LI.—*Notes on the Cupellation of Bismuth-silver Alloys.*

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THE loss of silver during the cupellation of lead-silver alloys has been the subject of a large number of experiments at various times, but comparatively few results have been published on the loss of silver by the cupellation of bismuth-silver alloys. It has been stated in Percy's "Metallurgy of Lead," that bismuth may be substituted for lead in the process of cupellation. A series of experiments was made, some years ago, in the Metallurgical Laboratory of the Royal School of Mines by Mr. Burbidge Hambly (*Chem. Gaz.*, 1856, 185—6) on the cupellation of lead-silver alloys, which proved that as the weight of the silver cupelled decreases, so the loss of that metal very slightly increases, provided the ratio of lead used is constant. His results also confirm the fact that with increase in the ratio of lead there is an increase in the loss of silver.

The following experiments were made in order to ascertain whether the loss of silver by cupellation was the same when varying quantities were used, the ratio in the amount of bismuth used in the place of lead being kept constant, and also to find the loss of silver when that of the bismuth used in cupelling was gradually increased.

The quantities of bismuth and silver taken were the same as those employed by Mr. Hambly for the experiment with lead and silver, which are given in Tables I and III.

The purity of the bismuth was a matter of first importance, and as commercial bismuth generally contains a small percentage of gold and silver, the bismuth was purified in the following manner:—

Refined bismuth was crushed to a powder, dissolved in warm nitric acid, and the clear solution diluted largely with distilled water so as to precipitate the bismuth. The nitrate was digested in a solution of potash, well washed with distilled water, dried, and reduced to the

* Unaffected by the presence of moisture, so far as the actions have been investigated.

metallic state by heating with charcoal powder in a clay crucible; the metal being cast into a flat ingot, which was subsequently crushed to a coarse powder.

The silver used in the experiments was fine silver, re-purified by being dissolved in dilute nitric acid, precipitated as chloride with hydrochloric acid, washed thoroughly with hot water by decantation, and dried. The chloride was reduced by fusion with sodium carbonate, cast into a small ingot mould, and rolled out to a thin sheet for convenience in cutting up. As the silver could not be wrapped up in the bismuth, as is the case when lead is used, the alloys were made by cutting the silver into small pieces and mixing it with bismuth in the form of a coarse powder. The weighed quantities were wrapped in a piece of tissue paper and carefully transferred to the cupels which were previously heated in the muffle.

In some cases the bismuth and silver were wrapped up together and transferred to the cupel, and in other cases the silver was wrapped alone in the tissue paper and placed upon the cupel, and the bismuth, also wrapped in tissue paper, added immediately afterwards.

It is well known that the process of cupellation is liable to be affected by a variety of circumstances, its results being especially affected by the temperature of the muffle during the operation (*cf.* T. K. Rose, *Trans.*, 1893, **63**, 700). In order, therefore, to ensure a proper adjustment of the heat, and thus obtain uniformity of temperature, the optical pyrometer devised by Messrs. Nouel and Mesuré was used. As the instrument is not capable of registering temperatures to a high degree of accuracy, it was used less to measure the temperature of the muffle than to follow, by observations comparable with each other, the variations of heat. The temperature was slightly lower than that usually used for the cupellation of lead-silver alloys, the melting point of bismuth, 270° being somewhat below that of lead, 334° . French cupels, manufactured by Deleuil, of Paris, were used.

The iridescent bands which pass over the surface of the silver buttons towards the end of the cupellation, and which are produced by extremely thin films of fluid litharge formed from the last traces of bismuth, appeared to be somewhat brighter in the cupellation with bismuth than in the case of lead. It is also interesting to note that when equal quantities of lead and of bismuth are cupelled in a muffle at the same time, the oxidation proceeds more slowly in the case of bismuth than in the case of lead, the cupellation of the lead being finished some minutes before that of the bismuth. In order to avoid the "spitting" of the silver buttons, the muffle was allowed

to cool slowly until they were set, after which they were cleaned and weighed. In all cases, the buttons were bright and well rounded. The following tables give the results obtained :—

TABLE I.—*Mean Results obtained by Mr. Hambly on Cupelling a Mixture of Lead and Silver in a Constant Ratio.*

Quantity of lead used.	Quantity of silver used.	Mean weight of silver globule obtained.	Calculated weight of silver per cent.	Loss of silver per cent.
250	25	24·733	98·932	1·068
100	10	9·886	98·865	1·135
10	1	0·988	98·775	1·225

TABLE II.—*Results obtained with Bismuth and Silver.*

Quantity of lead used.	Quantity of silver used.	Mean result of silver globule obtained.	Calculated weight of silver per cent.	Loss of silver per cent.
250	25	24·391	97·566	2·434
100	10	9·741	97·416	2·584
10	1	0·973	97·370	2·630

Mr. Hambly has concluded that, provided lead and silver be taken in a constant ratio, the loss of silver very slightly increases according to the decrease in the weight of the silver cupelled. From the above experiments, which are the mean results of a large series of cupellations, I think the conclusion may be drawn that a very much greater loss takes place when bismuth is present under the same conditions, instead of lead, although the ratio of the loss appears to be about the same.

