

Zinc-Dust Precipitation Tests

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THE use of zinc dust for precipitating the precious metals from cyanide solutions is well established now in many places, and has many advantages over the shavings method of precipitation. Although much work has been done on methods of testing zinc dust, as yet no absolutely positive test has been devised to determine the value of the material. Certain facts are known, but often it happens that results on a working scale are not as expected from the laboratory tests. The purpose of this paper is to record some observations made while testing a large variety of zinc-dust samples in the laboratory.

W. J. Sharwood¹ has described standard analytical methods, which have been followed, with the changes noted. The regular determinations include zinc oxide, by solution in ammonia and ammonium chloride, lead, and precipitating efficiency. In some cases cadmium was determined by a method similar to that described by J. E. Clennell.² I will discuss the precipitating-efficiency test in detail. The procedure is as follows:

"A solution of potassium silver cyanide is prepared by dissolving 10 grams of silver cyanide (AgCN) and 5 grams of '99%' potassium cyanide in a little water and diluting up to 1000 cc. It is then adjusted by addition of a little more KCN or AgCN until the solution indicates from 0.12% to 0.15% free KCN by titration with standard silver nitrate. The titration is best made by using a 10-cc. or 20-cc. sample, adding 1 cc. of 2% potassium iodide, and a slight excess of ammonia, as the end point is then sharper. Or 15 grams of pure crystallized KAg(CN)₂ may be dissolved in a liter of water and 1.5 grams KCN added.

"Weigh out 0.5 gram zinc dust into a 300-cc. beaker. Add a few cubic centimeters of water and stir until zinc is well mixed, then pour in 250 cc. of the prepared solution, stirring vigorously. See that all lumps are broken up, and continue stirring for fully five minutes. Stir occasionally (at least every 10 minutes) until the end of two hours from the addition of the solution. Then filter upon an 11-cm. filter, wash precipitate thoroughly, sprinkle with test lead, wrap it carefully in the paper, place in a scorifier with about 20 grams test lead, burn paper cautiously in muffle, scorify five minutes, cupel at low temperature and weigh silver. Milligrams silver obtained from 0.5 gram zinc \times 0.0606 = percentage precipitating efficiency."³

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¹ *Journal of the Chemical, Metallurgical and Mining Society of South Africa*, vol. xii, No. 8, p. 332 (Feb., 1912); reprinted in *Engineering and Mining Journal*, vol. xciii, No. 19, p. 943 (May 11, 1912).

² *Engineering and Mining Journal*, vol. xcvi, No. 16, p. 793 (Apr. 19, 1913).

³ W. J. Sharwood, *loc. cit.*

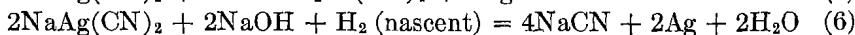
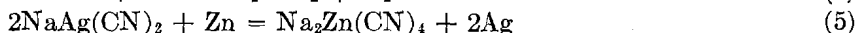
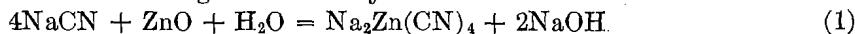
Recently I substituted the equivalent of sodium cyanide for the potassium cyanide, with no variation in the results.

A test was made with a gold solution that was equivalent to the standard silver solution. The efficiency shown was one-third to one-half that with the silver solution, in different trials. In one set of experiments a mixture of these gold and silver solutions in equal parts was used. The beads obtained were parted, and were found to contain about four atoms of silver to one of gold. The calculated efficiency was intermediate between those obtained with gold alone and silver alone, being somewhat higher than the average of the two values. This agrees with the fact that in practice gold is more difficult to precipitate than silver.

