Recovery of Silver from Speiss at Rio Tinto (SW Spain)

Within the frame of IAMS's Iberian Project, led by Professor Beno Rothenberg, the site of Las Arenillas in the region of the Rio Tinto mine, was explored and partly excavated in 1983–4 (IAMS *Newsletter* 7, 1984, p. 3). The archaeo-metallurgical finds from Las Arenillas are now under investigation by a research group of the British Museum Research Laboratory and the following report is the first publication of the rather unexpected results of these investigations. According to the authors of this report, 'there is now evidence that speiss was treated at the Roman site to separate the silver – the first time such a process has been recognised at an ancient site'.

Professor I. Keesmann, Institute of Geo-science, Mainz University, since 1986 the co-director of the Rio Tinto Project, sent us the following note: 'Silver extraction in the region of Rio Tinto was a very complex process. At most of the smelting sites of Rio Tinto the process remains represent only one or two steps of the whole complex process, and this fact makes the reconstruction of the extractive process at the stage somewhat tentative. It should also be noted that the findings at Las Arenilla are not identical with those at other sites in the Rio Tinto area, which are at present under investigation by the Archaeo-Metallurgy Research Group at Mainz University and other IAMS related groups'. (Editor)

Most silver from the Bronze Age onwards was produced from argentiferous galena (lead sulphide) (see IAMS *Newsletter* No. 9), but Rio Tinto lead is rather scarce and the main silver ore smelted there was jarosite. Jarosite is basically a mixture of iron and potassium sulphates with a variety of other metals such as tin, gold, lead and copper as well as the silver, and includes arsenic and antimony. These last two metals have a profound effect on the smelting process as they combine with the iron to form a mixed iron arsenide/antimonide which has the tendency to absorb substantial quantities of the silver. In Agricola's sixteenth century *De Re Metallica* it states:

> 'If pyrites are smelted the first to flow is a white molten substance injurious to silver for it consumes it. For this reason the slag which floats on the top having been channelled off, this substance is poured out or if it hardens this is poked out with a crooked bar.' (Transl. Hoover and Hoover, 1912, p. 408)

The Germans called this material, with its very distinctive silver-white metallic appearance, *Speiss*. The German metallurgist Lazarus Ercker (1580), defined it thus:

> 'The difference between speiss and slag-matte is supposed to be that, while in the latter sulphur exceeds arsenic, in speiss arsenic exceeds sulphur. This makes speiss whiter than slag-matte, and is the reason why it cannot be diminished much by roasting, whether in a strong fire or a moderate one. Neither can it be overcome by lead, it always shows up again, even if it is slightly diminished, though certainly not by much.' (transl. Sisco and Smith, 1951, p. 48)

Clearly, speiss was a problem! At Rio Tinto in the seventeenth and eighteenth centuries it was called *metal blanquillo*. In Rio Tinto speiss iron comprises over half of the total weight with arsenic and antimony making up most of the rest. It is a hard and dense material with a white crystalline fracture which rapidly rusts. Superficially at least, speiss has a strong resemblance to cast iron and indeed in the seventeenth century Spanish government officials, sent to investigate the possibilities at Rio Tinto, found the speiss in the heaps and suggested it could be used for making bullets, or even to replace tin in church bells (Salkield, 1987, p. 14).

However, the Spanish officials did note that the *metal blanquillo* contained about 2,800 grams per tonne (g/t) of silver, but concluded that it would be difficult to extract, a conclusion with which Ercker and Agricola would have heartily agreed. However, our investigation of material excavated in 1983–4 at the site of Las Arenillas, suggests that these difficulties may not have deterred the Romans (IAMS expedition to Rio Tinto, under the direction of Beno Rothenberg).

Las Arenillas, Site RT 103 on the IAMS survey map of Rio Tinto, called Cerro del Moro by the local people, is a prominent, steep hill next to the small mining town of Nerva, about 3km from the main slag heaps of the Rio Tinto mine. The site had already been noticed by Oliver Davies and described in his classic study '*Roman Mines of Europe*' (1935, p. 128) as follows:

> 'On a hill immediately to the south-east of Nerva is a Roman village fortified with a rude wall. Inside the enclosure are house foundations and I found a few sherds, a piece of glass, a fragment of coal and some slag probably from a smithy. The site may have been

Fig. 1. Small slag heap on the very summit of Cerro del Moro, the slags are different from those in the main heaps and suggest the treatment of speiss.

an agricultural village unconnected with the mines which are some distance away'.

The more detailed survey by the IAMS team discovered considerable quantities of speiss, lead and litharge scattered all over the hill, and a small slag heap was found in a trial trench (Fig. 1). The excavators were puzzled as to why speiss was brought to this area well away from the main heaps, and why a small smelting operation should have been conducted right on top of a very steep hill, where everything would have to be carried up several hundred metres.

Our preliminary analyses showed that the slag was not from the processing of iron, as assumed by Oliver Davies, although it seems different from the usual silver smelting slags of Rio Tinto. Since our analyses of the speiss (Table 1) showed that, unlike small speiss pieces from the main slag heaps, they contained no detectable silver, we assume that silver was being systematically removed form the speiss at Las Arenillas.

Fig. 2. Crucible used for roasting speiss as part of the operation to recover the silver.

The crucible

This assumption was strengthened by the discovery of a bowl of heavily slagged rough ceramic (Fig. 2), found on the slag heaps near the North Lode of the Rio Tinto mine. At first it was believed to be a large cupel for the separation of silver from lead, but the analysis showed that no lead was present. The vessel (19.0 × 8.0cm) was heavily slagged on both its inside and outside, and was originally heavily impregnated with speiss (now largely weathered); see Table 2. Clearly someone had been treating speiss!

