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Assay of copper matte for gold and silver

Walter E. Soest

Department: Chemistry; Materials Science and Engineering

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THESIS

FOR THE

Degree of Bachelor of Science

IN

Chemistry and Metallurgy.

SUBJECT:

Assay of Copper Matte for Gold and Silver.

W. E. SOEST, 1899.

Ores containing copper, and especially copper matte, have always been very annoying in assaying for the precious metals.

In assaying copper matte,and ores containing much copper,by the usual method of scorification,the losses of silver and gold are considerable,owing to the fact that in order to obtain lead buttons,which are soft and free from copper,repeated scorifications are necessary,and moreover it is impossible to obtain lead buttons which are entirely free from copper.

If the lead buttons contain copper,silver will be carried into the cupels when the button is cupelled.

The following is one of the methods carried out in case a very large percent of copper is present:-

One assay ton of the material is introduced into a beaker and 100 cc distilled water added,with stirring; 5o cc of nitric acid is now added, and the solution allowed to stand until the action of the acid has apparently ceased.

Then 50 cc more acid is added,and the solution is allowed to stand in a warm place until the red fumes are driven off. The solution is diluted with distilled water up to about 500 cc. and allowed to stand for several hours.

The solution is then filtered and the silver is precipitated with sodium chloride.

The solution is stirred and 10 cc. lead acetate added.

Then 2 cc. sulphuric acid was added (50%) and after stirring,the solution is allowed to stand for several hours.

When the precipitate has settled, the solution is filtered and the precipitate is washed into the filter, finally washing the precipitate to remove the copper salts.

The filter and precipitates are removed from the funnels, placed in scorifiers and dried in the front part of the muffle, and finally pushed back to destroy all the carbon and sulphur.

To the scorifier, containing the gold residue and the silver-lead precipitate, is added 5 grms. of litharge, 15-20 grms. test lead and one grm. borax glass.

The charge is now scorified, cupelled and the silver and gold determined as usual. (Furman's Manual of Practical Assaying p.250).

In cases where the percent of copper is not so high, repeated scorification will answer the purpose; but by this method each time we scorify, we lose from two to four percent of silver.#

As one will see, neither of these methods are desirable when rapid and very accurate work is required.

As the result of a large number of experiments conducted by myself, I propose a method which is more rapid than the above and at least as accurate.

The object of my work is to improve the assay of cupriferous materials,--mattes, ores, etc., especially in the case where the ordinary scorification process cannot be used on account of the small amount of gold present. !!

Transactions of American Institute of Mining Engineers 1894, p.575
1895, p.250

!! Of course one may assay many separate portions and unite the buttons.

Principles of Procedure.

I propose to use a crucible method on a charge of one A.T. of ore, thinking that a large mass of litharge might largely eliminate the copper from the button so as to cupel directly, or after one scorification.

Oxidation of Copper by Litharge.

That copper is oxidized by litharge is proven by the following data:

The same charge was used in each case, the only variable being the amount of copper taken, and the time of each fusion was 20 minutes.

The charge was as follows:

Borax	10 grams.
Sodium Bicarbonate	20 "
Litharge	60 "
Metallic Copper	Varying.

Following are the results obtained:

No	Wt. CU. taken	Wt. of Pb in Button	Wt.Cu in Button
1	3	2.065	1.2951
2	5	2.8192	3.3498
3	7	3.3182	4.6255
4	9	3.6142	6.7557

The first point to be proven is that the amount of copper oxidized is a function of the mass of litharge used.

The charge used was as follows:

Borax	10 grams.
Sodium Bicarbonate	20 "
Litharge	Varying.
Copper	5 grams.

From the following data, it is evident that the above mentioned facts can be deduced:

No.	Wt. cu Taken	Wt PbO taken	Wt. Cu. oxidized
1	5 grams	20 grams	.5513
2	5 "	40 "	1.1765
3	5 "	60 "	1.650
4	5 "	80 "	1.832

One will see at first glance that the copper is by no means entirely eliminated when the quantity of litharge is far more than the equation (2 $cu+PbO=Cu_2O+Pb$) requires.

We therefore suspect an easily reversible reaction, which was found in fact to be the case.

Reaction Between Cuprous Oxide and Metallic Lead.

The charge used is as follows:-

Borax	10 grams.
Sodium Bicarbonate	20 grams.
Cuprous Oxide	6 grams.
Metallic Lead	Varying.

Time of fusion for all charges in this experiment was 20 minutes.