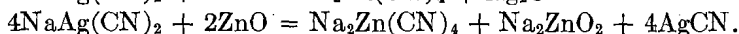
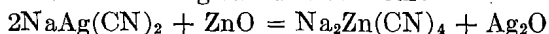
The following observations were made in the course of my experiments: Slight variations in the free cyanide present in the precipitating solution affect the results very little. However, if the free cyanide is reduced materially, to about 0.01 per cent., the results are very different. Tests agitated for short periods indicate that the rate of precipitation is much slower. In some cases exposure of the zinc to moist air for several hours so as to increase the oxide present seemed to increase the efficiency, although the amount of metal present in 0.5 g. was less. Also, in some cases, the addition of a little freshly ignited zinc oxide to the solution at the start of the precipitation increased the amount of silver precipitated. This seems to be due to the action of the oxide on carbonates in the solution. In this solution of low cyanide strength there is not enough free cyanide to dissolve all the zinc oxide, and the excess of zinc oxide would react with the alkali carbonates introduced from the cyanide used, forming zinc carbonate and caustic alkali. It is well known that the presence of caustic alkali in a solution increases the rapidity and completeness of precipitation.

As the solutions in practice are ordinarily free from carbonates, containing their alkali as lime, the standard method of preparing the silver solution was altered as follows: The solution is made up to double strength in silver. After adjusting the cyanide strength to about 0.2 per cent. NaCN, a slight excess of lime water is added to convert carbonates into hydroxides, and the solution filtered. It is then made up to the final volume, and tested for protective alkalinity. If this is not equivalent to about 0.01 to 0.015 per cent. NaOH, the solution is adjusted by the addition of a little acid. I have never found the alkalinity lower than desired, due to the alkali present in the cyanide as impurity. Although this adds to the work of preparing the solution, it is worth the trouble, as the results are more uniform, and come nearer to actual practice. Slight variations in the solution, such as the addition of neutral salts and changes in temperature, have much less effect than with the old standard solution.

The following reactions may occur:



The following two do not occur:



For all practical purposes, reaction (5) may be taken as the important one, whether it takes place by itself, or with (3), (4), and (6) as intermediate stages. Reactions (1) and (2) consume cyanide and alkali, interfering with (3) and (4), and thus indirectly interfering with (6). The free cyanide and alkali in the standard solution are sufficient to take care of more oxide than is usually found in zinc dust.

As precipitation is always better in the presence of reasonable quantities of cyanide and alkali, and is electrolytic in its nature, the addition of neutral salts as noted above would affect the solutions of lower cyanide and alkali concentrations much more than the standard solution. It is also well known that chemically pure zinc is very much less active than zinc containing a reasonable amount of metallic impurities. I will touch briefly on the common impurities.

Impurities in Zinc Dust

Zinc Oxide.—Zinc oxide is always present, varying from under 5 per cent. to over 20 per cent. Unless zinc dust containing over 15 per cent. of the oxide is unusually efficient for other reasons, it should be condemned, as the oxide only dilutes it and consumes cyanide. The oxide can rarely be seen in any quantity, even under the microscope, but the indications are that it occurs as a film on the surface of the particles, or in minute pits on the surface. It is present, sometimes in considerable quantities, in the small amount of coarse material, as well as in the finest part of the dust, so it cannot occur as separate grains disseminated through the mass of the zinc.

In regard to the oxidation of zinc dust during handling, in dry air it is practically negligible. In some tests, exposing a layer about $\frac{1}{2}$ in. deep to dry air, with occasional stirring, for several weeks, the oxide was increased only a very few per cent. On the other hand, in moisture-saturated air the oxidation may be very rapid, amounting to as much as 2 or 3 per cent. per day, but the rate falls off as the oxidation goes on, presumably due to the protection of the particles by a film of oxide. Exposure of a fairly large surface, however, for a reasonable time, does

not reduce the efficiency of the zinc as much as is commonly supposed, as only the surface layer would be oxidized, and to only a small extent. In a few cases exposure for a few hours seems to be of advantage, as will be explained later.

