

[Revised and Reprinted by the Author from the Journal of the Society of
Chemical Industry, 31 May 1894. No. 5, Vol. XIII.]

A JAPANESE PSEUDO-SPEISE (SHIROMÉ),
AND ITS RELATIONS TO THE PURITY OF
JAPANESE COPPER AND THE PRESENCE
OF ARSENIC IN JAPANESE BRONZE.

BY

W. GOWLAND, A.R.S.M., F.C.S., F.I.C.,
Late of the Imperial Japanese Mint.

In the separation of silver from copper by liquation with lead by the Japanese process, known as the "nambau fuki" method, an alloy of copper, arsenic, lead, and antimony, called "shiomé," is obtained as a by-product, in larger or smaller quantities, according to the nature of the copper treated.

As this substance is unique in composition among metallurgical products, as, besides, it forms an important constituent of some Japanese bronzes and allied alloys and has not hitherto been analysed or described, the following notes on its occurrence, composition, and uses will, I hope, be of interest to the members of our Society.

The process, too, in which it is produced will not be of less interest, as it possesses several important features and exhibits some curious relations or affinities of the metals copper, lead, arsenic, antimony and bismuth, under conditions which are not found in ordinary metallurgical operations,—affinities which have played a prominent part in the separation of the three latter metals from Japanese copper.

I propose now, with your permission, first, to describe the process in which the shiomé is a by-product, and its effects on the copper treated by it, and subsequently to consider the by-product itself.

The process of liquating copper with lead for the separation of silver is called, as I have stated above, "namban fuki," which signifies "melting after the style of the southern barbarians," the method having been introduced into Japan by the Portuguese. Since the date of its introduction, about the latter half of the 16th century, it has been continuously employed in the treatment of all copper containing sufficient silver to pay for its extraction.

As most of the copper ores of the country are more or less argentiferous the process has been and is still in extensive use, and very large quantities of silver have been extracted by means of it. Some gold also has been obtained, but only a part of that present in the metal treated can be liquated out with lead, a considerable proportion being always retained in the copper.

This process was not, however, introduced by the Portuguese in its present form. What they introduced was the old German method, known as "Das Saigern," only the principles of which have been followed by Japanese metallurgists, who, with these principles as a basis, developed the furnace, appliances, and method of liquation which are now in use and which are essentially Japanese.

Great credit is due to these metallurgists, especially to those of the early days, for the ingenuity they have exhibited in their radical alterations of the European method, for by these alterations they have not only made the process suitable for the work of the smallest mine, but have achieved results with it on all scales far surpassing in economy and in completeness of separation of the respective metals anything that had been accomplished by it in its original form.

Thus, for example, in the Japanese process less lead is required, a lead richer in silver is obtained, less lead and silver are left in the copper, and as small a quantity as 80 lbs. of copper can be treated at a time.

Copper suitable for liquation:—

The amount of silver in the copper which is necessary to make the liquation process a profitable one varies in different parts of the country.

In Tokio, 0·077 per cent. silver (25 ozs. 3 dwts. 1 gr. per ton) is said barely to pay the costs of the operation, but in other localities, where charcoal and labour are cheaper, this proportion of silver would be remunerative.

Generally speaking, in all districts when the copper contains 0·092 per cent. silver (30 ozs. 1 dwt. 2 grs. per ton) or more it is subjected to this process.

The following analyses show the proportions of silver contained in typical specimens of copper from different localities.

SILVER AND GOLD IN CRUDE COPPER.

Locality.	Silver.	Silver.	—
	Per Cent.	O s. per Ton.	
Province of Bungo..	0·060	19·60	Gold trace; nickel, cobalt, 0·251 per cent.
„ Echigo (Kusakura).	0·078	25·48	Gold trace.
„ Kozuke (Ashiwo).	0·094	30·70	„
„ Tosa ..	0·135	44·10	„
„ Uzen ..	0·140	45·73	„
„ Bichu ..	0·165	54·40	„
„ Hida (Takayama).	0·185	60·43	„
Yezo	0·230	75·13	Gold 0·003 per cent. (0·96 oz. per ton).
Province of Bichu ..	0·252	82·32	Gold trace.
„ Unknown..	0·527	172·15	„
„ of Rikuchu (Kosaka).	0·650	212·33	Gold trace, lead 4·09 per cent.
„ Iwami (Omori).	Trace	..	Gold 0·0165 per cent. (5·39 ozs. per ton).

Silver and Gold in Crude Copper—*continued.*

Locality.	Silver.	Silver.	—
Province of Rikuchu (Towata).	Per Cent. Trace	Ozs. per Ton. ..	Gold 0·0285 per cent. (9·31 ozs. per ton).
” ”	”	..	Gold 0·0436 per cent. (14·22 ozs. per ton).
” ”	0·011	3·60	Gold 0·0810 per cent. (26·51 ozs. per ton).
Korea.....	2·590	846·07	Gold trace.
”	3·000	980·00	”

Two specimens of copper from Korea are included in this table as they represent the most highly argentiferous crude copper I have met with in the East. The occurrence of such large percentages of silver in these specimens leads me to direct the attention of miners and metallurgists who may proceed to that country to the copper ores as sources of silver, as hitherto prospectors have confined their search for the metal to outcrops of galena and silver ores proper, and have not had the success which their energy deserved. The large amount of gold in the copper from Towata is worthy of note. About five tons of the sample containing 26·51 ozs. per ton were imported into the Imperial Mint as crude copper, the importer being ignorant of the presence of gold in it until he received the assay report.

THE LIQUATION PROCESS.

The operations of the Japanese liquation process are divided into two stages, each being conducted in a different furnace, viz. :—

A. *Preparation of an alloy or mixture of copper and lead.*

B. *Separation of the lead (and with it the silver) from the mixed metals.*

When, however, the crude copper already contains sufficient lead, stage A is omitted and it is submitted at once to the operations of stage B.

Several mines in the province of Hida, where the metal is obtained by smelting ores rich in galena, yield copper of this description, in which the amount of lead, as will be seen from the following analysis, occasionally reaches 39 per cent.

CRUDE COPPER CONTAINING EXCESS OF LEAD (PROVINCE OF HIDA).

	Per Cent.
Copper	58·87
Lead	39·28
Iron.....	0·08
Arsenic.....	Trace.
Antimony.....	Nil.
Sulphur	1·64
Silver	0·185
Gold	Trace.
	<hr/>
	100·055
	<hr/>

This is exceptional, and generally in most districts the addition of lead is required.

