before by dipping in water, so that the slag may be readily detached when cold. The refined button should be flat or only slightly depressed on its upper surface, with a thin film of an orange red colour; it should be soft, malleable, and tough; should break with difficulty and have a fine silky fracture. If impure, it has more or less the character of coarse copper.

(c) Cleaning Refinery Slag to extract the Copper.

Fuse the slag with 20 grains carbonate of lime, 30 of tartar and 10 of charcoal, and weigh the button of copper obtained with the refined button.

Refinery slag is either grey, flesh-coloured, pink, pale red, blue, or bluish green, from the presence of copper oxide, or deep red from the presence of cuprous oxide, which is probably due to the refining flux being too "sharp," *i.e.*, containing too much nitre.

The effect produced on copper by the presence of other metals may be seen by reference to § 26.

ASSAY OF YELLOW ORES OF COPPER.

§ 116. Pyritic ores are the most abundant ores of copper, and when pure may be represented by the formula (Cu_2S, Fe_2S_3) containing 34·81 per cent. of copper.

The dry assay of copper ores by the Cornish method is intended to give the purchaser an idea of the quality and quantity of metal that can be obtained by smelting, but the loss is greater in the assay than in the smelting on the large scale. The loss of copper in the dry assay is shown by the table on the following page.

The Cornish assay comprises the following operations:—1. Fusion for regulus. 2. Roasting the regulus obtained. 3. Fusion for coarse copper. 4. Cleaning the slag from No. 3. 5. Refining the coarse copper. 6. Cleaning the refining slag.

Assuming the ore to contain from 10 to 20 per cent. of copper, the following fluxes may be taken as a general guide:—400 grains of ore, 300 borax, 300 glass, 400 lime, 400 fluor-spar, and 100 nitre.

Borax may be used alone in many cases, taking about 1200 grains instead of the above mixture. If the ore be a very poor one, then 500 to 600 grains should be taken; if rich, 200 grains will suffice.

Copper Present.	Dry Assay.	Margin.
35	33·25	1·75
30	28·5	1·5
25	23·5	1·5
20	18·5	1·5
18	16·5	1·5
16	14·5	1·5
14	12·75	1·25
12	10·75	1·25
10	8·75	1·25
8	7·0	1·0
6	5·0	1·0
5	4·0	1·0
4	3·0	1·0
3·5	2·6	·9
3	2·1	·9
2	1·3	·7

(a) Fusion for Regulus.

Use the copper assay pot (Fig. 36 *b*) which has been previously annealed by placing over a hot furnace in an inverted position. The ore and fluxes must be ground to a fine powder, and sifted if necessary, as a fine state of division greatly assists in the chemical reactions which occur between the components of the mixture. The ingredients should be well incorporated, placed in the pot, and the whole covered with about 50 grains of borax. Then place in a hot fire, using same precautions as given in § 115. Only a moderate draught should be

allowed at first, which may be regulated by partly closing the damper, and drawing the back brick slightly forward, so as to allow a little air to enter without passing over the crucible; as the operation proceeds, the brick is pushed back so as to close the furnace and the damper opened. After a few minutes, effervescence occurs, producing large bubbles which may cause some of the ingredients to overflow the sides; these bubbles may be broken by touching with an iron rod. In about fifteen minutes all action ceases, and the mass settles down into tranquil fusion. The pot must then be removed from the fire by tongs, and a rotatory motion imparted to dissolve any particles from the sides, and cause the whole of the regulus to collect into one button; then pour the whole contents into a half-round mould. When the slag on the top has set, it should be slightly squeezed with the tongs in the centre to form a lip, so that it may be removed from the mould and dipped in water to make the slag brittle, and facilitate its separation from the regulus when cold. The mass should not on any account be left in the water till cold, otherwise the dampness will prevent perfect separation. Any slag adhering to the regulus should be carefully scraped off with a knife. Generally one or two small shots of regulus will be found round the edge of the slag, and must be detached and added to the main button. If the regulus cannot be easily detached from the slag, the latter should be re-melted with a little sulphur or iron sulphide to obtain another small button of regulus.

The slag from yellow ores is generally glassy and dark green or black in colour, due to oxide of iron. A good slag should be uniform throughout in colour and constitution, and not variegated or streaked; should be frangible and readily detached from the regulus. The addition of fluor-spar in the fusion facilitates the separation. Too much of the latter, however, produces a thick stony-looking slag which corrodes the crucible.

If the regulus is coarse and dull in appearance resembling sulphide of iron and if it is more or less flat, hard, and crystalline, with a brassy yellow colour, the slag will be free from copper, and may be thrown away.