Following are the results obtained:

No.	Wt. Pb. taken	Wt. Pb in Button	Wt. Cu. in Button.
1	3	.0965	1.8500
2	5	.1499	2.9019
3	7	.5477	3.5543
4	9	2.2976	4.3626

THE REVERSIBLE REACTION $Cu_2O+PB \rightleftarrows 2Cu+PbO$.

The equilibrium in this reaction was very difficult to study on account of the high and variable temperature, but though the results do not all agree, still some interesting points are brought out.

(a) Approximale time required for chemical equilibrium in the reaction $PbO+2Cu = Cu_2+Pb$ and the ratio of Pb:Cu in the buttons.

The same charge was used in each experiment, the only variable being the time of fusion. Chemical equivalents of both copper and litharge were used, and in this case 1/20 gram molecule of each.

The charge used is as follows:

Cu = 6.36 grms. = 2/20 gram molecule as equation requires 2 Cu.
PbO=11.15 " = 1/20 " "
$NaHCO_3$=20 "
Borax Gl=10 "

Following are the results obtained:

No.		Time of Fusion	Wt. of Button	Wt of cu in Button	Average	Ratio Pb:Cu in grams	Ratio Pb:Cu in gr.atoms
A	1	40 min.	8.076	5.874	5.885	1:2.6	1:8.57
	2		8.152	5.896			
B	1	60 min.	13.7822	6.152	6.152	1:.80	1:2.62
	2		13.78	6.152			
C	1	85 min.	12.2677	5.8291	5.829	1:.90	1:2.94
	2		12.2582	5.8291			
D	1	120 min.	11.5825	5.838	5.829	1:1.01	1:3.83
	2		11.5612	5.817			

Following are some results on the same reaction with two different fluxes, fusing 100 minutes.

Charge 1	Charge 2.
Cu = 6.36 grms. = 2/20 gr. mol.	Cu = 6.36 grs. = 2/20 gr. mol.
PbO = 11.15 " = 1/20 " "	PbO = 11.15 " = 1/20 gr. "
$NaHCO_3$ = 20 "	$NaHCO_3$ = 20 "
Borax Gl = 10 "	K_2CO_3 = 3 "

The results are as follows:

Charge1.					
No.	Wt. of Button	Color of Slag	Wt. Cu Button	Ratio Pb:Cu in grams	Ratio Pb:Cu in gr. atoms.
1	7.2287	Green	5.8622	1:4.29	1:13.9
2	7.9744	Redish Brown	5.8924	1:2.83	1:17.6

Charge 2					
No	Wt of Button	Color of Slag	Wt Cu in Button	Ratio pb:Cu in grams	Ratio Pb: Cu in gr. atoms.
1	8.3761	Red	5.8032	1:2.25	1:7.31
2	7.2478	Red	5.7734	1:3.91	1:12.7

Comparing the results we see that the total weights of copper oxidized are in fairly good agreement and for such work probably within limits of experimental error.

I fused the two last mentioned charges in covered crucibles and found the results to be practically the same.

From the preceeding results we see that the copper remains in great excess in all the buttons,and furthermore it is impossible to oxidize all the copper even if a large excess of litharge is present.

)b) Time Required for Chemical Equilibrium in the Reaction $Cu_2O+Pb=PbO+2Cu$;and the Ratios of Pb:Cu in the Button.

The same charge was used in each case,the only variable being the time.

The charge used is as follows:

Cu_2O = 7.11 grams = 1/20 gr. molecule.
Pb = 10.35 " = 1/20 " "
Borax Gl. = 10 "
$NaHCO_3$ = 20 "

Following are the results obtained.

No.		Time of Fusion	Wt. of Button	Wt.of Cu in Button.	Average.	Ratio Pb:Cu in grams.	Ratio Pb.Cu in Gr. atoms
A	1	40 min.	15.4927	6.8010	6.8006	1:.79	1:2.56
	2		15.3125	6.8002			
B	1	60 min	16.51	5.9134	5.9174	1:.55	1:1.78
	2		16.512	5.9214			
C	1	85 min.	16.3323	6.7335	6.7784	1:.71	1:2.27
	2		16.3413	6.8233			
D	1	120 min.	16.7140	6.8034	6.8078	1:.70	1:2.27
	2		16.3315	6.8122			

It should be particularly noticed that these results harmonize well with the ratios obtained in the reverse reaction (p 5).

I next experimented in the same direction using two different charges.