Metallic Impurities.—The only metallic impurities of any importance are lead and cadmium. In the samples I have examined, the lead varies from almost none to about 5 per cent., and cadmium from none to about 4 per cent. Both are probably present as metal alloyed with the zinc, as they are less easily oxidized than zinc. I know of no simple way to prove this point, but it seems self-evident in the case of lead. In the case of cadmium, a rapid extraction with the ammonia-ammonium chloride solution used for dissolving zinc oxide dissolves no cadmium, but metallic zinc would precipitate cadmium from this solution, if any were dissolved.

The nature of alloys of cadmium and lead with zinc has not been studied by modern metallographic methods, but the following statements can be made: It is known that lead is slightly soluble in zinc, and on cooling, about 1.3 per cent. of lead is left in the zinc, as a solid solution, any more lead segregating as a solution of zinc in lead. Therefore, if cadmium is absent, the metallic portion of the zinc may contain 1.3 per cent. of lead in solution, possibly in molecular form, while any excess must be in larger particles. This can be shown by preparing an alloy, and cooling it slowly, cutting out all parts showing segregations of lead, and analyzing the remainder. Cadmium is soluble in melted zinc in all proportions, and insoluble in solid zinc; but, separating only at the instant of solidification, does not segregate in large masses. Lead is soluble in melted cadmium in all proportions, and partly soluble in solid cadmium, the excess of lead not segregating as in zinc. The probability is that cadmium would increase the solubility of lead in solid as well as melted zinc, and would certainly diminish the tendency toward segregation. I prepared an alloy containing about 2 per cent. cadmium and 2.2 per cent. lead, and let it cool slowly in a muffle. It seemed perfectly homogeneous, and if there was any undissolved lead, it was so finely disseminated as to be invisible on etching the specimen.

Lead is known to increase the activity of zinc in cyanide solutions, as it has a much lower electromotive force, and remains undissolved. It is not known whether the dissolved portion (in the zinc) is more efficient than segregations, or *vice versa*. Cadmium also has a lower potential than zinc, and would probably also help, but would not be as advantageous, as the difference in potential is less. From several analyses of precipitates, the indications are that the cadmium remains in the precipitate, which has been proved to be the case with lead. It is to be hoped that the metallography of this system will be worked out soon so as to answer the question of the distribution of the impurities. The following

analyses show the variation in some samples of zinc dust from different sources:

Lead	Cadmium	Zinc Oxide	Total	Per Cent. of Metallic Portion	
				Lead	Cadmium
0.15	0.00	8.30	8.45	0.16	0.00
1.18	3.10	9.60	13.90	1.31	3.43
1.75	1.70	8.45	11.90	1.91	1.86
1.80	1.20	17.85	20.85	2.19	1.46
1.82	1.85	10.15	13.80	2.02	2.06
2.04	2.15	11.65	15.85	2.31	2.46
2.06	3.90	10.50	16.45	2.30	4.36
2.38	1.85	11.85	16.10	2.70	2.10
2.60	1.25	6.30	10.15	2.78	1.34
3.05	1.90	16.15	21.10	3.64	2.27
3.65	1.15	10.60	15.40	4.08	1.29
3.73	2.45	12.20	18.40	4.25	2.79
5.20	1.70	7.25	14.15	5.61	1.83

In calculating the columns headed "per cent. of metallic portion," it was assumed that 100 per cent. less the zinc oxide was the metallic part. The error, if any, would tend to make the figures as calculated lower than the truth. The table shows that practically any combination within the limits given for lead and cadmium may be expected to occur.

Other Impurities.—Other metallic impurities are negligible. Of the non-metallic impurities, nearly all samples contain a small amount of insoluble material, generally sand or fireclay; the amount is very small, and the only effect can be to dilute the dust with a trace of inert matter. Some zinc dust also contains a small amount of carbonaceous matter, such as coal dust, very seldom more than a small fraction of 1 per cent. This is also inert. This was demonstrated by intimately mixing 0.5 g. of zinc dust with 10 per cent. of finely ground coke dust in one case, and the same amount of graphite in another trial. In neither case did the amount of silver precipitated differ materially from that obtained when using the same amount of zinc dust by itself.