When the regulus is very fine grained, smooth, bright, and round on the external surface, with a dark colour, its fractured surface presenting a fine bluish-black colour with a glassy or compact structure, the slag is then liable to contain copper, and must be re-melted with a little sulphide of iron to obtain the copper as regulus.

A good regulus should be reddish brown in colour, moderately fine grained, convex on upper surface, readily frangible, and should contain from 50 to 60 per cent. of copper, which corresponds to the "blue metal" of the copper smelter.

A coarse regulus shows that more nitre was required for the fusion. A very fine regulus, that the sulphur was insufficient.

(b) *Roasting the Regulus.*

Reduce the regulus to fine powder in an iron mortar, preferably one with a lid having a hole in the centre through which the upper part of the pestle can pass to prevent particles being lost (Fig. 57), or the mortar may be covered with a duster, part of which is wrapped round the pestle. Then carefully brush the powder on to a sheet of glazed paper, remove any residue from mortar by rubbing in 5 grains of anthracite, and add this to the former. Introduce the powder into a clean No. 2 crucible and calcine till sweet. For this purpose the hot furnace is filled up with small coke and the crucibles (generally two assays are worked at one time) placed in an inclined position in the fire with the open end towards the operator. An iron rod (Fig. 15 *l*) flattened and smooth

Fig. 57.

at the end is put in each pot, being used for occasional stirring during the process. The operation should be commenced at a low red heat, and the temperature gradually increased to a clear red. For the first twenty minutes frequent stirring is necessary to prevent clotting, afterwards only occasional stirring will be required. If the temperature is too low at first, sulphate of copper is formed; if too high, the mass will frit together and prevent perfect oxidation. The completion of the roasting may be determined by removing the crucible from the fire and wafting a current of air across it with the hand, when no odour of sulphur dioxide will be perceived if the oxidation is complete. In order to decompose any sulphate which may have formed, 20 grains of finely-powdered anthracite is added, and the roasting continued with stirring for ten or fifteen minutes at a bright red heat. With a successful operation the powder should remain free from lumps to the end. If any lumps are formed by clotting, the regulus must be ground in the mortar again with a little anthracite, transferred to crucible, and again roasted. Any particles adhering to the stirring rods must be completely scraped off. Instead of a crucible, the roasting may be performed in a scorifier, previously rubbed with hematite powder, and heated in a muffle: this method requires less attention than the former.

(c) *Fusion for Coarse Copper.*
The roasted regulus is mixed with—
50 grains of carbonate of soda, 80 grains of tartar, and 30 grains of borax. Or, 80 grains of tartar, 30 of borax, and 20 of nitre, in the same crucible employed for roasting, which avoids any liability to loss as is the case when it has to be transferred from a scorifier. Put into a hot fire and proceed as described in § 115 (a).

(d) Clean the slag according to directions given in § 115 (b).

(e) Refine and clean refinery slag as in § 115 (c).
It should be observed that roasted regulus is a similar substance to a rich oxidised ore, and may be treated in the same way.

GREY ORES.

§ 117. Under this category are included all those ores which contain little or no iron, and require the addition of sulphur, sulphide of iron, or iron pyrites, to yield a proper regulus; such as copper glance (Cu_2S) (containing, when pure, 79·7 per cent. of copper, also known as "vitreous" or grey sulphide of copper) and Fahlerz, or true grey copper ore, containing antimony, arsenic, iron, zinc, lead, silver, etc. The following analyses collected by Dr. Percy show the composition of Fahlerz:—

	1	2	3	4	5	6
Copper,	38·42	37·98	39·18	40·57	38·63	30·73
Antimony,	25·27	23·94	23·66	21·47	16·52	17·76
Arsenic,	2·26	2·88	4·4	2·42	7·21	11·55
Silver,	·83	·62	—	·56	2·37	·10·53
Iron,	1·52	·86	6·99	2·92	4·89	1·42
Zinc,	6·85	7·29	—	5·07	2·76	2·53
Sulphur,	25·03	25·77	25·64	26·10	26·33	25·48
	100·18	99·34	99·87	99·11	98·71	100·0

Take 100 grains of ore, 100 grains sulphide of iron, 20 grains tartar, 200 grains lime, 200 grains fluor-spar, 150 grains glass, and 150 grains borax. Fuse for regulus and proceed as with yellow ores. The regulus from rich ores is very fine grained and rich in copper, with a great tendency to clot, so that great care is required in roasting, especially during the first fifteen minutes. When the ore contains lead the regulus is very liable to fuse, and it becomes extremely difficult to moderate the heat so as

to expel arsenic and sulphur, and at the same time prevent agglomeration of the powder.