Stage A.—Preparation of the mixture of lead and copper :—

The proportion of lead to be mixed with the copper varies at different mines and smelting works, ranging from 1 part of lead to 55 parts of copper at Ani (prov. of Ugo) to 1 part of lead to 3 parts of copper at Omodani (prov. of Echizen), the general ratio being about 1 to 4.

Both lead rich and poor in silver are used, the former being preferred when it can be procured, as more silver can be obtained from it than the old Japanese methods of assaying indicate, and the final cupellation is hastened.

The amounts of silver usually present in these two kinds of lead are as follows:—

SILVER IN JAPANESE LEAD.

Poor lead ...	0·063 %	silver	(20·56 ozs. per ton);	traces of gold.
„ ...	0·094 %	„	(30·71 „ „);	„
Richer lead..	0·312 %	„	(101·92 „ „);	„
„ ..	0·366 %	„	(119·56 „ „);	„
„ ..	0·424 %	„	(138·51 „ „);	„
„ ..	0·448 %	„	(146·35 „ „);	„

The furnace used is the typical Japanese smelting furnace shown in Fig. A. It consists simply of a rudely hemispherical hole about 16 in. diam. and 15 in. deep in a specially prepared portion of the ground of the smelting room, lined with a brasque of refractory clay and charcoal, and to which a blast is supplied through a clay twyer from the ordinary double-acting hand bellows in general use in China and Japan, which is placed behind the furnace.

Ignited charcoal is placed at the bottom of the cavity, which is then nearly filled up with fresh charcoal. Upon this the copper, which is in irregularly-shaped lumps, is placed, and more charcoal is heaped up over it.

The bellows are then started, more copper and fuel are added from time to time until the whole of the charge has been put in, and the blast is continued until all the copper has completely melted. The fire is then raked off, the metal skimmed, and the lead added and mixed thoroughly with the copper.

The alloy is then removed from the furnace by means of a curious tool consisting of a rudely spherical-shaped iron head about 4 in. or more in diam. attached to a long handle. This is dipped into the molten alloy, lifted out, and the adhering crust of metal knocked off and thrown into water. The tool is then cooled with water and another crust taken out, and this is continued until the furnace is emptied of its contents. This part of the operation is graphically shown in the Japanese drawing, Fig. A A. Six or seven charges, each of about 250—300 pounds of copper, are worked per day with a consumption of 20 per cent. of charcoal.

In a large copper refinery in Tokyo, erected after my designs, the copper is melted in charges of three or four tons, and is laded or run out in quantities of half a ton at a time into a large casting ladle in which the lead is mixed with it. The alloy is then cast in iron moulds into flat plates with intersecting furrows, so that it can be easily broken up when cold.

The former method is, however, that in general use.

The copper-lead alloy is now taken to the liquation department, where the second part of the process, stage B, is conducted.

Stage B.—Separation of the lead from the copper-lead alloy:—

The operations of this stage are carried on in a furnace of simple but ingenious construction.

A vertical section showing its general form, the arrangement of the twyer, and the curious fore-hearth is given in Fig. B.

Its exterior, as well as that of the fore-hearth, usually consists of flat stones set on edge, but in the mint and some modern refineries these parts are built of brickwork.

(In Dr. Percy's Metallurgy—Silver and Gold—Part I., p. 311, a drawing is given by Mr. Tookey of the brick furnace used in the mint in 1871.)

The interior is a circular cavity about 18 inches in diameter and 13 inches deep, with clay sides slightly converging towards the bottom, which slopes downwards towards the front side.

From the front side the fore-hearth projects in the form of a shallow trough in a line with the bottom and inclined at about the same angle. Below the end of the trough there is a shallow circular hole in the ground for receiving the liquated lead.

The interior of the furnace and of the fore-hearth is lined with the usual brasque of clay and charcoal.

The front side is open, but is partially closed during working with a fire-clay tile.

The top is covered with a clay slab excepting a small opening which is used for the addition of fuel, and is also covered during working with a movable tile.

The blast pipe is usually of clay, sometimes of iron, and terminates in a clay nozzle or twyer which passes through the

cover of the furnace. The twyer is bent sharply at an angle, the correct inclination of which is considered to be of great importance, its object being to direct the blast downwards and towards the middle of the back wall.

The furnace is placed under a hood for carrying off the fumes.

The charge of alloy weighing from 100—160 lbs. is placed on the bottom of the furnace, the larger pieces below, then a little charcoal, and then the smaller pieces. The front tile is now fixed in position, and the furnace almost filled with charcoal, the covering slab luted on, and the twyer adjusted.

Glowing embers are now put in, the charging opening is closed, and the bellows started.

The furnaceman then takes up his position, squatting on the ground in front of the fore-hearth.

Great skill is required in regulating the force of the blast, so that too high a temperature may not be produced, as the alloy must not be melted but merely brought to a pasty condition.

When it has reached this state it partly protrudes through the opening in the front on to the upper part of the trough forming the fore-hearth, and is there kept hot by the flame—which issues continually from this opening—passing over it.

The mass—a copper sponge saturated with lead—is now patted and squeezed by the workman with a tool consisting of a small block of wood about 5 or 6 ins. long and 3 ins. in diameter fixed on a hooked iron rod attached to a wooden handle, the lead trickling from it being collected in the hole in the floor (Fig. C.). As it becomes cool and lead ceases to exude, it is pushed back towards the hotter part of the furnace with a small iron rabble, and when sufficiently pasty it is again patted as before.

When the lead ceases altogether to flow from it the temperature is raised and the pasty mass is raked down the spout with further patting and allowed to solidify there.

The average duration of the operation is about $2\frac{1}{2}$ hours, and usually three to four charges are worked per day, with a consumption of from 40 to 50 per cent. of charcoal.

The products of this liquation process are: copper containing but little silver, argentiferous lead, and shiromé.

The specimen on the table is a sample of the copper in the form in which it is taken from the fore-hearth. Its composition is represented by the following analysis:—

COPPER AFTER LIQUATION.

