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THESIS

FOR

THE DEGREE
OF

MINING ENGINEER

A
COMPARISON OF
THE
FIRE AND WET METHODS
FOR LEAD.

G. W. DEAN.

A Comparison of the Wet and Fire Methods for Lead.

As has long been recognized by chemists, the fire assay method for lead is inaccurate and at best gives only comparative results. The condition of time, temperature, character of ore etc. affect the results so greatly that it is of little or no value in a strictly chemical sense. Still, with proper conditions of time, temperature, flux etc., it can be made to give constant results, which, while not accurate in a strictly chemical sense, are sufficiently accurate for the commercial purposes where great accuracy is not required.

The purchase and sales of all lead ores are made on the basis of the fire assay and, for this reason, it is very important that we should know with what confidence we can rely upon the results of the fire assay.

In the methods usually given in text books such as Furman, Ricketts, Brown, and others, the principal factors are short time, high heat, quick fusion. By any of these methods, I have been unable to obtain either reliable or constant results and with the so called "twenty minute fusions" have obtained results which were as much as three or four per cent too low.

In the method used throughout the Coeur d'Alene, and, I believe, in most of the Smelters, one which, on the whole, seems to give the most reliable and constant results, the principal factors are:- long slow fusion, rising to a high finish, Time, one to one and a half hours.

By carefully observing the proper conditions, very reliable results can be obtained.

The fluxes employed are of the ordinary type such as Winckler's:-

Flour	1 part
Borax Glass	1 part
Sodium Carbonate	2 parts
Potassium Carbonate	2 parts.

Some assayers prefer the following:-

Argols	1 part
Soda Bicarbonate	3 parts
Potassium Carbonate	2 parts
Borax(Dried)	1 part.

Either of the above fluxes will handle a great variety of ores very satisfactorily. They are mixed in quantity and kept in a tight box or can away from all moisture.

The method in detail is as follows:-

Fill a 10 gram crucible one third full of flux, weigh in ten grams of ore and mix thoroughly. Add the same quantity of flux on top and put in one or more nails as may be necessary, finishing with a salt cover one half to three fourths of an inch thick. Place in a muffle at low red heat, leave open. Gradually raise the heat so that at the end of half an hour the muffle will be a bright cherry red or even a dark orange. For the next half hour raise the heat a little more strongly so that the charge begins to sinter and fuse around the edges at the end of forty five or fifty minutes. At the end of an hour, the muffle should be a bright orange and white fumes should just begin to appear. Now close the muffle as tightly as possible and raise the heat rapidly until a bright yellow, holding at this until

fusion is complete which will be in twenty or twenty five minutes longer. Allow to remain a few minutes after the fusion is quiet, then pour, and break as usual.

A test of good work: The slag pours smoothly and cleanly, is bright glossy black when cold, and clings tenaciously to the button. If it breaks loose easily from the button leaving a bright surface, it will invariably give a low result as it is due to a very thin layer of undecomposed sulphide of lead which clings to the slag and is removed with it when the button is slagged. However, if the heat has been properly regulated, there will be no difficulty of this sort. Neither will there be any "Shot" lead in the slag as is often the case in short fusions.

It is important that it be given a high finish as this makes the slag more fluid which allows the particles of lead to settle perfectly into a single mass besides giving a clean smooth pour, thus lessening the danger of loss in the crucible or slag.

Another source of loss which must be guarded against is that which sticks to the nails when they are removed previous to pouring. They should be taken out with a pair of short tongs and ^{the lead} thoroughly removed by tapping on the side of the crucible dipping the point of the nail each time below the surface of the molten slag as this prevents oxidation and also facilitates its removal.

If the above conditions are carefully observed, results can be obtained which will not vary more than one or two tenths of one percent.

The Wet method most commonly employed is the Ammonium Molybdate method.

Take one gram of the finely pulverized ore and digest in a casserole with fifteen c.c. strong nitric acid. Boil until red fumes disappear. The residue should be yellowish white in color. In case there is much iron, there will be undecomposed particles in the residue in which case, add five c.c. of Concentrated hydrochloric acid and boil until red fumes disappear and examine the residue which should be flocculent and free from undecomposed particles. Sometimes a second or even third treatment with hydrochloric acid may be necessary. The residue should be yellowish white and flocculent while the supernatant liquid shows the characteristic color of ferric chloride.