GERMAN COPPER ASSAY.

§ 118. This operation differs from the Cornish method in several particulars; and the results obtained, as a general rule, are said to be a little higher.

The fluxes and re-agents employed are borax, glass, salt, charcoal, graphite, and black flux (obtained by deflagrating two parts of tartar and one of nitre), which is used as a reducing agent.

The method comprises the following operations:—

1st. Roasting to oxidise and remove volatile impurities.
2nd. Melting for coarse copper.
3rd. Refining the crude copper obtained from No. 2.

(a) Roasting.

About 60 grains of the finely-powdered ore is placed in a roasting dish or scorifier, which has been previously rubbed with an unctuous variety of hematite to prevent the ore sticking to the vessel, introduced into a red-hot muffle, and stirred for about fifteen minutes, or until no odour of sulphurous acid is perceived, using all the precautions mentioned in the English method. The dish is then removed from muffle, the powder brushed into an iron or bronze mortar, and mixed with 15 grains of graphite, and thoroughly incorporated by grinding with pestle. This mixture is then introduced into a peculiar egg-shaped crucible (Fig. 58), which is laid sideways in the hot muffle, with its open end to the front, and roasted till sweet, which generally takes ten to fifteen minutes. When lead and antimony are present, a low temperature, with careful stirring, is required to prevent clotting.

Fig. 58.

(b) Melting for Coarse Copper.

The roasted ore is mixed with 60 grains of black flux, and on the top are thrown 130 grains of black flux, 25 to 30 grains of powdered glass, and 15 to 20 grains of borax. The whole is covered with 150 grains of common salt, and on the top a piece of charcoal is added. When the ore is rich and free from lead, 10 to 15 grains of arsenic are added to produce a more fluid slag. The crucible is then covered, as shown in Fig. 58, and placed in muffle. The temperature is gradually raised to a very bright red, the operation taking about half an hour. The crucible is then removed, allowed to cool with its contents, and broken to obtain the button of copper. The slag should be a dark-green glass, and the button of metal free from any crust of regulus.

(c) Refining.

The coarse copper obtained in the last operation is wrapped in a piece of paper with an equal weight of borax, and placed in a small red-hot scorifier heated in the muffle. In a few minutes the copper melts, when the brick closing the muffle should be removed to allow a current of air to pass over it. The oxides of the foreign metals gradually pass from off the button of copper, which at last emits a greenish light, sinks beneath the borax, and solidifies. The vessel is now removed, partly cooled in water, and, when cold, the button of copper is detached from the slag. This refining of copper is based on the principle, that copper remains unoxidised as long as more oxidisable metals are present, the oxides of which unite with borax to form a fusible slag.

PLATTNER'S METHOD FOR THE VALUATION OF COPPER ORES, SLAGS, AND ALLOYS, CONTAINING COPPER, LEAD, BISMUTH, NICKEL, AND COBALT.

§ 119. (a) *Roasting.*

About 4 grammes of the ore, containing sulphides and sulphates, are taken for assay. Roast on a scorifier in a muffle till the sulphur is nearly expelled ; then add a little of ammonium carbonate, and heat until all the sulphur is expelled. Ores containing gypsum, heavy spar, and alkaline sulphides in combination with metallic sulphides, are first fused in a crucible with 4 grammes of vitrified borax, ½ gramme of colophony and the whole covered with 10 grammes of common salt. The crucible (Fig. 59) is covered and heated for thirty to forty minutes in a muffle. If the metals exist as oxides along with gypsum, etc., then 1 gramme of metallic arsenic is added to the above mixture. The sulphide of sodium produced by the action of sulphur on borax, passes into the regulus, and may be dissolved out with hot water.

Fig. 59.

(b) *Conversion into Arsenides.*

The roasted ore or regulus is mixed with 4 grammes of arsenic, and heated for fifteen minutes in a covered crucible (Fig. 59) placed in a red-hot muffle until all arsenical vapours are evolved.

(c) *Union of Metallic Arsenides into a whole, and Separation of Lead and Bismuth by Fusion with Suitable Fluxes.*

If the crucible used in the preceding operation is sound, the mass contained in it is covered with from ½ gramme to 1 gramme of iron wire, according to the amount of lead present, 8 grammes of black flux, and 2 to 3

grammes of vitrified borax, and the whole covered with 10 to 12 grammes of purified common salt, and a piece of charcoal on the top. The cover is put on crucible; then it is placed in hot muffle, when a gradually increasing temperature is used for twenty-five to thirty minutes. Remove, cool and break open the pot. The slag should be dark green or black, covered with a grey crust of common salt, and at the bottom or side is the reduced lead, which contains the silver, bismuth, and some of the antimony, if present, but no copper. The regulus may be detached from the lead with a knife, or by breaking it away with a pestle in a mortar. Bismuth acts the same as lead, but, being brittle, is more difficult to separate from the regulus.

