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A Rapid Determination of Small Amounts of Lead in Zinc

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A RAPID DETERMINATION OF SMALL AMOUNTS OF LEAD IN ZINC

GEORGE T. HANSON

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

MONTANA SCHOOL OF MINES
BUTTE, MONTANA
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INTRODUCTION

This investigation, carried on in the metallurgical laboratories at the Montana School of Mines, was undertaken with the desire to work out a rapid method for the estimation, or the determination, of the amount of lead in zinc.

There is a very definite industrial need for a fast, accurate method, and this thesis is a contribution to the zinc-producing industry, as well as a study of academic interest.

In the time available, no investigation was made of the effects of a third element; the alloy was confined to small amounts of lead in pure electrolytic zinc.
HISTORICAL

At the present time the determination of lead in zinc (spelter) is carried out in several ways, all requiring considerable time in the assay office. One plant(1) takes a 500 gram charge of spelter drillings, and analyses the sample by the volumetric molybdate method. Results are accurate to 0.004 percent, and check to 0.002 percent. The determination requires about four hours.

Other plants use the lead sulfate method(2), based on the weight of PbSO₄ obtained from the sample. An electrolytic method(2) is also used to determine the lead.

Some work had been done on this problem, mostly in connection with routine investigations of zinc spelter. Mr. R. D. Macdonald investigated the subject at the Montana School of Mines, but his results were not available in manuscript form. Mr. R. J. Smith(3) had worked on alloying lead with zinc, in-

1) Zinc plant, Anaconda Copper Mining Company Reduction Works, Anaconda, Montana.


3) Superintendent, Zinc plant, A. C. M. Company Reduction Works, Anaconda, Montana.
vestigating the segregation of lead in the zinc bath. His results are mentioned here, as they substantiate similar results obtained by the author.

W. M. Peirce\(^4\) did some of the early work on the equilibrium diagram of Pb-Zn. His work at the New Jersey Zinc Company indicated no solid solubility in alloys containing 0.05 percent lead, and he concluded from the literature that there was none below this value.

M. Hansen\(^5\), collaborating later work, obtained the diagram shown in Figure 1. He does not show any solid solubility.

J. L. Bray\(^6\), during recent investigations of high-lead alloys, obtained indications of a solid solution at about 0.05 percent zinc. The portion of the diagram worked out by him is shown in Figure 2.

Because industry today makes wide use of the


\(^{5}\) Hansen, M. Der Aufbau der Zweistofflegierungen. (1936) pp. 1007-1010.

microscope for fast and accurate quantitative analyses, it was felt that a microscopic method would be applicable to this thesis problem.

In the steel industry, the percentage of carbon in plain steels is readily determined by using a microscopic to estimate the amount of pearlite present in the sample. Another use of microscopic analysis is for determining the percentage of oxygen in copper, especially copper trolley wire. The oxygen content is determined by the amount of copper oxide eutectic present in the specimen.
Fig. 2
Zinc has a melting point of 419.4 °C and lead a melting point of 327 °C, so no difficulty was encountered in melting the materials. However, melting in air caused rapid oxidation of the zinc (also probably of the lead), so the composition of the resulting alloy was not accurately known. Various means were tried to prevent this oxidation, including cover charges, fluxes and melting under gas.

As covers, cerisin wax and a good quality transformer oil were tried, but their flash point was below the melting point of zinc.

Another cover charge used was a mixture of 60 percent NaCl and 40 percent KCl. The salts were melted at an estimated temperature of 600-700 °C. This formed a clean, molten cover, and effectively prevented oxidation. However, the specimens prepared were found to contain considerable material, either slag or a chloride(7), which could easily be mistaken for lead; also an indication of lead was obtained in specimens containing no lead.

Ammonium chloride is known to be a good fluxing agent, and efforts were made to use it as a flux and cover charge. It was found that the zinc combined with the NH₄Cl, forming a brown mass of lighter specific gravity. Oxidation was prevented, and a good clean casting was obtained, free from blow-holes and slag inclusions. When lead was present in the alloy, a grey-black mass was formed, which was shown by qualitative analysis to contain lead. The specimens, moreover, showed indications of a lead content not in agreement with that known to be present. This was due to the formation of ammonium zinc pentachloride(8) and lead chlorides(7), which would probably remain in the specimen and appear as lead.