	Per Cent.
Copper	99·12
Lead	0·52
Arsenic	0·04
Antimony	Trace.
Iron.....	0·04
Silver	0·034
Sulphur.....	0·02
Nickel.....	Trace.
Insoluble sandy residuc	0·06
	<hr/>
	99·834
	<hr/>

Sometimes when the process has been hastily or unskillfully conducted the amount of lead retained by the copper exceeds that in this specimen, but the greatest amount I have found has been 0·97 per cent.

The lead which has collected in the cavity in the floor contains varying quantities of silver according to the amount present in the copper and in the original lead used for the liquation.

Rarely less than 0·25 per cent. (81·66 ozs. per ton), frequently 1·3 per cent. (424·66 ozs. per ton), and occasionally as much as 2·2 per cent. (718·66 ozs. per ton), is present.

It also contains the whole of the bismuth, a little of the arsenic and antimony which may have been present in the copper, and small quantities of copper.

Usually only about 80—90 per cent. of the weight of the lead added to the copper is obtained, the remainder being lost, part being retained in the copper, shiromé, and slag, and part being volatilised.

The lead is sent to the cupellation department, where it is first submitted to an oxidising-melting process on a hearth of wood ashes and clay, and then is cupelled on a similar hearth of smaller dimensions, a cake of silver containing a little gold being obtained (see specimen).

SHIROMÉ.

The shiromé accumulates on the outside of the spongy mass of copper in the fore-hearth in irregularly-shaped semi-fused lumps, and is removed by the furnaceman from time to time during the liquation.

The amount yielded by any operation varies generally from 1—2 per cent. of the weight of the copper treated, but is entirely dependent on the purity of the copper; if this contains only traces of arsenic and antimony no shiromé is formed; if, on the other hand, much of these are present the proportion may greatly exceed 2 per cent.

When sufficient shiromé has accumulated in the liquation department it is twice treated by liquation with lead for the separation of as much as possible of the silver which it contains, but in spite of this treatment a considerable amount of silver is always retained in it owing to the arsenic, which is one of its essential constituents.

[*Note.*—The word shiromé (meaning “white solder”), the name of this substance, is unfortunately also used to designate antimony, the Japanese not having had any specially distinctive name for this metal excepting Iyo-shiromé or shiromé from Iyo (Iyo being the province in which the chief antimony mines were

situated) until recently, when "anchimoni" was adopted from the English word. Frequently "Iyo" was omitted and only shiromé written.

The term is also applied to ordinary tin and lead solder. I think it necessary to mention these three uses of the name, as they have led to much confusion in Japanese metallurgical books, and especially in translations from them. [Thus a careful and learned writer has conveyed a completely wrong impression of the composition of some Japanese alloys by translating shiromé as antimony when this copper-arsenic-lead-antimony alloy is meant.]

Shiromé as it is obtained after liquation with lead is in rough irregular-shaped, somewhat vesicular lumps. When melted and cast into ingots it is of a very dark bluish-grey colour. It is harder than lead, rather brittle, and can be reduced to a coarse powder by careful hammering in a steel mortar. Its fracture is dull, coarse grained, and free from crystalline structure.

The following complete analysis No. I. represents a sample taken directly from a liquation furnace at the smelting works of the Omodani mine (prov. of Echizen), which, as we shall see later, are noted for the purity of the copper they produce.

Nos. II. and III. are partial analyses of specimens from other districts, that from Iyo, No. II., having been liquated with lead for the separation of as much silver as possible.

The two determinations of lead and arsenic respectively were made in different portions of the specimen I., and they show that contrary to what might be expected it is tolerably homogeneous in composition. Its characteristic features, as will be seen from these analyses, are the presence of arsenic in considerable proportions, of antimony, of lead, and a large percentage of copper. In the specimen No. I the occurrence of the two former metals in such large amounts is specially noteworthy, as it demonstrates that without treatment by the liquation process, by which this shiromé was obtained, the Omodani copper would be seriously contaminated with both, and would be noted rather for its impurities than for its purity.

	I. From Omodani (Province of Kichizen).	II. From the Province of Iyo.	III. From the Province of Kaga.
Copper.....	72.70
Lead	8.53 { 8.75 8.32 }
Arsenic	11.37 { 11.50 11.25 }	7.64	9.18
Antimony	4.27	0.99	5.75
Tin	0.93
Iron.....	0.13
Silver	1.33	0.426	0.342
Sulphur.....	0.33
Zinc.....	Nil.
Gold	Trace.
	99.59		

I desire here to record the deep obligations I am under to my friend Prof. Roberts-Austen for having kindly placed the resources of the Metallurgical Research Laboratory of the Royal School of Mines at my disposal, so that I was able to make there not only the analyses of shiromé, but also to complete others which I had left unfinished in Japan.

After a very careful search I have failed to find any record of a metallurgical product approximating to shiromé in composition. A substance somewhat analogous to it in its mode of production is the Saigerdörner of the old German liquation process, but this, as will be seen from the accompanying analysis, differs entirely from it in composition.

*Saigerdörner (E. von Szamit):—

Copper	11·93
Lead	79·68
Antimony.....	7·30
Silver	0·213045
Gold	0·000465
	<hr/>
	99·123510

It is impossible to assign any definite chemical formula to this complex substance shromé, owing to its non-occurrence in a crystalline form, to the total absence of any crystals disseminated in its mass, and to its variability in composition at different works. It may, however, be regarded as an arseno-antimonide of copper and lead, in which an excess of copper and lead is held in solution, *i.e.*, as a pseudo-speise. The various copper-lead so-called speises, when they are the products of metallurgical operations, although differing from it in the relative proportions of their constituents, appear always to have this constitution, the amounts of arsenic and antimony present being less than sufficient for combination with the copper and lead. In this respect they are distinct from the true arsenical species containing nickel and cobalt, in which the arsenic is frequently combined with these metals in definite atomic proportions.

Having now described the method of liquating copper with lead, and the products which result from the operation, I will endeavour to point out as briefly as possible the influence which this process has had on the purity of Japanese copper.

INFLUENCE OF THE LIQUATION PROCESS ON THE PURITY OF JAPANESE COPPER.

The aim of the process is the separation of silver from copper, and to the success with which this is accomplished by it, it chiefly owes its importance and value in Japanese metallurgy. But another and almost equally important result accompanies its use, *viz.*, that by it copper containing arsenic, antimony, and bismuth is either entirely freed from these metals or has the proportions in which they are

* Percy. Metallurgy. Silver and Gold, Pt. 1, p. 325.

present so reduced that they no longer exercise any injurious effects on its physical properties or unfit it for use as a constituent of brass or other alloys. The action of the process in removing these metals may be explained as follows:—

Under the conditions which prevail lead does not form a definite alloy with copper. When the two metals are melted together in the first stage A, only a mixture, and not an alloy, results.

