from a photograph of crystals obtained by the spontaneous evaporation of a solution of the alkaloidal salt in ninety per cent. alcohol.

An examination of the resinous constituents of the plant is in progress, as well as a study of those of its constituents that are of interest to the vegetable physiologist rather than to the therapeutist.

A more extended report of this work is reserved for a future paper. Before closing this preliminary announcement, however, I wish to express my indebtedness to Dr. Wiley for much greatly appreciated assistance in the work, and to Dr. Brown for the aid that he very kindly rendered me in the preparation of the photographs used for the illustration of the article. I also desire to express my appreciation of the patience with which both Dr. Wiley and the gentlemen of the Bureau of Ethnology have awaited the progress of this work, which has been largely limited to spare moments not required by other duties.

WASHINGTON, D. C., May 11, 1896.

THE SULPHURIC ACID PROCESS OF REFINING LIXIVIATION SULPHIDES.[1]

BY FREDERIC P. DEWEY.

Received May 21, 1896.

THE time is fast approaching when more chemistry must be used in the extraction of the precious metals in the United States. The chief objections to chemical methods are the technical skill required in the management, the higher grade of labor necessary and the time required to turn out product, thus locking up large amounts of capital; but these difficulties are becoming less applicable all the time. Then too, the wonderful success attained in this country in extracting the precious metals by smelting with lead has retarded the application of chemical methods.

The chemical process of extracting silver by lixiviating, or leaching its ores with solution of hyposulphite of sodium, was introduced by von Patera in 1858, and has been variously improved, notably by the substitution of the calcium salt for

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the sodium salt. This process, however, had some serious disadvantages, the two most important being the necessity for a high degree of chlorination and the recovery of the precious metals in the form of sulphides.

In order to get a satisfactory extraction it was necessary to chlorinate thoroughly, and this was not always possible, especially in the presence of lime. Mr. E. H. Russell discovered, however, that the addition of a copper salt to the hyposulphite of sodium solution, resulting in the formation of a cuprous sodium hyposulphite, largely increased the solvent power of the solution for the ordinary silver minerals in ores, so that it was not necessary to roast with salt so carefully or so thoroughly; or, with equal care in roasting Russell's "Extra Solution," as it is called, will take out more silver than a plain hyposulphite solution. In other words, the use of the double hyposulphite increased the extraction of silver by the leaching process.

The Russell process can be applied to some ores without roasting, but in general the ores are roasted with salt. They are then charged into large vats and leached with water to extract soluble salts; they are then treated with a succession of hyposulphite solutions of varying compositions and strengths, according to the character of the ore, and are finally washed with water to displace the hyposulphite solution. The tailings are then run to waste. The various solutions carrying the precious metals are gathered up in large vats and precipitated with sodium sulphide. This produces a precipitate of sulphides of gold, silver, copper and a little lead. Most of the lead of the solutions is generally precipitated by a previous treatment with sodium carbonate.

The Russell process has also been applied with marked success to the tailings of other processes, such as amalgamation and the old process of lixiviation with plain hyposulphite. Under favorable circumstances, tailings can be lixiviated for $1.50 to $2.00 a ton.

The actual extraction of the silver by the Russell process reaches a high percentage of the total silver present in the ore. In one instance a mill treating nearly 23,000 tons a year averaged nearly ninety-four per cent. for the whole year. With tailings the extraction is not so high, being from fifty to seventy per cent.

Having brought the extraction of the silver from the ore up to a satisfactory figure there remains the question of dealing with the sulphide precipitate. For a long time this was admittedly the weakest point in the leaching process.

After going through all the operations of crushing, roasting, leaching and precipitating, the best we can say is that we have a rich concentrate, which requires further treatment to convert the precious metals contents into saleable forms.

It is true that these concentrates are often very rich and may even carry a higher silver percentage than the bullion produced by many amalgamating mills, or even by amalgamating the same ores, but the silver, as well as the other metals, are chemically combined with sulphur, and they are also in bad physical condition, being dry powders which are very susceptible to loss in handling, while their sampling and assaying present unusual difficulties.