Melting in an inert gas or a neutral atmosphere is a common procedure. Natural gas was used, in an apparatus constructed for this work, and proved to be satisfactory. Figure 3 shows the construction of this equipment. An ordinary cast-iron retort was used as the gas chamber, and fitted with a cover that had three holes, providing inlet and outlet for the gas and a hole for mixing.

Fig. 3

Sketch of Apparatus
A carbon crucible was used for the zinc pot. This permitted quenching the alloy without pouring or cooling it. Also, it is accepted that carbon is not soluble in zinc\(^9,10\). Because of its insolubility, a carbon arc electrode was used for the stirrer.

By regulating gas flow a slight pressure was maintained in the retort, and thus no air leaked in around the stirrer. The gas was burned at the exist pipe. No trouble was had with blow-outs or explosions. Oxidation was effectively prevented while using temperatures only slightly above the melting point. It was difficult to control the temperature of pouring, and a temperature too high caused oxidation during pouring.

Results with the apparatus seemed quite satisfactory at first, but it was soon found that segregation of the lead to the bottom of the melt prevented securing an alloy of uniform composition. The effect of quenching the well mixed alloy was investigated, but this was not satisfactory as oxidation occurred when the crucible was removed from


\(^{10}\) Hansen, M. Der Aufbau der Zweistofflegierungen (1936) p. 352.
the retort for quenching.

As none of these various methods of alloying permitted a knowledge of the exact composition, and as all required considerable time and care, it was decided to melt the zinc in a covered crucible, either carbon or graphite-coated, add the lead while stirring, and pour at once. There was some oxidation, but if the temperature was kept low, the amount of dross formed was not excessive. No attempt was made to apply a correction for this drossing, as identical conditions could not be maintained during each melt. This method gave an alloy whose composition was only known approximately, but great accuracy was not needed in this preliminary examination.
ETCHING REAGENTS

The literature lists several reagents for etching zinc, and zinc alloys, and several of these were tried during this investigation.

Schramm's Reagent

Jakob Schramm(11) has developed an etchant which colors the zinc rich constituents black, while the others, as magnesium, iron, copper, lead and nickel remain white. He used this reagent to show lead in spelter(12), and these results led to the use of this reagent. The effect of the etching is to precipitate copper on zinc, but not on the lead and those other metals which remain white.

Table I shows the reagents used in the preparation. Schramm's original article(12) did not state the percentage concentration of the reagents, so several sample solutions of the etchant were made, using different concentrations. The 50 percent concentration by weight was found to give a good etch. This concentration may not have been optimum, but another

11) Chemical Abstracts: vol. 31, 1748 (Mar.20, '37)
12) Schramm, J. Ein Atzmittel fur zink und zinklegierungen. Z. Metallkunde: Bd. 28, pp. 159-60 (1936)
factor prevented an accurate determination in any short period of time—the amount of citric acid added. Schramm states that the amount of acid should be varied a drop at a time until a satisfactory etch is obtained.

The effect of citric acid is probably to obtain a definite pH, and quite possibly determination of this pH would permit easier duplication and control of the etchant. The fact that the solution contains considerable cyanide would make the pH determination very difficult, although it could probably be secured by means of the glass electrode. The amount of citric acid was not found to be as critical as Schramm indicates.

During the investigation four different quantities of the etchant were made up. It was evident that each gave a different etch, although made up as closely as possible with identical proportions of reagents. More than likely this was due to varying values of the pH.

One 120 cc portion of the etchant was used over and over again for etching perhaps 50 specimens, over a period of six weeks. A slight change was noted in the etchs obtained after this time. If the effect of time was the decomposing of any complex citric acid ions, adding fresh citric acid should have remedied the trouble. This was not found to be so.
As copper was constantly being removed from the solution, this action may be an explanation for the slight change noticed. It seems more probable, however, that an equilibrium was maintained due to mass-action, hence the solution would give a constant etch until suddenly exhausted, when no etch could be obtained.

The time of etching was important although not particularly critical. An etch of 10 seconds usually gave the best results. Shorter times gave a light etch, that did not clearly distinguish the lead globules. A time of 15 seconds gave a dark etch, not as good for most specimens as the 10 second etch, but still satisfactory. When a 25 second etch was tried, the indicated lead content was low, but upon re-etching for 10 seconds a higher lead content was shown. The long etching period appeared to have bridged over the smaller lead particles, giving erroneous interpretations.