The experiments given in Tables III and IV tend to confirm the fact already known, that an increasing ratio of lead or bismuth produces an increasing loss of silver; the loss, however, being very much greater in the case of bismuth.

To determine with accuracy and in a thoroughly satisfactory manner the extent and exact ratio of the loss of silver in the cupellation with either lead or bismuth, a much larger number of cupellations are requisite.

As the loss of silver by volatilisation during cupellation is altogether inconsiderable, unless the temperature at which the operation has been conducted has been much too high, the loss is evidently due to the fact that silver is absorbed by the cupel.

TABLE III.—*Mean Results obtained by Mr. Hamblly on Cupelling Lead and Silver, Lead being taken in gradually increasing Ratio. The weight of the Silver used in each of the following Experiments was 5 grains.*

Lead.	Ratio of lead to silver.	Percentage of silver.	Mean result of silver obtained.	Calculated loss of silver per cent.
5	1 to 1	50·00	4·972	0·55
15	3 „ 1	25·00	4·955	0·90
25	5 „ 1	16·16	4·945	1·11
35	7 „ 1	12·50	4·941	1·18
45	9 „ 1	10·00	4·933	1·34
50	10 „ 1	9·09	4·924	1·52
75	15 „ 1	6·25	4·919	1·62
100	20 „ 1	4·76	4·916	1·68
125	25 „ 1	3·84	4·912	1·76
175	35 „ 1	2·77	4·906	1·88

TABLE IV.—*Results obtained with Bismuth and Silver. 5 grains of Silver was used in each.*

Bismuth.	Ratio of bismuth to silver.	Percentage of silver.	Mean result of silver obtained.	Calculated loss of silver per cent.
5	1 to 1	50·00	4·967	0·660
10	2 „ 1	33·33	4·964	0·720
15	3 „ 1	25·00	4·955	0·900
25	5 „ 1	16·16	4·940	1·190
35	7 „ 1	12·50	4·924	1·520
45	9 „ 1	10·00	4·909	1·820
50	10 „ 1	9·09	4·898	2·034
75	15 „ 1	6·25	4·878	2·428
100	20 „ 1	4·76	4·832	3·354
125	25 „ 1	3·84	4·808	3·840
175	35 „ 1	2·77	4·768	4·640

The bismuth was extracted from the cupels in the following manner:—After breaking off and rejecting the white portions of the cupels, the stained portion was powdered and passed through a sieve of about 60 holes to the linear inch. The powder was then mixed with sufficient charcoal powder to reduce all the oxide of bismuth present, and with fluxes in the following proportions.

Powdered cupels.....	1000 grains
Fluor spar	800 „
Sodium carbonate	400 „
Borax.....	200 „
Charcoal.....	45-50 „

The mixture was fused in a clay crucible in a wind furnace at a red heat, and the contents poured when the charge was in the state of tranquil fusion.

300 grains of the bismuth extracted from the cupels used for a large number of the experiments, when cupelled gave 0.294 grain of silver, equal to 0.098 per cent.

The following result was obtained by the cupellation of the lead extracted from a cupel upon which 175 grains of lead had been cupelled with 5 grains of silver.

Weight of silver button from 1st cupel	=	4.908	grains	=	98.160	p.c.	
" " " " 2nd "	=	0.075	"	=	1.500	"	
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Total weight of silver obtained		=	4.983	"	=	99.660	"
Loss			0.017	"		0.340	"
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		5.000				100.000	

The cupellation of the bismuth extracted from a cupel used for the cupellation of 175 grains of bismuth with 5 grains of silver gave

Weight of silver from 1st cupel	4.795	grains	=	95.900	per cent.
" " " " 2nd "	0.204	"	=	4.080	"
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Total weight of silver obtained	4.999	"	=	99.980	"
Loss	0.001	"	=	0.020	"
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		5.000		100.000	

The accompanying diagram helps to illustrate more clearly the losses which take place.