Charge 1	Charge 2.
Cu_2O = 7.11 grs.=1/20 gr. molecule Pb. = 10.35 " =1/20 " " Borax Gl=10 $NaHCO_3$ = 20 "	Cu_2O = 7.11 gr. =1/20 gr. mol. Pb = 10.35 " =1/20 " " K_2CO_3 = 3. " $NaHCO_3$ = 20 "

The results obtained are as follows:

No.	Color of Slag	Wt. of Button	Wt. of Cu in Button	Ratio Pb:Cu in grams	Ratio Pb:Cu in Gr. Molecules.
1	Red	4.7322	3.8563	1:4.48	1:14.3
2	Red	3.9062	3.8732	1:117.36	1:381.1
3	Red	5.9069	4.9786	1:5.36	1:32.92

	Charge 2.				
No.	Color of Slag	Wt of Button	Wt. of Cu In Button	Ratio Pb:Cu in grams	Ratio Pb:Cu in gr. molecules.
1	Red	5.0589	4.3784	1:.64	1:20.87
2	Red	5.9266	4.8489	1:4.49	1:14.59
3	Red	6.3752	5.0014	1;3.71	1:11.82

I also used the same charges and fused for two hours and fifteen minutes and obtained practically the same results.

We here again see that the ratio of Pb:Cu is variable.

The results here given as well as the others are not altogether trustworthy as experimental work of this kind is very difficult,it being impossible to always obtain the same temperature in the furnace,and as there is an equilibrium constant in each reaction for each temperature,I conclude that the variation in my results are due to the difference in temperature.

In the equation

$Pb+Cu_2O \rightleftarrows 2Cu+Pb$,we should expect that the reaction from left to right would be much more rapid and the equilibrium would consequently be sooner established because lead melts easily and liquids act on one another more rapidly.

Assay of Copper Matte.

I next turned my attention to the assay of copper matte,hoping still by a great excess of litharge to eliminate most of the copper from the button in a crucible charge.

My preliminary experiments show that the conditions necessary to drive as much copper as possible out of the button are, an excess of litharge and a long time of fusion.

Three different mattes were obtained,finely pulverized and sifted through a 100 mesh sieve.

The particles of metallic copper remaining on the sieve were set aside while that portion which passed through was taken for my experimental work,my object being to get enough of the matte for the required work and not the correct assay of the same.

The determinations of copper,silver and gold were made as directed in Furman's Manual of Practical Assaying (p.252).

The results of analysis are as follows:

Copper in per cent		Gold in oz. per ton	Silver in oz. per ton
No. 1 =	48.51	Trace	30.01
" 2 =	38.23	Trace	49.01
" 3 =	67.97	Trace	82.00

The figures given above are the average of three closely agreeing analyses.

Desiring a matte which contained very much copper,I used No. 3 and assayed it for gold and silver,using various charges.

Having found that the following charge was applicable to a copper matte with which I previously worked, I applied the same to Matte No. 3.

The following is the charge used.

Ore	.3 A.T.
$NaHCO_3$	20 grs.
K_2CO_3	7 "
Litharge	90 "
Silica	5 "
Borax Glass	20 "
Niter	7 "

The charge was fused 20 minutes then 15 grams of Argol added and the fusion continued 40 minutes longer.

The buttons obtained were very large, weighing 35.8226 grams.

The buttons obtained were then scorified with

4	grs.	PbO
5	"	Borax Glass.
7	"	Test Lead.

After scorification the buttons were thoroughly cleaned, put in a cupel and placed in the hottest part of the furnace.

The buttons opened very nicely but cupellation was impossible, there being too much copper present in the button.

After crucible fusion the buttons were found to contain 4.4748 grs. Cu and after scorification 4.0769 grs. Cu.

Other modifications of the crucible charge were tried, such as addition of less argol, omission of borax, the $NaHCO_3$ being increased to 40 grams, but none yielded buttons sufficiently free from copper to admit of cupellation.

Concentration of Gold and Silver into a Button from which the Copper is Removed by Solution.

Since the elimination of copper from the button was found to demand more litharge than could conveniently be employed, we tried the removal of copper from buttons obtained as previously described, by solution.

The plan was to dissolve the button in nitric acid and from the resulting small volume of solution to precipitate the silver.

The undissolved gold was added to this and a scorification and cupellation made as usual.

The charge used was:-

Ore	1 A.T.
$NaHCO_3$	20 grs.
K_2CO_3	5 "
Litharge	90 "
Borax Glass	20 "
Silica	5 "
Niter	10 "

Time of fusion 45 minutes.

Weight of Button obtained = 45 grams

The buttons thus obtained were cleaned and hammered out, cut into small pieces and dissolved in 50 cc. dilute $H\ NO_3$.