During this melting, however, there would seem to be a transference of the arsenic, antimony, silver, and bismuth from the copper to the lead, so that the copper-lead mixture, after being rapidly cooled, may be regarded as a solidified lead solution of the silver and bismuth as metals, of the arsenic and antimony as an arseno-antimonide of copper and lead, and through which comparatively pure copper is disseminated in granular or crystalline particles.

When this mixture is heated in the second stage B, and it is important to remember that the temperature never reaches the fusing point of copper, the lead solution of the silver and bismuth trickles away from the spongy agglomeration of the particles of copper into the receiver prepared for it, but as its temperature is lowered as it leaves the copper at the upper end of the fore-hearth below that required to retain the shromé in solution, this substance is gradually deposited there.

The greater part of the arsenic and antimony separates out in the form of this pseudo-speise. The whole of the bismuth, excepting mere traces, and nearly all the silver, passes into the liquated lead.

I am not acquainted with any other furnace process by which bismuth can be removed from the metal copper. The percentage when much is present may indeed be reduced by prolonging the ordinary-process of refining, but more than traces are always retained by the copper.

It is important to note that when the lead is subjected to the subsequent cupellation process much of the bismuth passes into the silver, communicating to it the greatest brittleness. As, however, a simple furnace operation suffices for its removal it is no longer a source of trouble to the metallurgist.

Several kinds of Japanese copper which have, and deservedly so, a high reputation for purity, would, but for this process, be unfit for most industrial purposes, and in demonstration of this I will ask for your attention to the consideration of the following examples. The first, which is specially noteworthy, is the copper from the mine of Omodani (prov. Echizen), previously alluded to, which is obtained by smelting ores containing fahlerz and native bismuth. The fahlerz occurs in such quantities that the roasting heaps at the mine are incrustated with arsenious anhydride and realgar. Yet the Omodani copper is free from more than mere traces of arsenic and bismuth and entirely so from antimony, and has been long regarded as the best copper in Japan for its malleability and ductility. In a recent report of the Director of Mines it is stated that it is the only copper now used in the Imperial arsenal for special copper work.

I have, unfortunately, no analyses of the metal before treatment by the liquation process, but from the composition of the shiromé obtained, given above, it must have contained about 0·20 per cent. arsenic and 0·08 per cent. antimony. The proportion of bismuth present would be variable, as the native bismuth is irregularly disseminated through the ore.

Its composition, after liquation and subsequent refining, is as follows:—

OMODANI COPPER.

—	Wire Bar.	Slab for Hammered Work.
Copper	99·80	99·67
Arsenic	Faint trace	Faint trace
Antimony	Nil	Nil
Bismuth	Nil	Nil
Lead	0·119	0·252
	99·919	99·922

(In these analyses a ft. tr. of arsenic means that when 13 grms. of the copper were taken, no weighable precipitate of ammonium magnesium arsenate was obtained in the final solution (measuring 60 to 80 cc.), but merely streaks on the sides of the beaker indicating its presence.)

Both analyses show a metal of great purity for copper which has not been electrolytically deposited.

The higher percentage of lead in the slab is intentional, as it is believed by the Japanese that the presence of lead in copper increases its malleability, and when it is not supposed to be present it is always added. The addition of lead to some kinds of copper have undoubtedly this effect, although the amounts sometimes added by the Japanese with excellent results so far as mere hand hammering is concerned, would be altogether detrimental to copper which had to be subjected to heavy forging.

The second example is a sample of copper which was sent to the Imperial Mint from one of the chief mines. I may say that before accepting any copper, or indeed, anything which could be chemically examined, I made an inflexible rule that it should be first analysed; a rule, the observance of which contributed largely to the success of many of the operations in the Mint.

This copper was partially analysed, and found to contain the following proportions of arsenic, antimony, and bismuth:—

ASHIWO COPPER BEFORE LIQUATION.

	Per Cent.
Arsenic	0·26
Antimony	0·16
Bismuth	0·10

The injurious effects of bismuth, the *bête noir* of the copper refiner, on the ductibility and malleability of copper are well known. As small a quantity as 0·06 per cent. sometimes will cause commercial copper to be so red-short as to be quite unfit for any purpose where forging is necessary. The effects of arsenic and antimony on the physical properties of brass and some other alloys are not less familiar to metallurgists.

The above copper was hence promptly rejected as worthless for the manufacture of hammered or rolled articles on account of the bismuth present, and for the manufacture of brass on account of the arsenic and antimony. It was then subjected to the liquation process at the works of the importer, after which it was again brought to the Mint, when on analysis it was found that these metals had been almost completely removed, the amounts present being as follows:—

ASHIWO COPPER AFTER LIQUATION.

	Per Cent.
Arsenic	0·04
Antimony	Trace.
Bismuth.....	Trace.

These two examples, I think, sufficiently demonstrate the important influence which the liquation process has on the purity of copper.

Unfortunately it is not applicable in England owing to the high price of charcoal and labour, although several brands of copper in the London market which are contaminated with bismuth contain sufficient silver for their economic treatment in Japan.

USES OF SHIROMÉ.

The application of the by-product shiromé to practical uses exhibits well the ingenuity and skill of the Japanese as workers in metal. Alone it is worthless, but as early as the beginning of the last century they discovered that not only could it be used as a constituent of some alloys, but that by its addition certain valuable properties were conferred on them.

The first official record we have of its use is contained in an edict of the Japanese Government in 1764, prescribing its addition to the copper-lead bronze to be used in the Mint for casting “Do-sen,” a small coin commonly known to Europeans as “copper cash.”

In 1768 we have another edict directing the minting for the first time of brass coins called “Shimon-sen” and the addition of

shiromé to the alloy to be used. These two kinds of coins, as shown by the following analyses, hence contain considerable quantities of arsenic and antimony.

The analyses of another coin, "Bunkiu-sen," which was chiefly a re-coining of "Do-sen" in 1863, is also given.

JAPANESE "COPPER CASH" CONTAINING SHIROMÉ.