(d) *Separation of Arsenide of Iron and Oxide of Zinc from the Arsenides of Nickel, Cobalt and Copper.*

The arsenides are placed with 2 to 3 grammes of borax in a scorifier, and raised to a white heat in a muffle. After a few minutes, the muffle is partly opened, and as soon as the assay has acquired a bright vapourising surface the temperature is so regulated that small films of oxide may form on the surface and pass into the borax. If the temperature is too high, the assay becomes bright ; if too low, the whole surface becomes oxidised. The process is complete when the surface becomes tranquil, and fumes of arsenic begin to escape. At this stage iron is scorified, and zinc volatilised. If the assay gets covered with a crust before the temperature falls, it shows an insufficiency of borax, and the operation must be repeated with more borax in another scorifier. The assay is removed, partly quenched in water, and cleaned from slag by tapping with a hammer.

(e) *Removal of Excess of Arsenic by Volatilisation.*

The button obtained from the last operation is mixed with 1 grain of borax wrapped in a little tissue paper, then

placed in a cavity scooped out of a lump of charcoal and melted in a closed muffle; when the metal exhibits a shining appearance and begins to evolve arsenical vapours, the muffle is partly opened to increase the volatilisation. When vapours cease, remove from muffle, and weigh the button, which should have a dull, black surface and contain the definite compounds—

$$Co_4As_2, Ni_4As_2 \text{ and } Cu_6As_2.$$
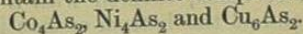
(*f*) *Separation of the Arsenides of Cobalt from the Arsenides of Nickel and Copper.*

The weighed button of speise is wrapped in paper and placed in a hot scorifier, containing about 1 gramme of borax, and heated nearly to whiteness; a current of air is then admitted to oxidise the cobalt, which is scorified by the borax. Two or three pieces of charcoal are placed in front during the coruscation. As soon as a green film of arsenide of nickel appears, the vessel is removed, partly quenched in water, allowed to cool, the speise detached and weighed. The loss represents the Co_4As_2, containing 61 per cent. of cobalt.

(*g*) *Separation of Arsenide of Nickel from Arsenide of Copper.*

The speise obtained from the last operation is treated with borax as before, heated till no more green films appear, and arsenical vapours begin to come off from the decomposition of arsenide of copper. The temperature must be gradually lowered as the arsenide of nickel is removed, because the arsenide of copper is more easily fusible. The button is again weighed; the loss representing the Ni_4As_2, and the arsenic volatilised from the copper; so that the nickel cannot be computed till the amount of copper is known.

(*h*) *Volatilisation of the Arsenic combined with Copper, and estimation of Nickel and Copper.*

The button of arsenide of copper is laid in the cavity of a piece of glowing charcoal placed in a muffle, and the latter closed till the speise is melted. The muffle door is then opened; the charcoal drawn near the front, which is partly blocked up with glowing coals and the temperature kept at a bright red, until films of cuprous arsenite begin to appear on the surface of the metal. The temperature is then raised until the metal exhibits the bluish green colour of pure copper, and the films which form upon it make their appearance at the top and not on the sides. The assay is then removed, quenched in water, and the button of copper, which should be malleable, weighed. The weight of copper obtained indicates the amount of copper present in the assay. To determine the nickel, the copper is calculated as Cu_6As_2; the resulting weight is deducted from the known weight of the arsenides of nickel and copper together and the difference gives the weight of Ni_4As_2, which contains 61 per cent. of nickel.

If the copper alloy is free from nickel and cobalt, as is often the case, then the operations (*f*) and (*g*) become unnecessary, and the process is reduced to the separation of arsenide of iron, including antimony and zinc, from the arsenide of copper. (Watt's Dictionary, page 63, vol. ii.)

## ASSAY OF LEAD ORES AND PRODUCTS.

§ 120. (*a*) This assay may be conveniently divided into two classes. The first, comprising all those which contain sulphur, phosphorus, and arsenic, such as galena, pyromorphite, etc. The second, including all substances other than the foregoing, which contain lead in an oxidised state, such as carbonates, oxides, etc.

(*b*) The fluxes and re-agents employed are:—Metallic iron, alkaline carbonates, black flux, nitre, tartar, sodium chloride, carbon, and borax.

