

PRECIPITATION OF COPPER

from Dilute Solutions Using Particulate Iron

by A. E. Back

In the search for lower cost methods of recovering copper from mine water, the use of sponge iron or particulate iron (as distinguished from iron powder used in powder metallurgy) as precipitants in place of tin cans, detinned scrap iron, or scrap iron is an intriguing possibility. The relatively faster copper precipitation rate obtained with particulate iron as compared to scrap iron promises economic and processing advantages when and if particulate iron becomes competitive cost-wise with available scrap iron. Kennecott has developed a precipitation cone,¹ Fig. 1, utilizing various particulate iron precipitants and has successfully demonstrated it in a prototype at a rate of about 1000 gpm of solution.

Initially, sponge iron produced at the Ray Mines Division for use in a leach-precipitation-flotation process was used in exploratory tests to develop a suitable apparatus to take advantage of the rapid precipitation rate and efficient iron utilization for the recovery of copper from dilute solutions. Here it was demonstrated that when sponge iron was added to a launder, the particles of iron collected in the bottom of the launder and tended to cement together. This resulted in incomplete precipitation of the copper and inefficient utilization of the iron.

Next, sponge iron was suspended in glass columns to study the dynamics of the precipitation reaction. Again it was observed that the particles tended to cement together at low solution flow rates while at higher flow rates large amounts of the precipitant overflowed the column resulting in loss of precipitant and an inefficient process.

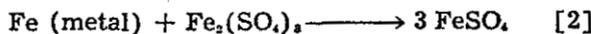
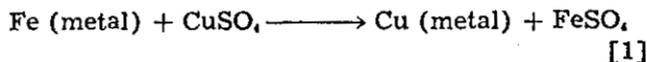
The next step was to suspend the precipitant in an inverted cone in a rising column of solution. We were successful: dynamic suspension of the solids was maintained at reasonable flow rates and the copper precipitation rate was rapid and complete with improved iron utilization. The first tests were conducted on a batch basis, and it was determined that a dynamically suspended bed of precipitant was necessary for satisfactory operation. More than 99% of the metallic iron could be converted to metallic copper by careful control of the residence time in the cone, and copper precipitation was essentially complete even when the available iron was almost depleted.

Several cones were built ranging in capacity from 1 to 200 gpm of feed solution, and finally a prototype

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cone was constructed which was 20 ft high and 20 ft in diameter with a capacity of 1000 gpm of solution. Tonnage samples have been evaluated in the prototype cone to confirm the results of small scale cone tests. We now have sufficient confidence in the small scale cone precipitation tests to predict the effectiveness of a precipitant using 10-lb samples in a series of amenability tests.

The following competitive reactions occur in the precipitation of copper from dilute acid solutions using metallic iron as the precipitant:



Reactions [1] and [2] proceed almost simultaneously in the cone precipitator followed by reaction [3]. In the solutions we have studied, the bulk of the iron is used to precipitate copper because of the relatively small concentration of ferric iron present. Because of the intimate contact in the cone between the metallic iron and the solution, copper precipitation is complete with less neutralization of the acid [3] by the iron than in a conventional launder plant. Thus, the cementation reaction is more efficient with respect to iron consumption and an iron factor (weight ratio of iron consumed to copper precipitated) approaching more closely the theoretical value of 0.9 is obtained. In addition, advantage is taken of reaction [3] to monitor the course of the precipitation reaction [1] by measuring the change in the rate of hydrogen evolution. Hydrogen evolution decreases as the amount of available metallic iron is diminished, and provides a sensitive measure for process control