—	"Do-sen."	"Shimon-sen."	"Bunkiu-sen."
Copper	77·30	75·62	83·10
Tin	4·32	0·73	3·21
Lead	15·33	2·85	11·22
Arsenic	1·14	1·99	1·50
Antimony	0·31	0·14	0·49
Zinc.....	Nil.	16·54	Nil.
Iron.....	1·01	1·76	0·27
Silver	0·06	0·016	0·06
Gold	Trace.	Trace.	Trace.
Sulphur.....	0·52	0·09	0·38
	99·99	99·736	100·23

The objects of its use in these cases were: to give additional hardness to the alloy without impairing its fusibility at moderate temperatures, and to obtain, when cast, a sharper impression of the mould than was possible with the copper-lead alloy alone. Additional hardness could also have been given by increasing the proportion of tin, but this would have had the disadvantageous effect of raising its melting point and of diminishing its fluidity when melted, both of which the Japanese desired to avoid, for two reasons—the first being

that their crucibles, owing to the absence of a good refractory clay, were incapable of sustaining long exposure to a high temperature, so that with metal of a high melting point they were soon worn out; and the second, that the coins were cast in very delicate moulds, made of a sand always more or less fusible, in which if metal with a high melting point was cast, the castings would be generally coated with a crust of semi-fused material not easily removable.

The specimens on the table demonstrate clearly the success with which the Japanese founders contended with the difficulties inseparable from the want of a refractory clay and non-fusible sand by thus modifying the composition of their alloys to suit these unfavourable conditions. I do not think any other alloy would give equally good results so far as sharpness of impression, clean surface, and hardness are concerned.

During the latter half of the last century—probably from an earlier date—and up to the present time, shiromé has been largely used by the bronze founders of Osaka and Kyoto, the chief centres of the metal industries, as a frequent addition to “Karakane,” a copper-lead bronze which is the principal alloy used in the manufacture of the numerous metal articles for ornamental and useful purposes in the production of which the Japanese are unrivalled. It is added to this bronze for the reasons given above for its addition to the old coinage alloys, but there is also another reason for its use, *i.e.*, it facilitates the production of the deep grey patina which is preferred for those vases or other objects which have to be decorated with inlaid line designs in silver (zogan work).

On the other hand, when a specially deep black patina was required in high-class bronzes, it was the practice of some of the best art founders to omit it from their mixtures for “Karakane.”

These last remarks apply solely to the older bronzes and not to the modern so-called “copies” of them.

In the old bronzes the colour and character of the patina is largely dependent on their composition.

On the other hand, in recent imitations—which however are not comparable with them in any way, excepting that they bear a slight but imperfect resemblance to them in superficial colouring—a false

patina of almost any colour may be given to any copper alloy, irrespective of its composition, and even to unalloyed copper.

The following analysis of an old bronze (Karakane) incense burner (date 18th century) affords an example of the use of shiromé.

INCENSE BURNER OF BRONZE CONTAINING SHIROMÉ.

	Per Cent.
Copper	86·85
Tin	1·76
Lead	9·13
Arsenic	1·15
Antimony	0·40
Zinc.....	Nil.
Iron	0·33
Silver	0·079
Gold	Trace.
	<hr/>
	99·699

From the proportion of arsenic present I should think that about 10 per cent. of shiromé had been used in making this alloy.

And here I wish to correct an error into which several writers have fallen who have accounted for the presence of arsenic and antimony in Japanese bronzes by assuming that it is due to the use of impure copper. Now no Japanese copper—and I have analysed some hundreds of specimens—ever contained, even when imperfectly refined, sufficient quantities of these metals to account for the percentages found in many bronzes.

The highest percentages I have ever found until the recent introduction of high blast-furnaces and modifications of European methods of smelting have been 0·085 per cent. arsenic and 0·090 per cent. antimony, and these amounts were quite exceptional. In fact, of all the samples received at the Imperial Mint during 16 years 96 per cent. contained less than 0·045 per cent. arsenic, generally only a trace being present, and 97 per cent. had less than 0·02 per cent. antimony, this metal being usually absent altogether.

So that when arsenic and antimony are found in large proportions in the older bronzes their presence is due to their addition to the alloy in the form of shiromé, and not to the use of impure copper

In some cases the arsenic has been added in the form of "Itakudo," a Chinese alloy of copper and arsenic, but these are rare. An interesting example of this is afforded by a sword guard, the composition of which is taken from a valuable series of analyses* of modern Japanese metal-work by my distinguished friend Prof. Roberts-Austen :—

SWORD-GUARD. COPPER ARSENIC ALLOY. (ROBERTS-AUSTEN AND WINGHAM).

Copper	98·060
Arsenic	1·066
Antimony	0·010
Lead	Nil.
Bismuth	Nil.
Iron	0·018
Nickel and cobalt	0·028
Zinc	Nil.
Tin	Nil.
	99·182

Another use for shiromé is as a cheap substitute for tin in the manufacture of metal mirrors, especially of the commoner kinds. This would seem to be a modern innovation, as in the older kinds I have not found arsenic and antimony in those proportions in which they would have been present had it been so used.

The following mixtures used in Tokyo are given in Ayrton and Perry's paper on "Japanese Magic Mirrors," read before the Royal Society 2nd October 1878 :—

Copper	81·3	71·5
Iyo shiromé (impure antimony)	2·4	..
Shiromé	16·3	28·5
	100·0	100·0

* Report on the analyses of various samples of Oriental metal work. Made under the direction of Prof. Roberts-Austen by Arthur Wingham. 1892.

I have not, however, found such mixtures in use in the chief foundries of Osaka, tin always forming a constituent of their alloys, for the following reason: that when shiromé is used without any tin the mercury amalgam employed in silvering the face of such mirrors produces a surface which is deficient in brilliancy, is easily tarnished, and has but little endurance.

I have endeavoured this evening to describe a process developed by the old metallurgists of Japan, an interesting by-product obtained in it, and the uses to which this by-product has been put; and I am sure you will all agree with me that the skill and ingenuity the smelters and founders of Japan have shown in accomplishing the results I have somewhat imperfectly placed before you are worthy of our warmest admiration.

SPECIMENS EXHIBITED IN ILLUSTRATION OF THE PAPER.

Argentiferous copper before liquation.

Lead used in the liquation process.

Copper after liquation.

Silver obtained from the copper.

Shiromé.

Japanese copper-lead coins "Do-sen" containing shiromé.