The silver and some of the lead were then precipitated with dilute solutions of NaCl and H_2SO_4 respectively.

This mixture was then allowed to stand in a warm place for lo minutes then filtered and washed several times.

The precipitate with filter paper was then placed in a scorifier and

4 grs.	Borax Glass
5 "	PbO
3 "	Pb added.

The weight of the button thus obtained was 10 grams.

It was cupelled in the ordinary manner. Weight of brads obtained:

No. 1 = 82.75 mgs. = 82.75 oz. per ton.
" 2 = 83.01 " = 83.01 " " "
" 3 = 82.73 " = 82.73 " " "

I slightly modified the last mentioned charge by adding only 5 A.T. ore and 7 grams niter, the other constituents remaining the same.

The results are as follows:

No. 1 = 41.48 mgs. = 82.96 oz. per ton.
" 2 = 41.56 " = 83.12 " " "
" 3 = 41.87 " = 83.74 " " "
" 4 = 41.76 " = 83.52 " " "
" 5 = 41.87 " = 83.74 " " "
" 6 = 41.57 " = 83.14 " " "

The gold in all these cases was in unweighable trace.

Thinking that possibly the beads might contain copper, I dissolved them in dilute HNO_3 and added HN_4OH.

Not the slightest coloration was produced which proves the absence of copper.

Five assays were made of Matte No. 2. which was previously assayed by Furman's Combination Method and found to contain 49.01 oz. of Ag+Au per ton of which the ore is an unweighable trace.

The results of my method are as follows:

One A. T. of ore was used.

No . 1 = 49.26 oz. per ton.
" 2 = 49.71 " " "
" 3 = 49.35 " " "
" 4 = 49.62 " " "
" 5 = 49.53 " " "

Comparison of the two Methods.

(a) At to time.

Furmans Method.

Solution of Copper in Matte	33	minutes.
Standing(as directed)	120	"
Filtering and washing	20	"
Addition of NaCl and Pb $C_2H_3O_2$	0	"
Standing as directed	120	"
Filtering and washing	12	"
Scorification	25	"
Cooling	7	"
Cupellation	25	"

Total 5 hours and 50 minutes.

This total is the time required for one assay and duplicate.

My method.

Fusion and cleaning the button	65 minutes.
Breaking and solution of buttons	20 minutes
Precipitation and standing	15 "
Filtering and washing	15 "
Scorification	25 "
Cooling	10 "
Cleaning and cupelling	33 "

Total 3 hours and 2 minutes.

This total is the time required for one assay and duplicate.

(b) As to Accuracy.

Average of results by Furmans Method = 82.034

Average of results by my method = 83.37

It can be seen that my method has an advantage as regards time and is at least as accurate.

The accuracy of my method is due to the fact that I have a very small bulk of solution to handle, so the precipitation of silver is carried on in a more concentrated solution and is therefore more complete.

The mattes I worked with contained too small an amount of gold to be weighed, but one would naturally suppose that this method would also be very accurate for the determination of the precious metal.

I therefore recommend the following method for the assay of Copper Matte containing a high percent of copper :

Ore	1 A.T.
$NaHCO_3$	20 grs.
Borax Glass	20 "
K_2CO_3	5 "
Silica	5 "
Niter	13 "
Litharge	80 "

Give this charge a slow fusion until the niter is decomposed and then a rapid fusion for 30 -35 minutes. Then hammer the button into as thin a sheet as possible and cut into small pieces.

If the button is brittle, that is if pieces of the button are liable to fly off on hard hammering, proceed more gently until the button is seen to crack, and then break up with the fingers.

Put the copper-lead alloy into a large casserole, add 35-45 cc dilute HNO_3, heat until a solution of the button is obtained, and add a slight excess of normal NaCl solution (a large excess should be avoided as AgCl is soluble in a large excess), and a dilute solution of H_2SO_4.

The resulting mixture is allowed to stand in a warm place for 10-15 minutes.

The solution is then filtered and the precipitate washed several times to free it from copper salts.

The precipitate, paper and all is then placed in a scorifier and

4	grs.	Borax Glass.
5	"	PbO
2	"	Pb added.

This is first placed in front of the muffle to dry the silver-lead precipitate and to burn the filter paper, then placed in the back part of the furnace and scorified as in the usual manner.

Then the contents of the scorifier are poured into a mould and the button is cleaned and cupelled as usual.

On some copper mattes and ores the assayer must use his own judgement as to the amounts of the different constituents for crucible fusion, taking care to make the excess of PbO and KNO_3 sufficiently large.