(c) *Metallic iron* completely decomposes sulphide and silicate of lead, as shown by the following equations :—

$$PbS + Fe = FeS + Pb.$$
$$2PbO,SiO_2 + 2Fe = 2FeO,SiO_2 + 2Pb.$$
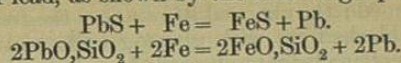
(d) *Sodium carbonate* partially decomposes galena, forming some metallic lead ; the remaining lead sulphide passes into the grey fusible slag, thus :—

$$7PbS + 4Na_2O = 4Pb + Na_2SO_4 + 3(PbS,Na_2S).$$
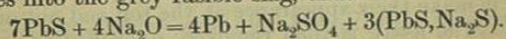
If iron be added along with the sodium carbonate, the reduction is complete.

(e) *Nitre* completely decomposes galena when present in the right quantity, but if in excess, the reduced lead would be oxidised.

$$2PbS + 2KNO_3 = SO_2 + K_2SO_4 + N_2 + 2Pb.$$
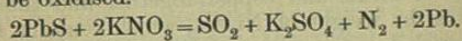
(f) *Tartar and charcoal* reduce oxides, and favour the reduction of galena, etc., by isolating a portion of the lead, and forming a quantity of alkaline sulphide.

FIRST METHOD.

§ 121. For this purpose take a sample of galena weighing about 12,000 grains ; dry ; powder in an iron mortar ; pass through a sieve with sixty meshes to the inch and well mix together. It may sometimes happen that malleable particles remain which will not pass through the sieve ; these must be put on one side and assayed separately, the proportionate amount of metal being added to each assay made from the above quantity.

(a) *Assay in Earthen Crucible.*
The pot used is about 3½ inches high and 1½ inches wide (Fig. 35 d). Take 400 grains of ore, 300 grains of

carbonate of soda, and 30 grains of tartar ; well mix and introduce into the crucible, then cover with another 100 grains of carbonate of soda, and insert a piece of hoop iron bent into a ∩ shape. Or, instead of 400 grains of carbonate of soda, 350 grains may be mixed with the ore and tartar, and 50 grains of borax placed on the top. Place the crucible into a hot fire containing no black coke, but all in the glowing state ; cover the mouth of crucible loosely with a piece of coke ; well pack round with hot coke ; cover furnace with bricks at top so as to exclude the air as much as possible during the operation, and heat for about fifteen minutes. Take hold of the iron with tongs, stir the contents of crucible with it, carefully shake into the pot any globules of lead adhering to the iron, and invert it so as to have the bow part at the bottom ; again cover with piece of coke, and heat for about ten minutes longer, when the liquid should be tranquil, and the reduction complete. Now remove the iron, taking care to detach any lead ; remove crucible from fire, and pour the contents into a dry, half-round mould. Allow to stand until perfectly cool ; then detach slag by hammering the button placed edgewise on a clean anvil so as to squeeze off the regulus and obtain the lead in a rectangular shape. Again hammer the edge so as to produce a rough square shape. Finally, hammer the corners so as to make it octagonal in shape, thus:— If the mass be at all hammered on the larger flat surface, some of the regulus will be forced into the lead, making it very difficult to remove, and thus giving too high a result. The metal thus treated will be soft and malleable if pure. A layer of glistening lead sulphide indicates, of course, that the reduction has been incomplete. If the heat is continued too long and air admitted, some lead will be oxidised and form silicate with the clay of the crucible, whilst some will be volatilised. A hard, brittle metal indicates the probable presence of antimony and arsenic.

Instead of the hoop iron bent in ∩ shape, two pieces may be used, placed so \/. Or three wrought-iron ⋇ nails, inverting as before at the end of fifteen minutes. On making experiments with hoop iron and nails, as described above, the following results were obtained from a sample of galena :—

1	2	3
78·50 per cent. 78.75 ,,	78·55 per cent. 78·75 ,,	78·75 per cent. 78·00 ,,

In the third case there is a tendency of the nails to carry away a little lead, especially if not reversed during the process.

Some assayers use iron filings, but this is not to be recommended, as particles of iron are liable to be retained by the reduced lead and increase its weight.

(b) *Assay of Galena in an Iron Crucible.*

In this case the addition of metallic iron is dispensed with, the crucible itself answering the purpose, being gradually worn away by repeated operations. For this purpose a piece of good wrought-iron plate about ½ inch thick is turned up in the form of a crucible, and the edges welded. The bottom is filled with a thick iron plug, which is then firmly welded to the sides, and the whole finished smooth by hammering on a suitable mandril. Such a pot may be used alone when assaying pure galena, but it is generally advisable to add fluxes as in a clay pot. When used alone, it should be heated to redness, and the powdered ore introduced by means of a copper scoop or a piece of clean sheet-iron bent in the form of a spout, then replaced in the fire, well packed round with coke, and covered also with a piece of coke.