„ brass coins Shi-mon-sen „ „
„ coins "Bunkiu-sen" a re-coinage of "Do-sen."
„ bronze vases containing shiromé.

„ „ „ not „ „

„ wire bars — { of pure copper obtained
„ cakes for hammered work { from arsenical and bis-
muthiferous copper by
means of the liquation
process.

DISCUSSION.

Professor ROBERTS-AUSTEN said he had listened with the greatest possible interest to this account of the working of those consummate metallurgists, the Japanese. No one could possibly deal better with the subject than Mr. Gowland, who, he was sure, could give more than one paper on this subject if he would. No one knew better than metallurgists who had examined Japanese alloys how marvellous was the skill with which they added a minute quantity of what we should call an impurity for the sake of producing a definite result in the way of patina. The very smallest quantity of gold would produce the most beautiful purple patina. He feared that in writing on this subject he might have said that the antimony and arsenic in Japanese alloys was not deliberately introduced, as they now knew to be the case, but found their way in from impurities in the copper. With regard to the process itself, Mr. Gowland said it was introduced into Japan in the middle of the 16th century, and the best account was that of George Agricola, who wrote in the middle of the 16th century, but that was not by any means the earliest period at which the process was known. There were earlier accounts of it, and quite recently, in some excavations made at Silchester, specimens of lead used by the Romans had been discovered, some of which were submitted to him and analysed by his assistant, and he thought there could be no doubt from their examination that in late Roman times this process of liquation was employed, and probably with success. There was one curious point about the bismuth, a very small quantity of which exercised a very deleterious effect on copper; some curious work which he did recently for the mechanical engineers showed that however small the proportion of bismuth in copper might be, it always remained free, it did not unite with the copper. It was possible by studying the cooling curves by means of an ordinary thermal couple to find veins of free bismuth, even although its amount did not exceed 0.1 per cent. or less. Mr. Gowland had thanked him for placing the laboratory of the School of Mines at his disposal, but seeing that Mr. Gowland had placed all the specimens there, the least one could do was to beg him to examine them

in situ. He confessed he should have thought the introduction of the shiromó would have had a tendency to make the copper cash brittle, but that did not seem to be the case, and there was no doubt an extreme sharpness given by its addition. He should like to ask if the Chinese used similar alloys, and whether such Indian tribes as used coins of a similar appearance used the same kind of alloys.

Mr. CLAUDE VAUTIN said this very interesting paper had cleared away what was always a mystery to him, viz., the removal of the bismuth from copper, which, as was well known to everybody connected with copper, was a very serious impurity. If he understood the process aright, the explanation was something of this kind: in the melting furnace the copper and lead were both brought to a state of fusion, the mixture was then removed by plunging in a cold piece of iron on which a thin layer of the metal was, as it were, frozen; that was knocked off, the iron cooled, and again dipped into the mixture. In the melting furnace, while the two metals were in a fluid condition, no doubt there was a transference of the arsenic, bismuth, silver, and gold from the copper to the lead. The sudden cooling on the surface of the iron prevented the copper re-uniting with the bismuth and arsenic. Then in the liquation furnace the copper was never allowed to become in a fluid condition, and the operation of the workmen in front of the hearth consisted in pushing back, working up, or puddling the material. In so doing they gave the lead an opportunity of running away in exactly the same condition as it was in the melting furnace without the copper ever having been in a sufficiently fluid condition to re-absorb the bismuth, antimony, and silver. He should like to know if this was the correct rationale of the process; if so, it might have very important consequences. Personally, he was engaged a few years ago with a copper company in trying to remove bismuth from the copper, the presence of which reduced the value of that metal in the London market by 8% a ton. On one occasion a remarkable result was obtained which unfortunately was never repeated, but of which he thought they had an explanation. They granulated some copper containing the bismuth and melted it with lead; he did not think it

Fig. A A.