The time was dependent to some extent on the amount of citric acid. For varying amounts of acid, varying times of etching were required. But if the amount of acid was not correct, the error could not be corrected by adjusting the time.

All specimens were polished in a standard manner.
It was very difficult to obtain a good polish, but only the deeper scratches showed after etching. The poor polish did not affect the estimation of the lead content, as far as could be determined by preliminary investigations.

The sample was sawed and filed to a plane surface, then ground on emery paper, dry, from "0" through "0000" sizes. Final polishing was done on a revolving felt wheel, using levigated alumina, and cleaning was done on a similar wheel, using plenty of water. It was recognized that a tendency existed for the lead to be torn out of the specimen, but polishing high-lead alloys, 1 and 10 percent Pb, did not seem to indicate this as a source of trouble. The extent of this tendency has not been established, however, and should be investigated further.

Etching was accomplished by completely immersing the specimen in the etchant for the desired time, pouring off the liquid, and then washing the specimen in running tap water. It was necessary to dry the surface to prevent oxidation; this was done without rubbing by washing the surface with absolute ethyl alcohol.
If the etched surface was scratched a white streak was formed, and similar streaks were caused by uneven rubbing (see below).

The polished surface had to be quite clean when etching. Grease or oil, such as was easily rubbed off of the fingers, prevented a uniform etch.

**Chromic acid.**

Previous investigators\(^{(4, 13)}\) of zinc and zinc alloys had used a chromic acid-sodium sulfate solution as an etchant. This etchant was tried, and good etches were obtained. Etching was by immersion for 10-20 seconds, using 10 grams of C.P. chromic acid and 1.5 grams of C.P. anhydrous sodium sulfate in 100 cc of water.

The grains of zinc showed up well, but it was difficult to differentiate the lead. This was due to the cross-hatching of the individual zinc grains, caused by mechanical twinning\(^{(14)}\). Many brilliant and varied colors were noted on the individual grains.

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14) Reference 13, p. 317.
grains, due to iridescent filming\(^{15,16}\).

**Acetic acid and Hydrogen peroxide.**

Approximately equal portions of glacial acetic acid and \(\text{H}_2\text{O}_2\) were mixed, and the polished specimens etched by swabbing with this reagent for 10 or 15 seconds. The grains of zinc were well defined, but the etchant brought out so much detail in the grain structure that estimation of the lead content was nearly impossible.

The lead was probably oxidized, and it showed as black globules between the grain boundaries of the white zinc. This would be a basis for estimation if the grain structure was not so complex\(^{14}\). Annealing to secure large grain growth might be a solution of this difficulty. But annealing would lengthen the time of estimation beyond that allotted to a "rapid method". Slow cooling did not allow time for a large grain growth, but it indicated a definite improvement.

15) Gaudin, A. M. The identification of opaque solids by selective iridescent filming. Part II "Physical Chemistry and Crystallography".

Nitric acid

Nitric acid was used during a few preliminary investigations, but the etch obtained was not very satisfactory; at least it was not a good etchant for distinguishing the lead.

Ammonium polysulfide

It was thought that ammonium polysulfide would be an etchant, as the PbS formed would show up well against the white zinc (or white ZnS). This etchant did not prove satisfactory for small amounts of lead, although some black spots were visible that were different than the polish pits. The fact that a very good polish is needed for this etchant practically eliminates it, if a fast method is to be secured.
Schramm's reagent was used in all studies of the alloys prepared, and several of the results recorded in this part of the thesis might well be included in the discussion of that reagent.

The segregation of the insoluble lead to the bottom of the zinc casting was noted in all preliminary specimens. This segregation made knowledge of the exact composition unknown, so studies were made of some of the factors effecting it.

Segregation occurred to some extent in all alloys. The low lead alloys showed the segregation as a continuous increase in lead to the bottom of the casting, but high lead alloys (10 percent Pb) segregated into two separate layers. The upper layer was zinc containing a considerable number of lead-zinc globules. Mathewson\(^\text{(17)}\) and Pierce\(^\text{(18)}\) both gave the composition of these globules as 3.5 percent zinc and 96.5 percent lead; Pierce also explained their occurrence. More recent work by Bray\(^\text{(6)}\) indi-


cated that their composition was only 0.5 percent zinc.