The temperature is then gradually raised, during which the contents become liquid, giving off quantities of gas. In ten to fifteen minutes the sides of the pot should be scraped with an iron rod to detach any particles of metal which may adhere to it. The crucible is again covered and left in the closed furnace another five minutes, then removed, and the contents poured into a half-round mould. The sides are then scraped with an iron rod to obtain any particles of lead remaining, which particles are cleaned from slag, and added to the main bulk of metal, and the whole weighed.

(c) As wrought-iron crucibles are expensive, pots made of malleable cast-iron may be substituted, but the temperature must not be allowed to get too high, or the crucible itself will melt.

For fusion in an iron pot with fluxes, the following proportions may be used :—

I.		II.	
Ore, - - 500 grs.		Ore, - - 500 grs.	
Sodic carbonate, 500 ,,		Sodic carbonate, 450 ,,	
Tartar, - 50 ,,		Tartar, - 50 ,,	
		Borax, - 50 ,,	

With the first proportions, about 50 grains of carbonate of soda are left to cover the mixture after placing in the pot. In the second case the 50 grains of borax serve this purpose.

As before, the crucible is made red hot, removed from the fire to introduce the assay mixture and then replaced. The operation is conducted in precisely the same way as when the iron crucible alone is used.

Operating on the same ore as mentioned in § 121a, the following results were obtained from two assays :—

78·60 per cent. and 78·88 per cent.

(d) Assay of Pyromorphite, known as Green Linnet.

Phosphate of lead ores are treated with the following proportions of fluxes, and assayed in an earthen crucible. Either of the two following proportions may be used:—

I.			II.		
Ore,	-	300	Ore,	-	300
Carb. of soda,	-	350	Carb. of soda,	-	400
Tartar,	-	100	Charcoal,	-	25
Borax,	-	30	Borax,	-	30

The first three substances are well mixed together, placed in clay crucible, and covered with the 30 grains of borax. The temperature should be gradually raised, and care should be taken to obtain a uniform heat in all parts of the pot, as a somewhat violent reaction occurs, and the substance is liable to boil over, when the assay would be vitiated.

The general temperature should be higher than with galena, and a good bright red heat obtained to finish with. The lead is detached from slag as before, and weighed. The following results were obtained with the above mixtures:—

1st mixture, 62·23 per cent.	2nd mixture, 61·96 per cent.
„ „ 62·16 „	„ „ 61·66 „

## METHOD EMPLOYED IN THE UPPER HARTZ.

§ 122. 5·7 grammes of the finely powdered ore is mixed with three or four times its weight of dry carbonate of potash, placed in a clay crucible of the Hessian shape, and the mixture covered with a layer of common salt about ¼ inch thick. The lid is then put on, and the pot put into a hot muffle, which is then raised to its highest heat. To prevent undue accession of air, the mouth of the

muffle is surrounded with glowing coals. In from twenty to thirty minutes the mass will be perfectly fused; the damper is then partly closed, and the muffle opened until the temperature has fallen to a low red heat, and the vapours have disappeared. The temperature must all the while be maintained sufficiently high to keep the mass in perfect fusion. The assay is left at this point, for another fifteen minutes, then removed, allowed to cool, the crucible broken, the slag detached, and the button of lead weighed.

If the assay has been successful, the button of metal has the characteristic colour, malleability, and softness of pure lead. If the slag shows on the surface of separation from the metal lead-grey spots with a metallic lustre, there will generally be glistening lead sulphide undecomposed on the surface of the button of metal, which then has a dark colour and high metallic lustre. If the button is laminated, brittle, and white in fracture, there has been an insufficiency of flux, or the metal contains antimony and arsenic. When successful, the lead should have a bluish appearance, rather dull than brilliant. The slag should be homogeneous and well settled down towards the bottom of crucible, showing that there has been proper fusion. The sodium chloride covering forms a thick light-coloured slag overlying the thick dark coloured slag which contains the metallic oxides. A porous slag containing metallic globules indicates too small a quantity of flux or too low a temperature; a brilliant vitreous slag, too high a temperature and scorification of lead.

§ 122A. Lead Matt (PbS) and Lead Fume are smelted with the addition of borax and coal dust to the potassium carbonate, and the first heat continued longer than when assaying ores. The potash of the carbonate is reduced to potassium, while it yields its oxygen to the sulphur of the matt forming sulphuric acid; the liber-

ated potassium takes up sulphur from another portion
of the matt forming potassium sulphide. The matt
would in this way soon lose all its sulphur if a com-
bination—a sulphur salt—of potassium sulphide with
lead sulphide did not form, and resist all further action
of the potassium carbonate thus :—

$$4K_2CO_3 + 7PbS = 4Pb + 3(K_2S,PbS) + K_2SO_4 + 4CO_2.$$
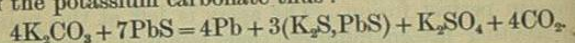
SECOND METHOD.