Another impurity that may occur is carbon dioxide, combined with the zinc determined as oxide. If the dust has been exposed to moist air, it is reasonable to assume that some zinc carbonate would be formed. As the solution being precipitated contains lime, the carbonate would cause the precipitation of calcium carbonate on the zinc grains, preventing efficient contact with the solution. All precipitates contain some calcium carbonate, but ordinarily, if there has not been much chance for the access of air to the solution, the amount is so small as to make the effect of carbon dioxide in the zinc dust very slight.

There is one other material that is found in many lots of zinc dust that may be of some importance. This material is oil of some sort. If present, it may be detected by extraction with ether. I do not know how it is introduced into the dust. It may be deposited in the cooler part of the condenser, and come from the reducing agent used, or it may be added later to diminish the tendency toward oxidation. On dissolving oily zinc dust in dilute acid, the action is very slow, due in part to the protection by a film of oil, and also to an effect similar to flotation methods of concentration, the dust being floated in a rather compact mass. An oil-free dust can be oiled by moistening with a solution of paraffin or some heavy oil in ether, and evaporating the solvent, and then it acts like the oily dust. It is the dust containing appreciable quantities of oil that seems to be benefited by some exposure to air; possibly the formation of a film of oxide removes the oil from the surface and leaves clean metal for precipitation.

Screen Analyses of Zinc Dust

Ordinarily from less than 1 per cent. up to nearly 5 per cent. will remain on a 200-mesh screen, and from one-fourth to three-fourths of this will remain on a 100-mesh screen. The coarse particles are partly sand, bits of fireclay, and similar things; usually there are some coarse particles of zinc. The amount that passes through a 200-mesh screen does not indicate the real fineness of the zinc dust, as much depends on the average size of the through-200 portion. A further separation may be made by clutriation.⁴ Much may depend upon the composition of the various fractions.

In some cases lead determinations were run on the separate fractions. In one lot the fine portions contained progressively less lead, and in another contained more than the coarser fractions. Cadmium determinations were not made on these fractions. As a rule, the fine portions contain higher percentages of zinc oxide, and there may be enough to outweigh the effect of a high proportion of fines. In other lots, however, the zinc oxide was fairly evenly distributed through all the sizes. It may be that determinations of metallic zinc in the fractions would be of value. The difficulty in determinations of this sort is the chance for oxidation during the manipulation, especially the drying of the fractions.

Substitutes for Zinc Dust

There have been several zinc products proposed as substitutes for dust, but none of those so far suggested have been of any consequence. They have been mechanically made, of the nature of chips or cuttings;

⁴W. J. Sharwood, *loc. cit.*

or they have been similar in character to test lead, of varying degrees of coarseness; some have been finely crystalline. All that I have seen have the same failing of coarseness. The efficiency of various substitutes ranges from 5 to 20 per cent. of the efficiency of an average dust, by the silver-precipitation method.

Conclusions

Zinc dust satisfactory for precipitation of precious metals from cyanide solutions should satisfy the following requirements: It should be fine; that is, most of it should pass through a 200-mesh screen, and the fine portion should be very much finer than the screen opening. As the surface exposed per unit weight varies inversely as the diameter of the particles, and the number of grains varies inversely as the cube of the diameter, if the average diameter of one lot of dust is one-half that of another, the finer would have twice the surface and eight times the number of particles. The dust would remain in suspension better, and, if uniformly distributed, the distance between grains would be half that of the coarser material.

The oxide should be low, but very low oxide does not necessarily indicate a good zinc. There should be a reasonable amount of lead, over 1 per cent. As high as 4 per cent. may do no harm. Cadmium is usually present, and some cadmium may take the place of part of the lead. If oil is present, it should not be in such quantity as to prevent good mixing of the dust with the solution. Precipitation with a standard solution of silver cyanide gives a rapid method for approximating the value of a particular lot of zinc dust. If the efficiency is well over 40 per cent. (100 per cent. being the theory for complete replacement of pure zinc by silver), the zinc is satisfactory. If under 30 per cent., the dust will probably give poor results.

