when dissolved in sulphuric acid left no trace of gold.

These experiments throw light on the statements often made that it has been possible to extract the gold from the ore but not from the solution. A person trusting to the above-described reaction, might easily throw away such a solution after twenty-four hours' contact with bright metallic zinc, even though it contained \$603 per ton.

The next experiments were made with lathe-turnings from the same sheet-zinc which, in the polished state, had failed to precipitate gold. With potassium-aurocyanide containing 0.1 per cent., or \$603, gold per ton, which had failed to precipitate at all on the bright sheet-zinc, the gold was entirely precipitated from the solution in twenty-four hours by filtering it through a very large excess of zinc-shavings (over four hundred times the weight of the gold present). The filtrations were repeated through the same shavings four times.

When the solution contained only \$10-worth of gold per ton, the precipitation was only 82 per cent. of the gold in solution in a single filtration which lasted twenty-four hours. In each case the solution was allowed to remain in contact with zinc-shavings, four hundred times the weight of the gold in solution, until a color of gold appeared on the shavings; then the solution was allowed to flow from the filter drop by drop, the shavings being continuously submerged. The conditions were, therefore, much more favorable for complete precipitation than could be maintained in practice.

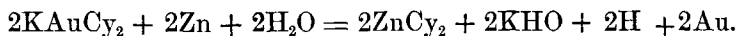
These differing results are very difficult to explain on the simple substitution-reaction usually accepted. If the gold precipitates on the shavings, why should it not do so on the same

sheet of burnished zinc from which the shavings were made? There is a larger surface of contact, it may be suggested. But even the smallest fragment of a zinc-shaving will precipitate gold on itself, while, in the same solution the freshly-scraped surface of sheet-zinc, many times its area, is either entirely or practically without action. It may be thought that the turnings had a cleaner surface than the scraped zinc, but this cause was carefully eliminated.

All the indications point to the phenomena of "polarization," so well known in electrolytic work, where the formation of invisible traces of films on the surface of the electrodes puts a stop to further action, either by preventing contact, or by setting up an opposite electromotive force.

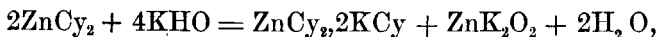
I have not had time to establish firmly the following explanation of the phenomena which I have observed, but there seems some evidence in its favor.

There is no doubt that, besides the tendency of the potassium-aurocyanide to split up into KCy and Au and Cy , which is assumed in the reaction by substitution, there is also a tendency for it to split along another line, viz., into K and AuCy_2 , the latter playing the part of an acid-radical. Now, if this takes place in the presence of zinc and water, the water will be attacked by the potassium, forming caustic potash and hydrogen, and the AuCy_2 will be attacked by the zinc, forming zinc-cyanide and metallic gold, according to the following reaction;

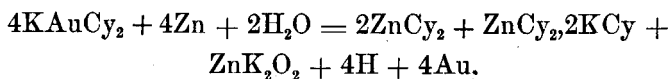


There is no doubt that a certain tendency to form this reaction exists, for electrolysis proves it. It can only take place here by setting up a condition of polarization on the surface of the zinc, owing to the film of occluded hydrogen set free on its surface. If this be so, it is now very clear why the zinc turnings act, while the smooth zinc does not. The turnings have an infinite number of ragged edges, which favor the escape of the hydrogen gas, and the relief of the condition of polarization, and thus allow the reaction to proceed. The hard, smooth surface of the rolled sheet-zinc is very unfavorable to the formation of gas-bubbles from its surface, and hence to the continuation of the reaction.

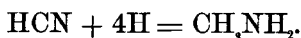
Of course, when the reaction once sets in as above, there is a further reaction between the caustic potash and the zinc cyanide, by which a part of the latter is dissolved, and potassium zinc cyanide and potassium zincate formed. Thus:



as already pointed out by Mr. J. S. C. Wells in a valuable paper (*Eng. and Min. Journal*, December 21, 1895). The complete reaction would then be :



The turning-point would seem to be, is hydrogen formed as these reactions require, or is it absent, as called for by the substitution-reaction? Numerous experiments have always shown that by the action of a solution of potassium aurocyanide containing only 50 mgs. of gold and zinc-turnings, hydrogen gas is set free in sufficient quantity to give a well-defined flame (4 or 5 c.c.). The hydrogen does not form in noticeable quantity at first; but as the gold begins to come down, on shaking the zinc-turnings, fine bubbles of gas escape, and may be easily collected in quantity. It may be objected that the replacement-reaction took place, and that the hydrogen was evolved by the subsequent reaction of the $2\text{KCy}, \text{ZnCy}_2$ on the zinc. Experiment shows that the double cyanide of zinc and potassium acts very slightly on zinc-shavings, but that when the latter have been partly plated with gold, hydrogen is then set free. So that the presence of hydrogen at the end of the reaction may be due to this cause, at least in part. It is also probable that the KCy is, to a certain extent, dissociated (KHO and HCy being formed). It seems likely that the nascent hydrogen will be partly absorbed by the HCy with the formation of methyamine, thus:

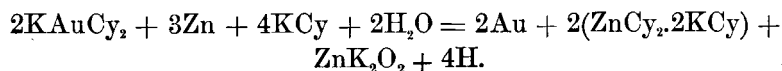


Another curious fact remains to be recorded. When zinc-turnings are placed in distilled water containing a drop of phenolphthalein no coloration takes place. When phenolphthalein is added to pure potassium-aurocyanide, no coloration takes

place. This shows the aurocyanide to be but little dissociated. When the latter solution is poured upon the former, at first no change occurs; but as the gold begins to separate upon the zinc, a deep purple stain surrounds the zinc-turnings where the gold has separated out, showing that the reaction has become alkaline. Whether this is due to the formation of caustic potash, methylamine, or the double cyanide of zinc and potassium, I have not demonstrated with certainty. The fact, however, that zinc cyanide seems to separate out early in the reaction indicates the explanation I have suggested.

Yet another point remains to be mentioned. When to a solution of potassium-aurocyanide which has been left for twenty-four hours in contact with zinc-strips, without action, a little free cyanide of potassium is added, the gold comes down at once, and the precipitation is soon complete. This fact seems an additional confirmation of the reaction that I have suggested. It will be remembered that the formation of the insoluble cyanide of zinc is a feature of this reaction. If this occurs, it is certain that a film of this substance, perhaps infinitely thin, must cover the surface of the zinc, and, in addition to the film of hydrogen, prevents the contact necessary to continue the reaction. The presence of free cyanide of potassium, of course, readily dissolves this film, and the reaction is free to continue.

The reaction which actually takes place in precipitating gold from solutions containing free cyanide of potassium will then be something like this:

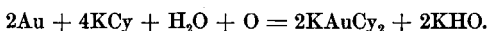


It will be remembered that according to the substitution-reaction, one atom of zinc replaces two atoms of gold, or 1 ounce of zinc should precipitate 6.2 ounces of gold; whereas, as every one knows in practice, 1 ounce of zinc will precipitate only from $\frac{1}{5}$ to $\frac{1}{15}$ of an ounce of gold, or thirty to ninety times less than the amount called for by the reaction by substitution. According to the reactions I have suggested, in the absence of free cyanide of potassium and caustic potash, 1 ounce of zinc should precipitate 3.1 ounces of gold. In the presence of a moderate excess of cyanide of potassium it should precipitate

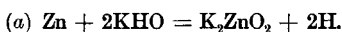
2.06 ounces. The apparent discrepancy that seems still to remain between theory and practice is in reality due to the facts: first, that the free alkali (potash in particular, formed in the solution of the gold, or added to neutralize the free acid in the ore) also dissolves the zinc as potassium zincate; second, that an excess of potassium cyanide dissolves the zinc on its own account, both as the double cyanide and as the zincate of potassium; third, it should also be remembered that water containing dissolved oxygen attacks metallic zinc quite vigorously, forming hydrate of zinc.

I do not consider the reactions which I have suggested as demonstrated. I have considerable work outlined on this subject which is not yet finished, and the opinions here expressed are provisional. It is not improbable that the reaction by replacement, and the more complicated one that I have suggested may both take place under certain conditions of concentration and temperature, which are not yet understood. It is also possible that the nature of the reaction changes after the first deposition of gold.*

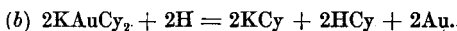
* Mr. Alfred James, in a valuable paper on the "Cyanide Practice," read before the Institution of Mining and Metallurgy, London, England, May 25, 1895, calls attention to the inadequacy of the substitution reaction in explaining the precipitation of gold in the zinc-boxes. He doubts the action of KCy on the zinc, at least to any appreciable extent, and calls attention to the fact that KHO is always present in the solution, as per Elsner's reaction:



He then suggests the following reactions in explanation of the precipitation of gold in the zinc-boxes:



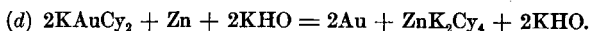
"Then, as Feldtmann has pointed out, the nascent hydrogen reduces the gold:"



Then he adds that a subsequent reaction takes place as follows:



When we come to study these reactions, however, it must be evident that we may combine reactions (a), (b) and (c) together into one reaction, for they are in reality simultaneous. We have then:



It must be further evident that the 2KHO remains unaltered throughout the

However the theory of this subject may finally turn out, and even granting that, given indefinite time and zinc-shavings, it may be possible to remove all the gold from an aurocyanide-solution in the absence of free cyanide of potassium, it is still practically true that it is impossible to remove all the gold from a cyanide-solution in a reasonable time, say twenty-four hours, unless there is an excess of about $\frac{1}{10}$ or $\frac{2}{10}$ of 1 per cent. of free cyanide of potassium. This is all the more necessary in large-scale work, as fine ore-silt and the oxidizing effect of dissolved oxygen nearly always leave the shavings in the zinc-boxes more or less coated with films, which increase the difficulty of an intimate contact of the solution with metallic zinc.

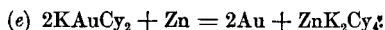
8. *Recovery of Cyanide of Potassium from Strong Solutions by Zinc Sulphate.*

As objection will be made to the cuprous method of gold precipitation when strong solutions of potassium cyanide must be used, it is necessary to consider the recovery of the cyanide from such solutions previous to the precipitation of the gold.

A careful study of the ferrous sulphate method of recovering the cyanide from strong solutions, previous to the recovery of the gold, by means of copper solutions, as suggested by Prof. de Wilde, has led me to regard it as entirely impracticable in most cases that occur in practice. I have therefore sought another method besides the one already set forth (by means of sulphuric acid and aeration). This I have found in the use of sulphate of zinc. I find, however, that an American patent had been already granted, October 15, 1895, to Bertram Hunt, of Wickenburg, Ariz., for such a method of recovery. According to the patent-claims, he

“Precipitates the cyanide in the waste or spent liquor by adding a solution of sulphate of zinc containing some free sulphuric acid, whereby a cyanide precipi-

reaction, and we may, therefore, subtract it from both members of equation (d). When we do this, we have :



In short, it appears that the explanation of Mr. James brings us back to the old substitution reaction which he started out to avoid. His reactions also fail to explain the increase of free alkali which every one recognizes as taking place in the zinc-boxes.

tate is obtained ; then drawing off the supernatant liquor ; then mixing with the said precipitate a quantity of sulphuric acid more than sufficient to decompose the cyanide of zinc contained in said precipitate, then subjecting the mixture to a distilling operation."

The following statements are founded on my experiments made with a solution containing 1 per cent. of free KCy and 0.1 per cent., or \$603, gold per ton. When a chemical excess of sulphate of zinc is added to such a cyanide of potassium solution, a white precipitate of cyanide of zinc forms, which readily settles, and may be decanted or filtered. [If alkaline sulphides are present, they may be first removed by treating the solution by means of lead sulphate.] If less than an excess of zinc sulphate is added, the precipitate separates very imperfectly from the solution, and is difficult either to decant or filter. When the zinc sulphate contains a little free sulphuric acid, very little gold comes down with the zinc cyanide, and when an excess of the zinc sulphate is used, the precipitate separates in a manner leaving very little to be desired.

When the cyanide of zinc is acidified with sulphuric acid, and treated either, as I have already described, by pumping air through it, or by distilling it, the cyanhydric acid may be very completely recovered by collecting it with caustic potash. The latter may be entirely saturated without loss by using two vessels for condensation, the first receiving the saturated and the second a weaker solution.

A certain amount of gold will usually be found in the zinc sulphate-solution (as HAuCy_2). After crystallizing out the zinc sulphate to be used over again, the gold may be recovered from the mother-liquor by precipitation with sulphurous acid and copper sulphate, as before described. The amount of gold that comes down at this point seems to depend on the amount of free acid contained in the zinc sulphate. Sometimes only traces come down ; sometimes nearly half of that originally present in solution.

From the filtrate from the zinc cyanide precipitate the gold may be recovered by sulphurous acid and copper sulphate, or cuprous chloride direct, as already described.

This method of treating stronger solutions, such as 1 per cent., as would be used in treating rich gold-ores, leaves very little to be desired, working on a laboratory-scale. It is in

every way superior to that described by Prof. de Wilde, with sulphate of iron. Still, it may be questioned whether such a method could be carried out in a mining camp. There is one serious difficulty that it would meet. When the ore-solution contains ferrocyanide of potassium, as it is likely to do, a ferrocyanide of zinc forms, which is of the consistency of white lard. This substance is hard to settle, and practically impossible to filter. It is insoluble in acids, but easily soluble in alkalies or potassium cyanide. In the presence of this substance, the simple acidification of the solution, followed by the removal of the HCy, by circulating air through it and condensing in caustic potash, would probably be a more successful method of recovering the cyanide.