§ 123. The assay of oxidised ores and products free from
sulphur, arsenic, and phosphorus, is a simple operation, if
care be taken that sufficient carbon or carbonaceous matter
is added, to reduce the oxide to the metallic state. The
metalliferous matter must be ground and passed through
a fine sieve.

(a) Take 400 grains of ore, mix with 600 grains of dry
carbonate of soda, and 15 to 20 grains of charcoal, place
in a clay crucible, which should not be more than half full,
and cover with a layer of common salt. The crucible
should be placed well down in the fire, and must be
kept at a moderate temperature, carefully watched
through the space between the two bricks to see if any
portion through swelling up of the fluxes passes over the
sides. In such a case, the draught should be checked
and the bubbles broken as they form, by means of an
iron rod ; but if the crucible is placed well down in the
fire, and all parts at the same temperature, this nuisance
will be avoided. In a few minutes the boiling will cease,
and gas will no longer be given off ; then raise the tem-
perature for a few minutes, when the mass will soon
settle down into tranquil fusion. Remove from fire,
impart to crucible a rotatory motion to shake down all
particles of lead, so as to form a single button at the
bottom, and pour into a dry mould, which has been

blackened to prevent the metal sticking. When the
operation has been successfully performed, the cooled
slag will present a smooth concave surface with a vitreous
lustre. A safer plan is to allow the contents to cool in
the pot, and break the latter to obtain the lead. The
button, with its adhering slag, is then hammered on an
anvil to squeeze off the slag ; some small portions cannot
always be separated by mechanical means. They may be
removed by boiling in water containing sulphuric acid,
and brushing the metal with a hard brush.

(b) Instead of the assay mixture given above, equally
correct results may be obtained by either of the follow-
ing :—

I.		II.	
400 grains ore.		400 grains ore.	
500	,, carbonate of soda.	800	,, black flux.
200	,, tartar.		

Each of the above mixed and covered with borax.

ESTIMATION OF SILVER IN LEAD.

§ 124. As many ores of lead contain silver, this metal is
always tested for, and its amount estimated in a sample
whose character is unknown. This information is ascer-
tained by subjecting the lead obtained to the process of
cupellation. This method is based on the fact that lead
heated in a current of air is oxidised, while silver
remains unaltered (except that it absorbs some of the
oxygen mechanically), and when this is effected in a
porous receptacle, the oxide of lead is completely ab-
sorbed, leaving the silver on the surface in the unalloyed
state, or alloyed only with gold and members of the
platinum group.

(a) The assay for silver is conducted in shallow vessels made of bone ash called cupels, a description of the manufacture of which is given in § 22. The cupels are placed in a hot muffle, and left for a few minutes to attain the same temperature, which should be of such a degree that the lead may melt in a minute or two after its introduction. The lumps of metal are weighed and then charged into the cupels. When melted, the muffle door is closed until the operation is completed. If the temperature is too low, the lead will oxidise instead of melting, forming a thick crust on its surface, then when the temperature is raised, the lead is spirted up through this crust causing loss. If the temperature is too high, dense fumes will arise from the volatilisation of lead carrying with them particles of the molten metal, hence causing a loss of silver. When the right degree of heat is secured, the lead will have a bright and convex appearance, the vapours arise gently, and be promptly carried away by the draught, but there will be no violent projection of liquid particles, and the film of oxide as it forms will be carried from the top to the base of the liquid button, there being absorbed by the bone ash. Towards the completion of the process, the film of oxide becomes much thinner, producing a display of iridescent colours. In a short time these disappear, and the silver remains bright. During this stage the temperature should be raised by opening the damper, so as to remove the last traces of lead from the silver. The phenomenon of "flashing," which is quite distinct from brightening, then takes place. The button cools down below its solidifying point without actually becoming solid, and then suddenly emits a bright light or "flashes," and then becomes solid.

(b) Success also depends on the quantity of air passing through the muffle in the draught. When the air current is too rapid, the cupel is cooled, and the lead

being oxidised faster than the oxide can be absorbed by the cupel, the oxide may completely cover the metal and protect it from further oxidation. When the current is too feeble, the completion of the assay is unnecessarily delayed.