Data obtained on the effects of the rate of solidification were mostly inconclusive. Schramm's reagent did not bring out the lead clearly in the quenched specimens. This may have been due to a dispersion of tiny lead globules among the fine grains of zinc, which, being so small, were easily "bridged over" by the etchant. It was not determined if this dispersion effected segregation.

The presence of slag (or ZnO) in the specimen had an undesirable effect. The slag did not etch black, and hence was mistaken for lead. It had a different appearance, however, and could be distinguished from lead when the two were present in one specimen. The slag was usually irregular, while the lead globules were round and quite uniformly distributed. If much slag was present, the specimen was of no value.

Pure zinc did not etch well with the reagent. This was due to the absence of a galvanic couple, similar to the inability of pure zinc to dissolve readily in acids.

Polished cathode zinc showed many white spots when etched. The polished surface was examined under high-power, and found to contain many pinholes.
These pinholes were probably caused by gas accumulations on the cathode during electrolysis. A melt of cathode zinc was fluxed with ammonium chloride, and the resulting melt was cast, polished and etched. A fair etch was obtained and no white spots were visible. Examination showed that pinholes had been eliminated.

Some specimens etched well in immersion in the etchant, and showed the white lead spots clearly in a dark black-brown field. Most of the specimens, however, showed the spots in a field containing innumerable dull white patches, not slag inclusions. These patches, probably due to iridescent filming, made estimation of the lead content difficult.

Rubbing the surface of the specimen with a smooth material, such as Kleenex, eliminated this difficulty. Part of the film was removed, thus giving a light, uniform brown field, against which the white lead globules showed distinctly.

In an attempt to eliminate the polishing steps, and thus the possibility of tearing out the lead globules, the molten alloy was cast in heated porcelain crucibles. The castings were usually very smooth. When these specimens were etched, the iridescent filming was very pronounced. One grain of the zinc would remain nearly white, while an adjacent grain might be jet-black. The lead showed
up quite well, however, except along the boundaries of the white grains.

It was not possible to study the effect of the etchant on a third element in the alloy. The problem is particularly important to an industrial application of this method of determining the percentage of lead, as various impurities are usually present, and some metals are frequently added to the spelter.

Schramm's results[12] indicate that certain of these metals would appear as lead. Maintaining a certain pH value may permit a differential etch, that would not be too limited in its application in an industrial plant.
SUMMARY

1. A suitable etching reagent (Schramm's Reagent) exists for distinguishing small amounts of lead in zinc.

2. It is possible to estimate the percentage of lead present in the specimen.
PHOTOMICROGRAPHS

Various alloys, etched with Schramm's reagent and lightly rubbed.

Appendix A
Fig. 1
10% Pb  88 x

Fig. 2
0.1% Pb  185 x
Fig. 3
0.5% Pb 185 x

Fig. 4
0.5% Pb 370 x
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Appendix B
TABLE I

Etching Reagent for Zinc and Zinc Alloys-- Schramm

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<th>Substance</th>
<th>Quantity</th>
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<tr>
<td>Concentrated KOH</td>
<td>51 cc</td>
</tr>
<tr>
<td>Distilled water</td>
<td>50 cc</td>
</tr>
<tr>
<td>Concentrated Cu(NO₃)₂</td>
<td>20 cc</td>
</tr>
<tr>
<td>Powdered KCN</td>
<td>25 grams</td>
</tr>
<tr>
<td>Concentrated citric acid</td>
<td>2.5 cc</td>
</tr>
</tbody>
</table>

Preparation of Reagent

The water and then the copper nitrate are added to the hydroxide, and the mixture allowed to stand until the blue precipitate which forms has turned black. The powdered cyanide is then added very slowly, shaking the solution constantly. The last small addition of cyanide dissolves all the black precipitate. The solution is then filtered, and allowed to cool to room temperature. The citric acid is added, and the solution of the reagent is kept in a cork stoppered bottle.
ACKNOWLEDGEMENTS

I wish to thank Dr. Curtis L. Wilson and Dr. Ettore A. Peretti for their aid and advice during this investigation.

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