The improvement in leaching, introduced by the Russell process and the success of this process has stimulated the development of processes for refining the sulphides. In the early days several processes of dealing with the sulphides were proposed and some of them tried more or less, but the business finally settled down to sending the sulphides to the smelters for treatment, although this was well known to be troublesome and expensive. In 1891 Mr. C. A. Stetefelt introduced at the Marsac Mill, Park City, Utah, an unpatented process which was built up out of the general fund of information available. The process consisted in matting the sulphides, grinding, roasting, grinding again and dissolving the copper out in dilute sulphuric acid, then melting the silver and crystallizing the bluestone. It did not yield fine bullion, but the bullion had to be refined as well as parted, besides there was some loss. This process was thoroughly tried at the Marsac Refinery, and then a year's run was made, the net results of which was that it did not prove sufficiently better than sending the sulphides to smelters.

In 1893 the Dewey-Walter Refining Company undertook the refining of the Daly sulphides in the the Marsac Refinery by the sulphuric acid process, upon which a United States patent has been issued to the writer. Naturally difficulties were encountered in starting a new process and much of 1893 was taken up in getting the process into smooth working order, but in 1894 a run was started in which all the regular sulphides produced by the Marsac Mill in 1894 were refined and thus a complete set of statistics of the operation of the process was obtained.

Broadly speaking the process consists of six main operations:

First. Boiling the sulphides with strong sulphuric acid in an iron pot.

Second. Dissolving out the sulphates of copper and silver in a lead lined tank, leaving a residue containing the gold and lead of the sulphides and also rich in silver.

Third. Precipitating the silver out of the filtered solution by copper plates.

Fourth. Sweetening, drying, pressing and melting the cement silver.

Fifth. Treatment of the solutions after the removal of the silver to crystallize the sulphate of copper and recover the excess of acid for reuse.

Sixth. Treatment of the gold-bearing residues.

The 1894 run of the Marsac Leacher produced 116,519½ pounds of regular sulphides, which were treated by this process. For convenience they were divided into twenty-five lots, mostly from 4,500 to 5,500 pounds in weight. As reported by the assayer of the Daly Mining Company, these lots varied in composition as follows:

COMPOSITION, DALY SULPHIDES FOR 1894.

	Silver. Ounces per ton.	Gold. Ounces per ton.	Copper. Per cent.	Lead. Per cent.
Maximum	11,127	14.8	32.9	0.2
Minimum	7,835	7.6	20.3	0.6
Average	9,827.4	11.225	27.17	0.33

The totals were:

Silver	572,544.4 ounces.
Gold	646.1 "
Copper	31,585.3 pounds.
Lead	385.6 "

THE PLANT.

The plant required is simple and all of it is well known. It is easily managed and no especially skilled labor is required. It consists of two ordinary iron pots, such as are used in parting bullion; a series of twenty-one lead-lined tanks for dissolving, filtering the solutions, precipitating the silver and filtering off and sweetening the cement silver, together with crystallizers to recover the bluestone, and evaporators to concentrate the mother liquors for reuse in the pot; a dryer and press for the cement silver; furnace for melting the bullion; four storage tanks for acid; and pumps for handling the liquids. The large pot for boiling the sulphides is forty-six inches in diameter and three feet deep. It is hung by its rim on a cast iron plate and is enclosed in brick work over a fire-box. It stands fourteen feet from the floor and is provided with a suitable hood and stack to take off the fumes. The smaller pot is used for boiling the residues. The tanks are arranged in steps to allow the descent of the solutions from one to the other by gravity.

THE PROCESS.

The process consists in boiling the sulphides in strong sulphuric acid to convert the sulphides into sulphates. The sulphate of silver is soluble in strong sulphuric acid, but the anhydrous sulphate of copper is practicably insoluble. Owing to the large percentage of copper, averaging twenty-seven per cent. in 1894, in the sulphides a large quantity of insoluble sulphate is produced, and this is one of the most serious difficulties of the process. After boiling the charge is removed to the dissolving tank, in which are put wash water and weak solutions. Here the copper sulphate goes into solution along with the silver. The solution is filtered into the precipitating tanks where the silver is precipitated by metallic copper, after which the solutions are concentrated and go to the crystallizers to recover the bluestone. Periodically the cement silver is removed to the filter, sweetened, dried, pressed and melted. The mother liquors are concentrated, crystallized and the recovered acid finally sent back to the pot. The residue in the dissolving tank is taken out, washed somewhat and reboiled in acid to remove as much as possible of the silver that it contains.