(c) When properly conducted, the assay button should be round, bright, and smooth on its upper surface, and when cold, easily removed from the cupel by a pair of pliers. Any matter adhering to the bottom may be removed by squeezing the button with the pliers, or tapping on the edge with a hammer, and brushing with a hard tooth brush.

Silver contained in lead or ores is reported in this country in troy ounces, dwts., and grains, per ton of 2240 lbs.

(d) The following are the results from two buttons of lead obtained from the assay of 400 grains of galena in earthen crucibles mentioned in § 121.

Lead obtained	-	312·0	313·8
Silver "	-	·202	·204

$$\text{Wt. of Pb.} \left. \right\} : \left\{ \begin{array}{c} \text{No. of grains} \\ \text{in 1 lb.} \end{array} \right\} :: \left\{ \begin{array}{c} \text{W. of Ag} \\ \text{obtained.} \end{array} \right\} : x.$$

$$312 \quad : \quad 7000 \quad :: \quad ·202 \quad : 4·532.$$

lbs. in 1 ton.

$$1 \text{ lb.} \quad : \quad 2240 \quad :: \quad 4·532 \quad : 10152.$$

One ton of the above lead therefore contains 10152 grains Ag, and this is reduced to oz. and dwts. thus :—

$$24 = \begin{cases} 6 & | \ 10152 \\ 4 & | \ 1692 \\ 2,0 & | \ 42,3 \\ \hline & 21·3·0. \end{cases}$$

The lead contains 21 oz. 3 dwts. of silver per ton. The amount of silver per ton of ore is calculated in same way, substituting 400 in the first proportion for 312, and both results shown as follows :—

			Per Ton of Lead.			Per Ton of Ore.		
		grs.	oz.	dwts	grs.	oz.	dwts	grs.
1. Wt. of ore 400 „ lead 312 }	Wt. of Ag ·202		21	3	0	16	9	22
2. Wt. of ore 400 „ lead 313·8 }	„ ·204		21	4	16	16	13	5

§ 125. Table showing amount of silver contained in one ton of ore corresponding to the weight obtained from 400 grains :—

If 400 Grains of Ore yield fine Metal	One Ton of Ore will give			If 400 Grains of Ore yield fine Metal	One Ton of Ore will yield		
gr.	oz.	dwts.	gr.	gr.	oz.	dwts.	gr.
·001	0	1	15	·200	16	6	16
·002	0	3	6	·300	24	10	0
·003	0	4	21	·400	32	13	8
·004	0	6	12	·500	40	16	16
·005	0	8	4	·600	49	0	0
·006	0	9	19	·700	57	3	8
·007	0	11	10	·800	65	6	16
·008	0	13	1	·900	73	10	0
·009	0	14	16	1·000	81	13	8
·010	0	16	8	2·000	163	6	16
·020	1	12	16	3·000	245	0	0
·030	2	9	0	4·000	326	13	8
·040	3	5	8	5·000	408	6	16
·050	4	1	16	6·000	490	0	0
·060	4	18	0	7·000	571	13	8
·070	5	14	8	8·000	653	6	16
·080	6	10	16	9·000	735	0	0
·090	7	7	0	10·000	816	13	8
·100	8	3	8				

When the silver obtained in the above processes contains gold, it is separated by dissolving out the silver in nitric acid, and the weight of the gold is deducted before computing the amount of silver present.

ASSAY OF SILVER ORES, PRODUCTS, AND ALLOYS.

This assay may be conveniently studied under three heads, viz. :—

I. Treatment of bullion, coin, and plate.
II. Ores of all kinds containing silver.
III. Various products and waste matters containing silver, such as litharge, slags, sweep, etc.

First Method. BULLION, COIN, AND PLATE.

§ 126. This assay is effected by means of cupellation which has been partly explained under the assay of argentiferous lead. Care must be taken that the sample employed represents the whole mass from which it is obtained, as alloys of silver and copper are liable to undergo liquation, so that different parts of the same ingot will give discordant results.

(a) Professor Roberts-Austen has made a special study of this subject. He cast the alloys in cubical fire-brick moulds, in which they could be cooled either rapidly or slowly. His results are embodied in the following table :—

No.	Name of Alloy.	Parts of Silver in 1000 of Alloy.	Rate of Cooling.	Maximum Variation of Silver in different parts.
I. a I. b }	British standard coin	925 }	rapid slow	12·8 per 1000 1·4 ,,
II. a II. b }	Old French standard coin	900 }	rapid slow	10·1 ,, 1·3 ,,
III. }	Levol's homogeneous alloy	718·93	slow	1·2 ,,
IV.	AgCu	630·3	slow	21·1 ,,
V.	AgCu₄	333·3	slow	12·8 ,,