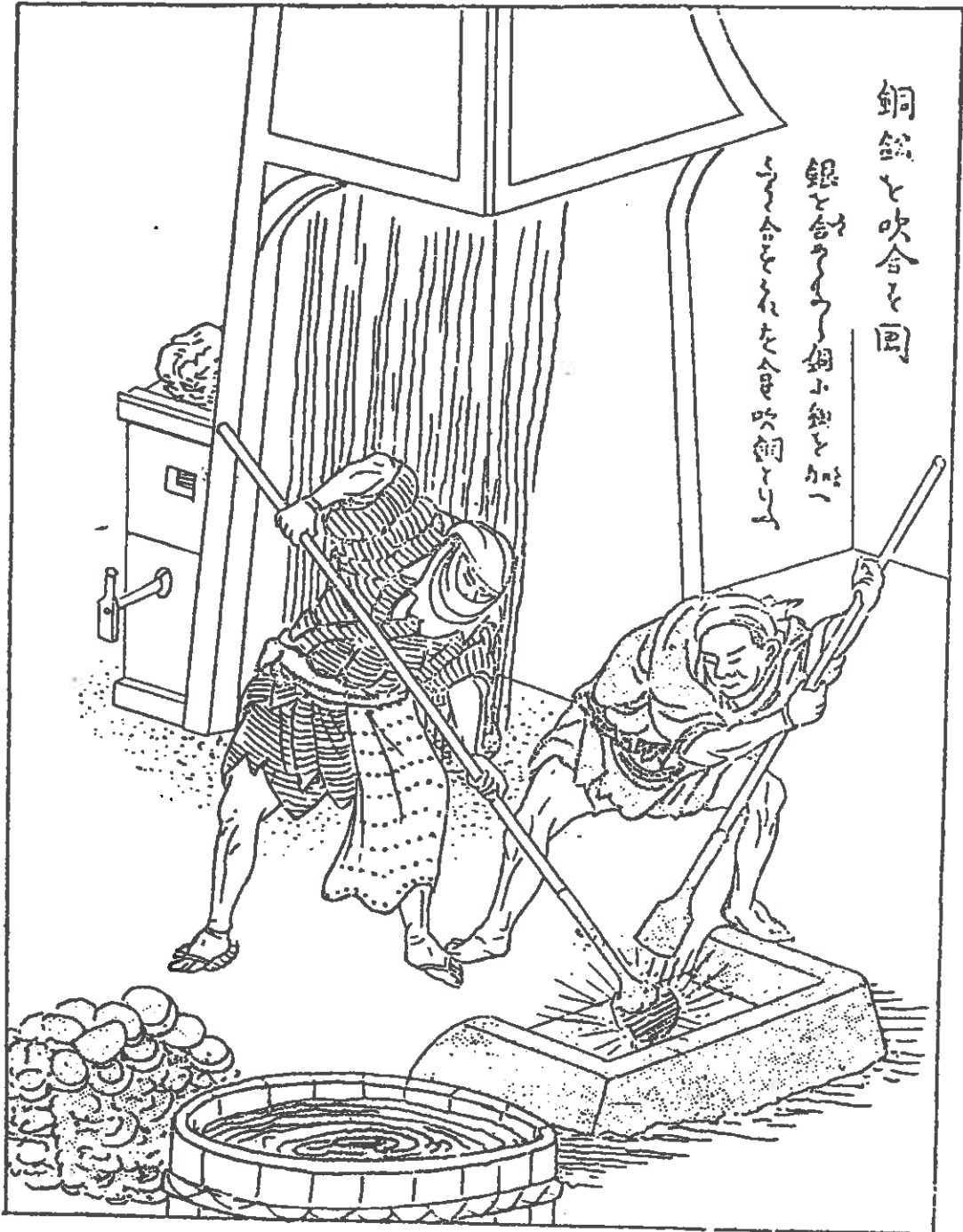
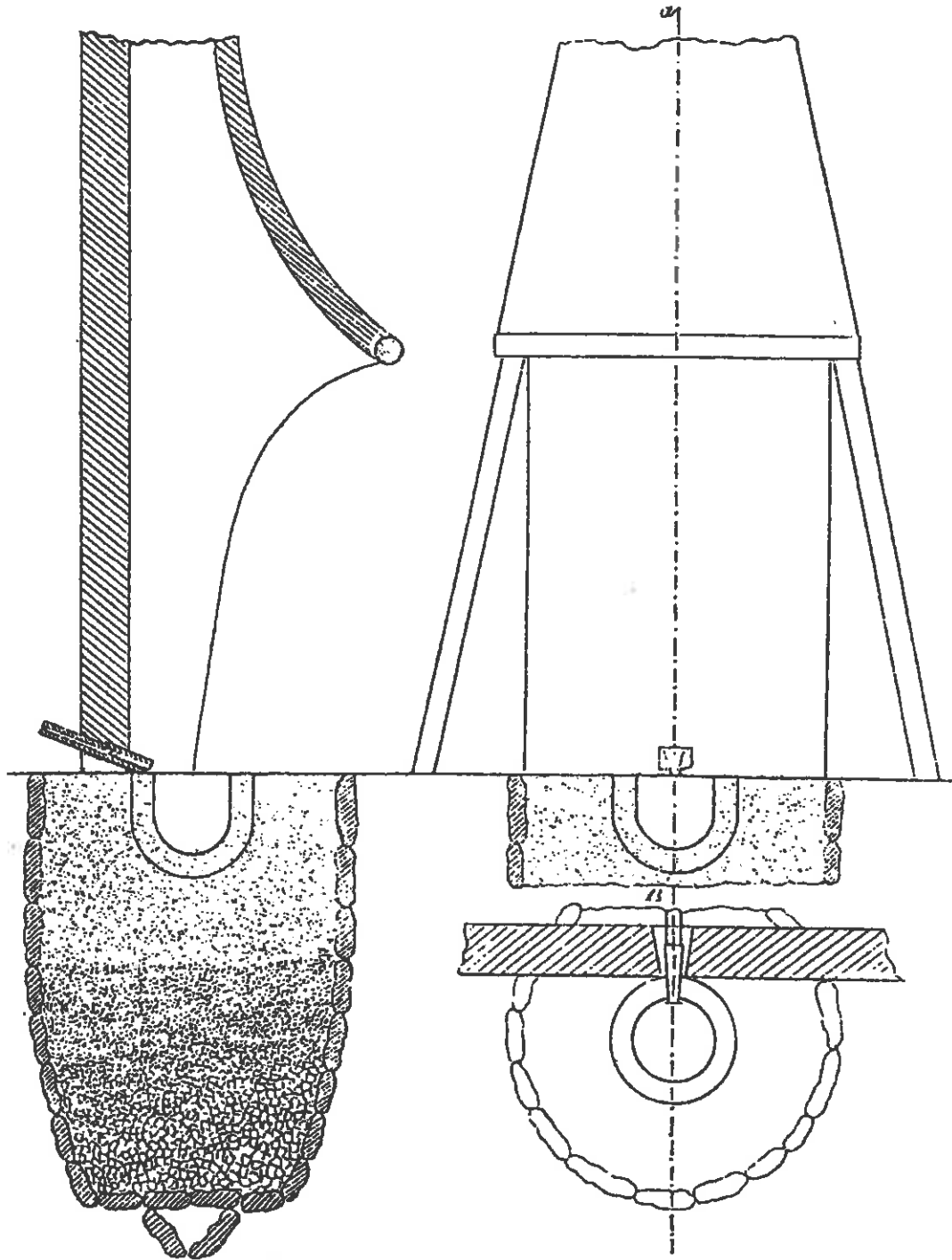
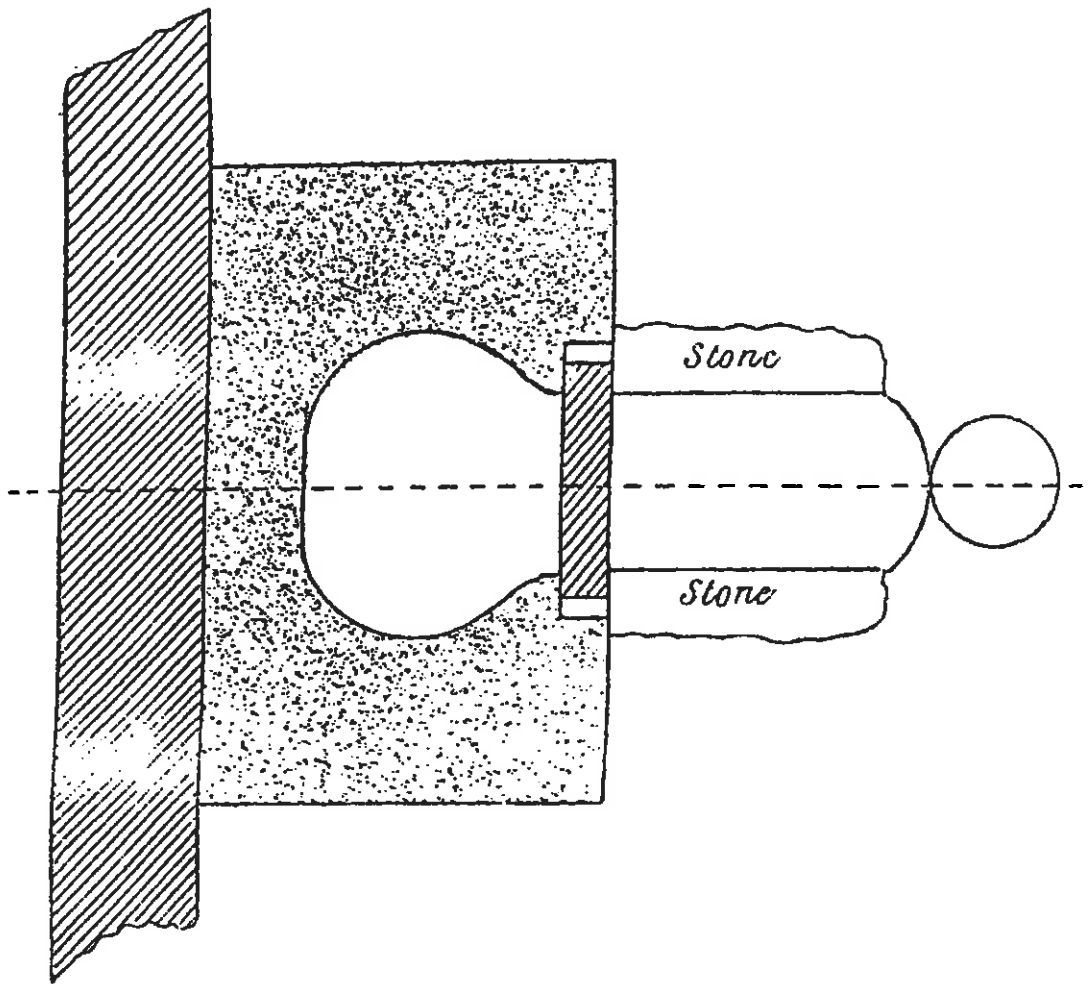