PRACTICAL OBSERVATIONS.

A charge of about 975 pounds is put into the pot in the morning with about 1,000 pounds of 66° acid and thoroughly mixed and the charge heated. At first the reaction is rather violent; sulphur dioxide is copiously evolved and the fumes carry considerable sulphur, which gives them a yellowish color. At this stage a steam jet may be required to increase the draught. After a while the reaction settles down and the normal charge boils quietly until near the end. As soon as the charge gets stiff, more acid, about 100 pounds, is added, until about 3,000 pounds have been added. Toward the end, evaporated acid is used. As the boiling goes forward anhydrous sulphate of copper is formed in large quantities which separate, forming granular masses. This necessitates frequent stirring of the charge and this in turn is hard on the pots. A net-work of cracks develops and finally the acid finds its way through, when the pot must be replaced. In the 1894 run nine pots were used, two of which were short-lived. Better results have been obtained since.

The progress of the operation can be watched by taking out a small sample of the charge, treating with water and adding hydrochloric acid to the solution ; but this is not necessary after getting familiar with the process, since the color changes from black to brown or dark gray. About ninety per cent. of the total acid used is added before the charge begins to show soluble silver salts. Then the charge foams violently and must be constantly stirred while the fire must be lowered. In about an hour the foaming is over and the charge is finished. This usually occurs in the afternoon of the day after starting. On the second morning the charge is warmed up, generally with the addition of some acid and, as it is rather thick, it is ladled out into a trough which delivers it to the dissolving tank. The pot is then started on a new charge.

The dissolving tank is filled with cold water within six or eight inches and tightly covered, since the introduction of the charge generates much heat. After the charge is in, the cover is raised and the solution stirred with a paddle and boiled with steam, after which it is settled and drawn into the filters. The first tankful of solution contains most of the copper. It is run into a small precipitating tank and kept separate from the rest of the solution. The charge now resembles thick white mud and is washed eight or ten times with weak acid solutions to remove the silver, after which the residue is thrown into a filter. This residue varies very much, running from 5,000 to 19,000 ounces silver per ton and fifty to 100 ounces gold, the balance being mainly sulphate of lead.

The filters are three to four inches of clean quartz sand on a foundation of lead plates, cocoa matting and asbestos cloth, resting on lead strips, giving a space below. It is impracticable to settle all the very fine residue in the dissolving tank, so some of it passes over into the filters and chokes them up. In about two weeks the filters must be washed by a stream of water from below and the muddy water pumped off the top.

The solution has a reducing action and immediately a separation of metallic silver begins in the dissolving tank, often with the formation of beautiful growths upon the surface of the liquid, and this reaction continues in the filters. By this reaction metallic silver is found in the first residue and some 10,000 ounces may accumulate in the filters during a year's run.

From the filters the solution goes to the precipitating tanks, where the silver is precipitated by copper, cathode plates from an electrolytic refinery being used. The first or copper solutions require a long time to precipitate, sometimes eighteen hours, but ordinary solution is precipitated in four to five hours. During precipitation the solution is stirred by air and heated by steam. When the precipitating tank is cold and the hot solution of silver sulphate runs in, there may be a separation of silver sulphate which may go into the solution again as the solution is heated up, but some of it may also remain with the cement silver and be removed in washing the silver, in which case the wash water must be treated with copper.

When about 20,000 ounces of cement silver have accumulated in the precipitating tanks, it is removed to the sweetening tank and washed with hot water and then with acidulated hot water until the ammonia test shows no copper, which takes about fifteen hours. The wash water runs through a guard tank containing scrap iron and then to waste.

The sweetened silver is put into sheet iron pans and dried about twenty-four hours in a steam dryer, pressed into cakes, dried again and melted. In 1894 the melting was done in crucibles holding about 2,400 ounces, or two bars, and about a pound and a half each of borax and niter were used to a crucible. The melted silver was poured into heated and greased light cast steel moulds. After pouring a little sugar was thrown on the liquid silver and the mould covered by a tight fitting cast iron cover. This gives a very smooth surface to the bar. When cool the bars are hammered up and marked. The average fineness for 1894 was 999.4 silver with no gold, 446 bars were shipped, of which 401 were 999.5 fine and forty-five were 999.0 fine.