9. *Precipitation of Aurous Cyanide by Means of Zinc Chloride.*

An American patent has been taken out on this method by Frederick Rinder, June 18, 1895. In this method:

“The solution containing gold and silver in solution is first treated by iron sulphide, whereby the silver is removed as a sulphide; chloride of zinc is then added to the filtrate, whereby the gold is precipitated as a double cyanide of zinc and gold.”

I have also investigated this method. When chloride of zinc was made by boiling an excess of metallic zinc in hydrochloric acid till the action ceased, and this was added to a solution of potassium aurocyanide, nothing more than a trace of gold was precipitated. But when the chloride was formed by treating oxide of zinc with hydrochloric acid, the former in excess, so that one had in reality to do with a solution of oxychloride of zinc, 99.37 per cent. of the gold present was precipitated. It should be mentioned that both solutions of chloride of zinc had a slightly acid reaction to litmus-paper.

As, however, an excess of either acid or alkali dissolves the gold precipitate, this method must remain inferior to the method of precipitation as cuprous aurocyanide; for this precipitate seems almost absolutely insoluble in dilute sulphuric acid. The latter, therefore, possesses a sharpness and completeness that the zinc-method can never have.

10. *The Advantages of Precipitating the Gold by Means of Cuprous Salts.*

It must be evident to those who have followed the progressive

development of the cyanide-process that, as the method is better understood, the constant tendency is towards the use of more and more dilute cyanide-solutions. While in the beginning a solution of 1 per cent. was used, this was first reduced to one-half, then one-quarter, and finally to one-tenth, and even one-twentieth of 1 per cent. As the action of the so-called "cyanicides" contained in the ore is better understood and prevented, it seems not unlikely that the strength of the solution in potassium cyanide may be reduced to one one-hundredth of 1 per cent. or even lower. It should be remembered that much of the material treated by this process does not assay over \$3 per ton, or only half of one one-thousandth of 1 per cent. gold. So that a ton of solution of 0.01 per cent. potassium cyanide solution contains 30 times as much cyanide as is needed to dissolve \$3 worth of gold in a ton of ore.

The present methods of precipitation, the electrical and the zinc-shavings method, both find in these dilute solutions their great difficulty. In the electrical process the resistance of such solutions is something enormous. In the case of the zinc-shavings it is practically impossible to precipitate the gold from such a solution unless it contains one- or two-tenths per cent. free cyanide of potassium. This fact alone prevents the cyanide from being utilized to the best advantage.

In order that the cyanide should be utilized to the full, we should form the maximum of KAuCy_2 and leave a minimum of free KCy in the solution. This, as has been pointed out, is fatal to the precipitation by zinc-shavings. But it is just here that the cuprous method of precipitation comes into play most efficiently.

In the treatment of such solutions with a bare excess of potassium cyanide, there is no method of precipitation yet invented that can compete with it. In such a case there is not enough cyanide of potassium in the solution to bother about saving it.

The method of procedure would then be as follows: The solution would be made slightly acid by sulphuric or sulphurous acid, as might be most convenient. Then there would be added a copper sulphate solution with common salt, which had been saturated with sulphurous acid. This solution should be added until the filtered solution gives a red precipitate with potassium

ferrocyanide. The whole solution should be thoroughly stirred before this end-point is determined. A neat way to determine the end-point is to place a few drops of the stirred mixture on a double layer of fine filter-paper. On removing the upper layer, a drop of ferrocyanide of potassium will give a red precipitate of cuprous ferrocyanide on the wetted spot of the lower layer when the end-point is reached. This method avoids the delay of filtering the solution in the ordinary way. It would, of course, be best to determine the end-point beforehand, with a liter of solution, and then add the copper-salt to the mass of solution, after a preliminary calculation as to how much is required.

The solution should be allowed to stand for at least twelve hours, when it should be filtered. The filtrate should stand another twelve hours to see if any further precipitate forms; or it may be filtered first through CuS, to remove any suspended or dissolved gold, and then through old scrap-iron to throw down any copper-contents.

For the recovery of the gold from the cuprous aurocyanide, Prof. de Wilde suggests three methods as follows:

“First method: Roasting in a reverberatory furnace. One obtains thus a residue of gold and of oxide of copper (CuO). This latter is then dissolved in sulphuric acid diluted to 20° Beaumé (or in dilute nitric or hydrochloric acid), and the gold remains in the residue as pure gold.