Add fifteen C.C. Sulphuric acid (diluted in the proportion of one to one as this can be added to a hot solution without danger of spattering) and evaporate until dense white fumes of sulphuric anhydride appear. A good test is made by allowing the drop which collects on the watch glass cover to flow down the side of the casserole. As long as it hisses when it comes in contact with the hot acid, the reaction is incomplete.

Remove, cool and wash down the sides of the casserole with water. Dilute to twenty or thirty cc and add about four or five grams of tartaric acid. Boil vigorously for three or four minutes, remove, wash down the sides and watch glass cover, ^{with} cold water. Cool thoroughly, dilute to about one hundred cc. and filter through a fine-grained filter, such as Munktell's, pouring back the first few C. C. as a precaution in case any lead sulphate should run through the filter.

The tartaric acid dissolves any ferric sulphate which may have been formed and which is but sparingly soluble in water.

It is important that the precipitated lead sulphate should be thoroughly cooled as this insures the perfect precipitation of the lead and lessens the danger of its running through the filter.

After filtering wash thoroughly several times with cold water allowing to drain off each time. Heat fifty C.C. Ammonium acetate (made from aqua ammonia and acetic acid) to which ten C.C. thirty percent acetic acid has been added, to boiling in a beaker, remove the filter from the funnel, unroll it and wash the sulphate of lead into the beaker with hot water finally putting in the filter also as it does not interfere with the reaction and insures no loss of lead.

When thoroughly dissolved, dilute to about two hundred and fifty C.C. with hot water, heat to boiling and ^{titrate} ~~dilute~~ with standard solution of Ammonium Molybdate using a one percent solution of tannic acid as an indicator.

The standard solution of Ammonium Molybdate is made by dissolving the required amount of the salt in luke warm water adding fifteen C.C. strong ammonia per liter of standard solution as this clarifies it and ~~renders~~ it more stable.

It is very convenient to have the standard solution of such strength that one C.C. equals one percent lead, as results accurate to one tenth of a percent can be easily obtained in this way which is sufficiently accurate for work of this kind and danger of error in calculation is avoided besides lessening

the time required which is often and important factor.

Checking the fire method as given above with the wet method, we find a very regular difference in the results, increasing of course with the lead contents of the ore.

The following table shows results from several hundreds of assays, ~~as~~ taken as to cover as wide a range as possible:-

Fire.	Wet.	Difference.	Fire.	Wet.	Difference.
16.0	16.4	0.4	51.0	52.6	1.6
30.7	31.5	0.8	54.9	56.8	1.9
34.8	35.8	1.0	55.2	56.9	1.7
34.9	36.0	1.1	60.9	62.8	1.9
37.1	38.3	1.2	62.9	64.8	1.9
39.9	41.1	1.2	64.0	66.0	2.0
41.9	43.1	1.2	65.1	67.1	2.0
42.1	43.3	1.2	70.0	72.2	2.2
45.2	46.5	1.3	72.7	75.0	2.3
49.9	51.5	1.6	78.2	78.7	2.5

Plotting the percentage as given by the two methods, we get a straight line No.1 passing through the origin. This is what we would naturally expect as the results approach each other as the percentage decreases.

Now plotting the fire results and the differences, we obtain a straight line No.2 not passing through the origin as before, but cutting the ordinate at about four percent. This means, simply, that, within the limits of accuracy with which we are working, there is no perceptible difference in the fire and wet results until we reach five or six percent.

By use of curve No.2, the difference for any percentage may be easily obtained and the results for the wet method calculated or taken directly from No.1,

With careful work it proves very satisfactory and may be relied upon where an accuracy greater than one tenth percent is not required.

I have used it continually during the past ~~two~~ months and find that it gives perfect satisfaction except with ores containing a large percent of zinc when the differences are generally greater than those obtained from the curves although I have not yet been able to determine to what extent the zinc influences the results.

I wish to acknowledge my obligations to Mr.P.J.Schuman who has assisted me greatly in my work and has also furnished a part of the data from which the curves were obtained.

Respectfully

Geo. A. Dean

*Wallace Idaho
May 8th 1900.*