The bluestone solutions are concentrated to about 35° to 37°B, and run into ordinary crystallizers provided with lead strips and allowed to stand two days or more, when it is pumped back to the evaporators and run up to 42° B. It goes back to the crystallizers, and a crop of crystals containing iron and but little bluestone is obtained. The solution goes back to the evaporator. The crystallizers are filled with cold water, which dissolves most of the iron and only a little of the copper. This solution goes through the guard tank to waste. These bluestone crystals are very small, but answer well in the leacher in preparing extra solution. The mother liquid is brought up to 50°–52° B. and then allowed to stand in a crystallizer several days to separate iron. It is then pumped to storage tanks for use in the pot. While concentrating, considerable iron separates in the evaporators. Periodically this is washed out and the solution run to waste through the guard tank.

After boiling five charges of sulphides, about 750 pounds of wet residue are obtained. This is put into the pot and boiled with a little more than its own weight of acid, after which it is washed and the final residue dried. This residue is very complex in composition, although it is mainly sulphates of silver and lead. There appears to be some acid sulphate, for the sulphuric acid present is far more than sufficient to form normal sulphates, and yet the sample is so dry that the excess of acid cannot all be free. It contains the gold of the sulphides. During 1894 this residue was shipped away to the smelters for treatment, but at the present time it is being melted on a hearth.

SUPPLIES.

Sulphuric acid is received at the refinery in iron tank cars holding 40,000 to 50,000 pounds. It is stored in two lead-lined wooden tanks and is elevated by a mountejus to two iron receivers above the level of the pots from which it is drawn to feed the pots. In the 1894 run 389,439 pounds were used, being an average of 3.34 pounds per pound of sulphides treated, or 0.68 pound per ounce of silver. Copper to precipitate the silver is used in the form of cathode plates, and 16,832.5 pounds were used, one pound of copper precipitating 2.27 pounds of silver, or 33.1 troy ounces. The ordinary local coal is used and 159,000 pounds were used in the 1894 run. The regular labor required was a superintendent and two men, with an extra man to assist the superintendent in melting bullion. Occasionally some extra labor was required, particularly in shipping residue and making the annual clean-up. Mechanics were also required for special work occasionally, but the lead burning was done by one of the regular men.

RETURNS.

It is a well known fact that, in assaying, some of the precious metals pass into the slag, and some are absorbed by the cupel, causing a loss in the determination. In the case of ordinary ores, this quantity per ton is generally small, although the percentage of the total silver is large. In the case of rich materials, however, the percentage is low and the actual quantity per ton becomes considerable, and when the rich material carries copper the loss of silver per ton becomes quite respectable. In our business transactions, the sulphides are always settled for upon an assay corrected for slag and cupel absorption, which shows from 100 to 200 or even more ounces per ton more than ordinary uncorrected assay shows. Even on the corrected assay the actual amount of silver returned by the refinery on the year's work was 2,078.81 ounces more than the assays called for, showing very plainly that even the corrected assays do not show all the silver really present. This silver was divided as follows:

116,519.5 pounds sulphides contained 572,544.45 fine ounces of silver.

PRODUCT RETURNED.

	Fine ounces silver.	Per cent. total silver.
Fine bullion, free from gold	551,329.89	96.29
Residue	15,773.41	2.79
Cleanings	5,328.87	0.93
On hand	2,191.09	0.38
Total	574,623.26	100.36
Plus clean-up	2,078.81	0.36

All weights of sulphides and products, excepting one covering less than 200 ounces, and all the assays are the originals made by the Daly Mining Company.

It is regarded as an extraordinary showing for a chemical process on the large scale to recover more than the best assay possible calls for.