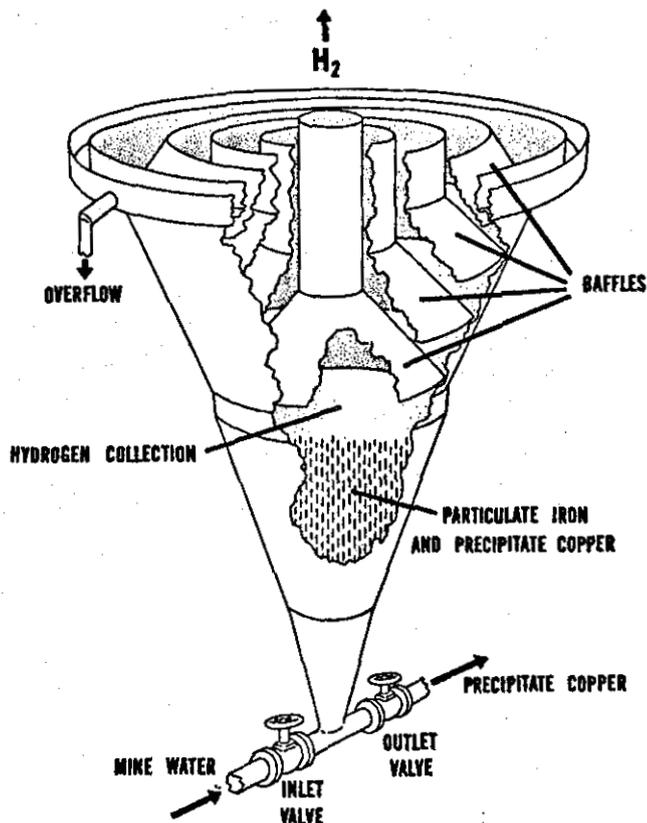


Fig. 1—Relationship of baffles to distribution.

batch of precipitant to the cone, with continuous discharge of barren solution at the overflow and intermittent discharge of the precipitates from the apex of the cone, was found to be most desirable.

During the period of this investigation, some fourteen different samples of particulate iron from various companies and individuals have been evaluated as copper precipitants. Various samples of directly reduced iron, iron powder, iron turnings and chips, and granulated iron have been tested. Pertinent analyses are given in Table I.

Table I—Typical Analysis of Particulate Iron Samples Tested and Grade of Copper Precipitate, %.

Analysis		Reduction	Calculated Grade of Copper Precipitates with 0.9 Iron Factor
Fe (Metal)	Fe (Total)		
97.6	99.2	98.4	97.8
96.0	97.1	98.9	96.4
93.8	94.4	99.4	94.4
93.8	96.0	97.7	94.4
93.0	98.0	94.9	93.7
92.0	94.4	97.5	92.8
86.8	90.7	95.7	88.0
86.6	93.0	93.1	87.8
83.6	97.4	85.8	86.6
79.4	87.5	90.6	81.0
65.4	83.4	78.4	67.7
55.2	71.6	77.1	57.8
48.8	64.2	76.0	51.4

The samples contained variable amounts of copper, sulfur, carbon, and silicon which are not listed. The grade of precipitate theoretically recoverable is shown graphically in Fig. 2 with theoretical 0.9, 1.5, and 2.0 iron factors. The presence of a significant quantity of copper in the precipitant would result in an increase in the grade of the precipitate.

In general, each of the particulate iron precipitants is satisfactory for the recovery of copper from dilute solutions in a precipitation cone. The dense iron samples require finer grinding, i.e. to minus 35 mesh, than do the spongy iron samples, which are suitable if ground to minus 10 mesh. An excessive amount of minus 200 mesh material is undesirable because this favors reaction [3] slightly over reaction [1]. However, as long as the bed of precipitant is maintained in dynamic suspension by adjusting the rate of solution flow into the cone, variations in particle size can be accommodated and reaction [1] is favored. A high degree of reduction of the iron precipitant is desirable because of the resultant high grade precipitate. However, the cost of obtaining such a precipitant often prices it out of the market, and a compromise between reduction costs for the precipitant and smelting costs for the precipitate must be resolved.

The prototype cone that is now in operation at the Utah Division precipitation plant and is equipped with a variable speed feeder so that the precipitant feed rate can be varied to meet the requirements of the process. The facility is automated so that the progress of the consumption of the available iron can be followed by the decrease in the evolution of hydrogen from the reaction



As the hydrogen evolution decreases and comes to a predetermined low value, a system of valves be-

30-sec to precipitate from the lower portion of the cone. Then, the valve closes and fresh iron is fed into the cone simultaneously with the influx of fresh copper-bearing solution. The precipitates are filtered and then transferred to a conveyor for subsequent treatment.