Fig. A.

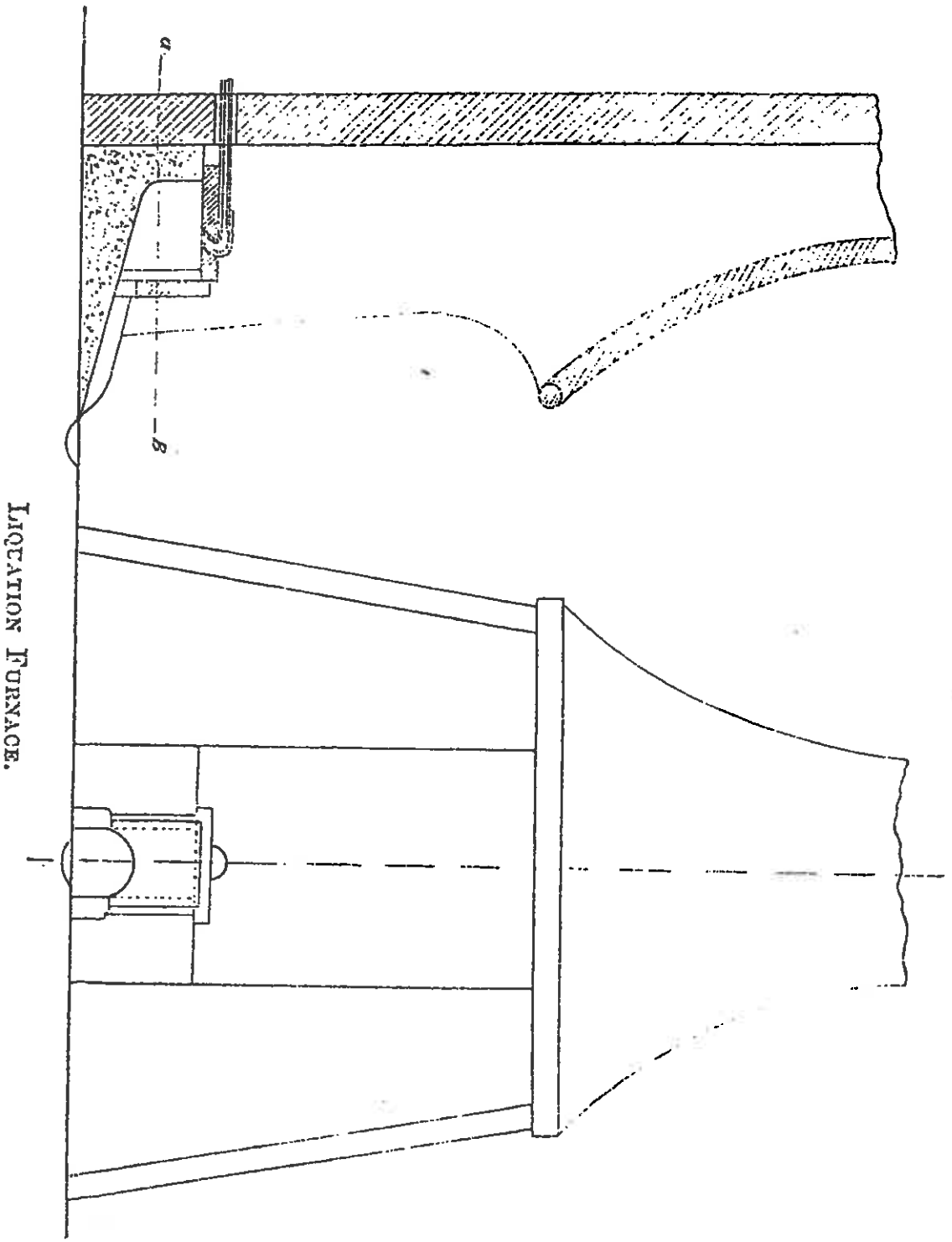


MELTING FURNACE.



SECTION ON A B (FIG. B) (ENLARGED).

Fig. B.



IRRIGATION FURNACE.

Fig. C.