“At the same time the sulphate of copper is regenerated, which will serve to precipitate the gold in subsequent operations,* and the same quantity of copper may continue to serve. Owing to the sharpness of the reactions, the loss of copper will be insignificant.

“Second method: Solution of the cuprous cyanide in dilute chlorhydric or nitric acid; there remains a residue of aurous cyanide which, after washing and drying, is decomposed by heat and pure gold is left behind.

“Third method: The precipitate is heated with 60° Beaumé sulphuric acid in a porcelain or iron pot; it is entirely decomposed, leaving a residue of pure spongy gold. After cooling water is added, the precious metal is washed by decantation, dried and melted. The copper has been transformed into sulphate.

“The first method appears to me the most rational, the roasting being attempted once or twice a month only. It is an inexpensive operation, and the sulphate of copper is thus regenerated.”

* “The sulphate of copper thus regenerated should be crystallized by cooling the solution, and the crystals drained from the adherent acid mother-liquor. A solution of sulphate of copper containing a notable quantity of sulphuric acid is not adapted to the precipitation of gold. The mother-liquors, after being strengthened by the addition of sulphuric acid, serve very well for the attack of the mixture of oxide of copper and gold.”

In this matter I agree with Prof. de Wilde. After being carefully dried the conversion of the cyanide takes place very quietly at a low red heat, and the spongy, porous, black residue readily dissolves in the sulphuric acid, leaving the gold very clean. Care should be taken not to alloy the gold and copper by a reducing atmosphere and too much heat.

A fourth method would be to dissolve both gold and copper cyanide in a strong KCy solution, and precipitate pure gold by the dynamo. With less than 2.5 volts and a strong solution of KCy this is possible, the copper remaining in solution.* This I have verified. All the objections to electrolysis apply, except that the bulk of the solution would be small, and it would be concentrated.

In many cases it would probably prove more advantageous for the reduction-works to ship this precipitate without attempting to reduce it, as the technical skill to do this occasional work is hard to get in mining camps.

The methods here outlined will certainly fail in the hands of those without chemical knowledge and engineering skill, and many unforeseen difficulties will probably have to be overcome before they can be utilized in practice. Nevertheless, I feel very confident that in some of the methods here outlined for the precipitation of gold by means of cuprous salts will be found the missing link in the chain of operations necessary to utilize the extremely dilute solutions of cyanide of potassium, which have been found effective in extracting gold from low-grade ores. If this should prove to be the case, and the usefulness of the method should be extended, particularly in California, my native State, I shall feel amply repaid for this long labor.

III.—THE TREATMENT OF ORES.

I have here reached the limit laid out for myself in the present paper. Still a few words on the application of the process to ores may not be out of place. In the first place, it should be said that the usual extraction from the South African tailings averages only from 60 to 70 per cent. While such results on low-grade products that can be treated in no other manner may be eminently satisfactory, they should be regarded as deci-

* H. Freudenberg, *Zeitschrift für Physikalische Chemie*, xii., p. 97, 1893.

dedly unsatisfactory for rich ores and concentrated sulphurets, assaying perhaps \$100 per ton or upwards. It is to the treatment of such products, particularly the latter, that I have given the most attention. Although at first I could obtain extractions at most averaging not more than 70 or 80 per cent., I was finally able to reach uniform extractions that were eminently satisfactory with quite a wide range of ores. Thus, with the concentrated sulphurets from the Idaho Mine, Grass Valley, assaying \$120 per ton, I began with 70 per cent. and finished with 98 and 99.45 per cent. With the Alaska Treadwell concentrates, assaying \$50 per ton, I began with 75 per cent. extractions, and finished by extracting all but a trace. In a lot of concentrates from the Bald Eagle Mine, Alaska, assaying \$280 per ton, I was finally able to extract up to 97 per cent. On the other hand, with a lot of sulphurets from the Bay State Mine, Amador county, California, assaying \$160 per ton, 90 per cent. is the best result yet obtained.

Each one of these ores demanded a long and painful study before these results could be obtained with any certainty, and there still remain some difficulties to be overcome before they can be reached on the large scale. Still there seems a strong probability that this will be accomplished. And while it is unlikely that the cyanide process will displace any of the standard methods of gold-extraction it will certainly supplement them where they are weak, and will perhaps enable low-grade ores to be worked that will not now pay for chlorination.

I cannot close without a warning to those who expect extravagant results from this method in the hands of persons utterly ignorant of chemistry. No process was ever introduced requiring a more thorough and subtle chemical knowledge, and without it success is absolutely impossible. But engineering skill and experience are also equally indispensable, and success can only follow where these agents co-operate to produce the final result.