Channeling of the hydrogen or reaction gases toward the center of the cone into a central exhaust system is essential because particles of copper adhere to the hydrogen bubbles and, if they are near the overflow of the cone, the particulate copper is transported into the tailings. Thus, it is necessary to install a battery of baffles in the upper part of the cone to divert the gas towards the center, and allow the bubbles to burst and release the particulate copper to settle back into the bed. As this copper settles back into the apex of the cone, it is subjected to attrition and peening so that it is necessary to discharge the bed of the cone periodically. This prevents attrition of the particulate copper to form a colloid, which would not settle and would report as a loss in the tailings overflow.

It has been found that to obtain the best operation of the precipitation cone on a batch-continuous basis, approximately 50% of the iron requirement should be fed into the cone during a five-min time interval. The remainder of the iron is fed during the next 15-min period at a gradually decreasing rate. In this manner, a bed is built rapidly within the cone so that effective fluidization of the particulate iron and efficient utilization of the metallic iron as a copper precipitant are obtained. Under these conditions, the competing reactions between copper, acid, and metallic iron are regulated, the precipitation reaction being favored over the iron dissolution-hydrogen evolution reaction. In this manner, the pH range of the effluent solution in a precipitation cone is from 2.5 to 3.0 pH (while in a conventional launder plant it might range from 3.0 to 3.5 pH).

ADVANTAGES OF PARTICULATE IRON

The advantages of a cone precipitation plant over a launder precipitation plant are many. For example, a cone precipitation plant capable of treating 10 million gpd of solution would require an area of 10,000-sq ft, whereas a launder plant similar to the Utah precipitation plant at Bingham Canyon would require an area approximately ten times as great. Handling of the precipitant is time consuming in a launder plant because of the large bulk per unit weight of iron. The bulk density of the particulate iron samples varies from approximately 75 to 200 lb/cu ft, and the material is free flowing so that it can be handled with conventional materials handling equipment. In a cone precipitation plant, the copper precipitates are discharged automatically into a filtration system while in the launder plant the precipitates are washed manually from the launders. We have found generally that the iron efficiency in the cone plant is superior to the launder plant. In fact, in treating similar solution through the launder plant and through the prototype cone, it was found that savings of 0.5 to 1.0 lb of iron per lb of copper could be realized. In addition to this saving in iron, essentially all of the soluble copper is precipitated from the solutions

so that a circulating load of dilute copper solution to the leaching system is eliminated.

In the operation of the prototype precipitation cone, it has been demonstrated conclusively that the decrease in the rate of hydrogen evolution is a sensitive indirect measure of the completeness of the precipitation reaction which can be used for process control. The only chemical analyses required are for accountability because of the completeness of the precipitation reaction within the cone. Another advantage in collecting the hydrogen in a central exhaust system is that operation is under a slight pressure of nascent hydrogen, which seems to accelerate the copper precipitation rate and to prevent reoxidation of iron.

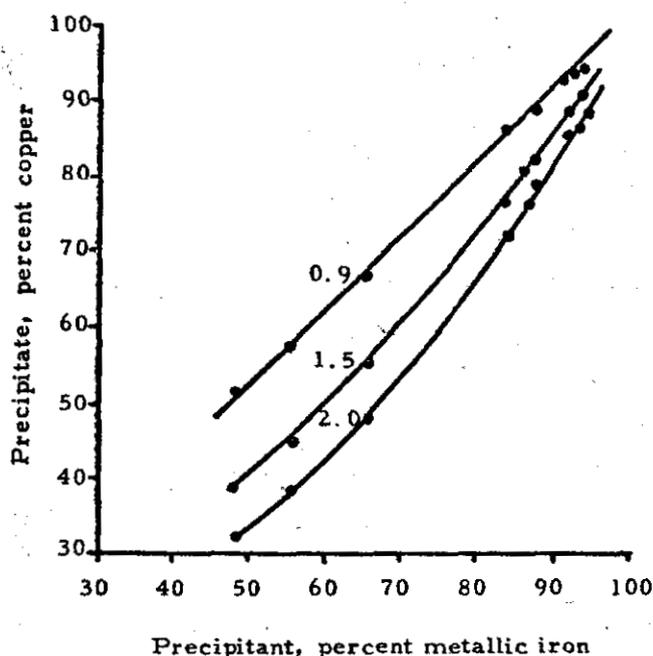


Fig. 2—Relationship at different iron factors.