As to the recovery of gold, I cannot see any reason why it should not equal the silver recovery, but the figures upon the point are not satisfactory. The actual return of gold for the year was 606.9 ounces. The original assay of the Daly Mining Company called for 654.8 ounces, but their re-assay on some of the samples reduced this to 646.1. This left an apparent shortage in the returns of 39.2 ounces. The same samples were assayed by Mr. Charles Earl under my directions, and while the silver result showed a satisfactory agreement with the Daly assays, yet his gold determinations called for only 602.9 ounces, showing a plus clean-up on the year's work of four ounces. After the close of the year's business a general sample was prepared by taking proportionate weights of each of the check samples of the twenty-five lots, and the Daly Co.'s assay of this sample called for 605.9 ounces, and showed a plus clean-up of one ounce. Mr. Earl is no longer with me, so I cannot add his figures on this sample. There are especial difficulties in determining such small quantities of gold in the presence of so much silver.

The conditions of the process are such that I do not see how we could gain so much on the silver and lose on the gold, so that I am satisfied that the process practically recovers all the gold that goes into the operations, although the assays may not always show this.

The bluestone produced amounts to 175,809 pounds, or 3.63 pounds per pound of copper, including the copper in the sulphides and the copper used to precipitate the silver. About 125,000 pounds of bluestone were used by the leacher in preparing extra solution, leaving 50,000 pounds to be sold to outside parties. No particular care is taken to prepare fine large crystals of bluestone, and it is not necessary to purify the solutions from iron except as above described. Most of the bluestone produced goes to the leacher and the size of the crystals is of no moment whatever, while the small amount of iron present does no harm. The best grade showed 0.34 per cent. of protoxide of iron, the medium 0.69 per cent., and the worst, of which only a small quantity was produced, 3.89 per cent.

THE FOLLOWING TABLE SUMMERIZES THE STATISTICS FOR THE YEAR BY THE DEWEY-WALTER PROCESS OF BOILING RUSSELL SULPHIDES IN STRONG SULPHURIC ACID.

First charge of 1894 sulphides to pot, February 20, 1894.
" " " 1895 " " " February 27, 1895.
Sulphides treated, 116,519.5 pounds.
" contained silver by corrected assay, 572,544.45 ounces.
" " copper, 31,585.3 pounds.
" " lead, 385.6 pounds.
" " silver average ounces per ton, 9,827.44.
" " copper average per cent., 27.1 per cent.
" " lead average per cent., 0.33 per cent.
Acid used, 389,439 pounds.
" " per pound sulphides, 3.34 pounds.
" " per ounce silver, 0.68 pound.
Coal, 159,000 pounds.
Copper used to precipitate silver, 16,832.5 pounds.
Total copper, 48,417.8 pounds.
One pound copper precipitated silver, 2.27 pounds.
Bluestone produced, 175,809 pounds.
" " per pound copper, 3.63 pounds.
Regular labor, superintendent and two men.

Extra labor, one man at bullion melting to assist superintendent, laborers for clean-up and shipping residue, etc., mechanics for special work occasionally.

136,519.5 pounds sulphides contained 572,544.45 fine ounces of silver.

PRODUCT RETURNED.

	Fine ounces silver.	Per cent. total silver.
Fine bullion, free from gold·······	551,329.89	96.29
Residue·····························	15,773.41	2.76
Cleanings···························	5,328.87	0.93
On hand·····························	2,191.09	0.38
Total··············	574,623.26	100.36
Plus clean-up······················	2,078.81	0.36

All weights of sulphides and products, excepting one covering less than 200 ounces, and all the assays are the originals made by the Daly Mining Company.

The advantages of this process are the phenomenal percentage of silver recovered, and that it is an entirely liquid one from beginning to end, so that there is no loss from handling dry products. There is no roasting to cause loss. A large percentage of the silver is recovered as very fine bars, ready to enter the market. It is so simple and so easily carried out, and the plant is so small and inexpensive that it can be installed at individual leaching works.

Finally, the cost of operating is small; in fact, the value of the bluestone recovered returns a large proportion of the operating expenses.

NOTES ON THE ELECTROLYTIC DETERMINATION OF IRON, NICKEL AND ZINC.

By H. H. Nicholson and S. Avery.

Received May 15, 1896.

THE experimental part of this work was undertaken in the spring of 1892. During the progress of the work various articles on the electrolytic deportment of these metals have been published. Some of these investigations are closely related to those carried out by us. As, however, they differ in some important particulars and as some observations have been made which, so far as we are aware, have not as yet been reported, it