The condition of the metallic impurities may have much influence. It is quite possible that the composition of different particles may vary according to the time in the distillation when they were condensed, or because of mixing of lots of dust of decidedly different composition. In a case of this sort, the precipitation test is the only simple method of determining what may be expected in actual work.

DISCUSSION

GILBERT RIGG, New York, N. Y. (communication to the Secretary*).—The following statement by Mr. Herz, if not properly qualified, is apt to be misleading:

"The nature of alloys of cadmium and lead with zinc has not been studied by modern metallographic methods." This statement is quite

* Received Dec. 29, 1915.

true so far as the ternary system Pb-Cd-Zn is concerned, but the binary systems Pb-Cd, Zn-Cd, and Pb-Zn have been studied by several investigators. Furthermore, sufficient metallographic work has been done on spelter itself to give us a very fair knowledge of the high zinc corner of the Zn-Cd-Pb diagram. A list of references is given at the end of this discussion.

Mr. Herz continues: "It is known that lead is slightly soluble in zinc, and on cooling, about 1.3 per cent. of lead is left in the zinc as a solid solution, any more lead segregating as a solution of zinc in lead. Therefore, if cadmium is absent the metallic portion of the zinc may contain 1.3 per cent. of lead solution, possibly in molecular form, while any excess must be in larger particles. This can be shown by preparing an alloy and cooling it slowly, cutting out all parts showing segregations of lead, and analyzing the remainder."

Now it is quite true that in a bath of lead and zinc kept only slightly above the melting point of the latter, the upper (zinc) layer will contain approximately the amount of lead stated by Mr. Herz (about 1 per cent.). As the temperature of the bath increases, the upper layer—the solution of lead in zinc—will become increasingly richer in lead as Spring and Romanoff have shown. With falling temperature, however, the solubility of lead in zinc rapidly diminishes. Arnemann, and Heycock and Neville have placed the limit of solubility of lead in zinc at a temperature of 418°C. at 0.5 per cent. lead. At this temperature, of course, the mixture begins to freeze. Doubtless the reason that we are unable to reduce the lead content of spelter below about 1 per cent. by liquation methods is due to the fact that at the freezing temperature the metal is somewhat viscous, and holds the lead which has been thrown out of solution (above about 0.5 per cent.) in the form of an emulsion—a suspension of minute globules. Microscopic examination of spelters confirms this. Spelters containing from 1 to 1.5 per cent. lead under higher powers of the microscope show the lead as distinct globules. If Mr. Herz will prepare the "unsegregated" parts of his lead-zinc alloy, etch with nitric acid, and examine under the microscope, he will be quite convinced that the 1.3 per cent. of lead is not present as a solid solution.

Mr. Herz also states: "Cadmium is soluble in melted zinc in all proportions and insoluble in solid zinc, but separating only at the instant of solidification does not segregate in large masses." Such investigations as have been published are rather conflicting regarding the presence or absence of solid solutions of cadmium in zinc; some investigators claim that they are absent, while others indicate their presence to a limited extent. My microscopic examination of spelters containing cadmium has invariably shown the presence of solid solutions. On the other hand, with very slow cooling the cadmium separates as a definite constituent. This, of course, only applies to cadmium less than 1 per cent. In other

words, in the stable system, produced by slow cooling, solid solutions are absent; but in the metastable system, which is practically the universal case with spelters containing cadmium, solid solutions are present due to the rapid cooling.

Mr. Herz's statement: "The probability is that cadmium would increase the solubility of lead in solid as well as melted zinc," possibly is true. Under the microscope, lead is not as easily discerned in spelters containing considerable amounts of cadmium as in those free from it.

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¹ The references under the heading Cd-Pb are incomplete. The article referred to, however, gives full data on the system.