It is interesting to note that when particulate iron is used as the precipitant, copper recoveries from solution are in the range of 95% before a bed of dynamically suspended precipitant is established and, after the bed has been established, recoveries of more than 99% are common regardless of the type of precipitant used and the amount of metallic iron available for precipitation. Thus, it is possible to precipitate 99% of the copper even when less than one % metallic iron is available in the partially spent precipitant, which insures excellent iron efficiency.

After a batch of precipitant has been added and is essentially utilized, a system of valves is actuated. The solution flow continues and the precipitate that collects in the lower portion of the cone flows out of a valve into a receiving tank, from which it flows by gravity into a filter. The precipitate slurry is dewatered in a filter from approximately 15% to 50-60% solids. The filter cake is then discharged as a moist cake onto a conveyor for the next step.

SOURCES OF PARTICULATE IRON

Sponge iron produced by the direct reduction of magnetite concentrates, iron ore, or pyrite cinders may be considered as sources of high-grade reactive precipitants. Some 10 different sources of this directly-reduced iron have been made available for testing at the Research Center and at the Utah Cop-

per Division in the prototype cone. All of these precipitants were found to be suitable for the process. Factors of cost and tonnage availability remain to be resolved before any of these are used as the source precipitant. Commercial high-purity iron powder is also satisfactory; however, the cost of such a precipitant is not competitive with other indicated sources. Detinned scrap or burned tin cans are suitable precipitants for launder plants or for the cone precipitator described by Spedden, Malouf, and Prater.² Because of the necessity of keeping the entire bed of precipitant in dynamic suspension and maintaining a clear overflow, it is not possible to suspend large pieces of scrap iron satisfactorily. Cast iron or steel chips have been considered a potentially inexpensive source of precipitant; however, they are covered with grease and are relatively coarse. Degreasing of the chips and grinding them to approximately 35 mesh is required to prepare them for use in the precipitation cone, thereby adding to the cost of iron. This procedure has also been tested in the pilot plant.

At the present time, Kennecott is investigating the recovery of a suitable precipitant from reverberatory slag. Selective reduction of the slag with coke and pyrite yields a metallic product that is relatively brittle. Products of varying composition have been tested in the prototype cone, and again it was determined that this type of iron is a suitable precipitant with the same favorable characteristics of copper precipitation and iron utilization as the other iron samples that have been evaluated. Several potential producers of directly-reduced iron have graciously supplied samples, some of which were tonnage samples for evaluation in the prototype cone.

Other smaller samples have been evaluated in a cone precipitator with flow rates of about 1 l/min. In these small scale tests, fluidization characteristics of the particulate iron samples are determined and the particle size of the precipitant is evaluated. Generally it is necessary to have a particulate iron of minus 35 mesh size. However, when sponge iron is used and a spongy product with a relatively high specific surface area is used, a 10 mesh product is satisfactory.

SUMMARY

At the present time, a prototype precipitation cone is being operated. The goal is to establish operating parameters and to develop engineering data for the installation of a 400,000 lb per day copper recovery cone precipitation plant that will use particulate iron as the precipitant. Simultaneously, an economic source of iron precipitant is being developed.

Several potential suppliers have submitted samples that are satisfactory; however no contract has been signed. Current scrap iron prices are more than competitive. In addition, Kennecott is now evaluating the process mentioned previously—that for recovering iron precipitant from copper reverberatory slag. Since this is a captive source it would obviate the requirement of outside supply.

REFERENCES

- 1 A. E. Back, K. E. Fisher, and J. Kocherhans: "Process and Apparatus for the Precipitation of Copper from Dilute Acid Solutions," U. S. Patent 3,154,411, October 27, 1964.
- 2 H. F. Spedden, E. E. Malouf, and J. D. Prater: "Use of Cone-Type Copper Precipitators to Recover Copper from Copper-Bearing Solutions," *Mining Engineering*, 1966, Vol. 18, pp. 57-62.