The slags

The small slag heap found *in situ* in a trial trench on top of Las Arenillas was about two cubic metres in volume and completely insignificant compared with the main slag heaps of the mining region. The heap was made up chiefly of broken slag pieces up to fist size. Three samples were selected at random for further investigation and analysis (Table 2). Although they are of the usual fayalite type, they are rather different in bulk

Table 1

Speiss from main slag heaps at Corta Lago	%	Fe	As	Sb	Pb	Mo	Sn	Ag
CL-79 T2 layer 4 17		33.5	39.0	19.5	2.3	0.5	4.3	1.0
CL-79 T2 Box 17		50.5	40.5	6.0	0.83	0.15	1.7	0.27
CL-79 T2 Layer 15 69 H8 419		52.5	38.0	7.2	0.8	0.5	0.8	0.07
Speiss from Las Arenillas								
RT 103 HP 507 site E		72.7	18.6	7.2	0.6	0.1	0.6	<0.02
RT 103 surface		72.4	20.0	6.6	0.5	0.12	0.5	<0.02
Silver from Las Arenillas		Ag	Au	Bi	Cu	Pb	Fe	
		84.0	1.75	15.4	0.12	0.14	0.01	
				Zn, Sn, Co, Sb, As, Ni not detected.				

Table 2

Slags from main heaps RT19a	%	SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	PbO	BaO	$P_2S_2O_3$
Plate slag 180		23.2	2.66	42.0	0.3	1.9	0.07	0.7	0.05	25.0	<0.5
Plate slag 181		30.66	4.46	36.57	0.7	3.75	0.2	1.75	1.12	12.0	<0.5
Ropey slag 182		28.42	5.91	50.54	0.2	0.15	0.13	0.7	0.66	1.4	<0.5
Slag from small heap on Las Arenillas											
RT 103 D2A Layer 4 14 HP567											
BMRL 27963		24.0	4.7	60.4	<0.5	1.4	<0.5	1.2	1.7	2.8	<0.5
BMRL 27964		23.0	4.1	60.5	<0.5	1.8	<0.5	0.9	2.5	2.9	<0.5
BMRL 27965		34.73	5.2	45.6	<0.5	0.4	<0.5	1.4	1.8	4.2	<0.5
Impregnated ceramic matrix of crucible		23.4	15.3	51.0	<0.6	<0.2	0.9	3.0	<0.4	—	4.2

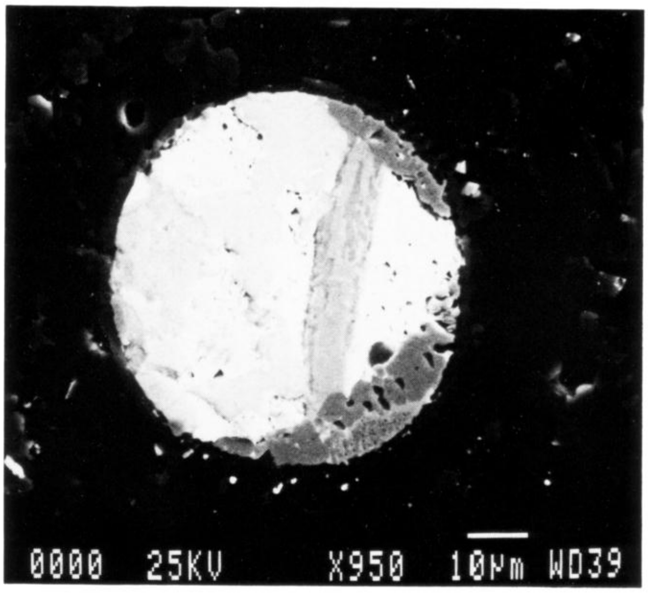

Fig. 3. Micrograph of a section of slag from Las Arenillas showing a globule of speiss. It is made up of at least four phases: Pb with some Sb, Cu-Sb, FeAS and areas rich in Pb and Sb with some S. Ag is included in the lead-rich phases .

composition and inclusions from the slags of the main heaps; their iron content is somewhat higher and the high barium contents encountered in most of the smelting slags of the main heaps are not found here. One of the samples contained numerous globules of plumbospeiss which is not typical of the slags of the main heaps. The globules were internally heterogeneous with at least four major phases present (Fig. 3): lead (with some antimony and the silver), a copper-antimony phase, iron arsenide and areas rich in both lead and antimony with some sulphur. Typically these inclusions contain about 30–50% of lead, 26–45% of antimony, 2–15% of iron, 1–12% of arsenic and about 3% copper and 1% tin, etc. Silver was concentrated in the lead-rich phase and in one case the lead contained 1.3% of silver.

Lead, litharge and silver

Samples of lead, litharge and silver from Las Arenillas were examined. the lead and litharge are now both heavily corroded and the exposed surfaces are covered with lead carbonate, cerusite ($PbCO_3$). The litharge pieces tended to be quite rich in antimony and also have some copper, absorbed during the cupellation processes, whereas the lead is uniformly pure. The analysis of one piece of silver is given in Table 1; note the extraordinarily high bismuth content – raw silver from Rio Tinto normally contains only about 1 to 5% of this element. The other elements are quite typical for Rio Tinto silver.

The process of speiss treatment

Speiss was treated at Las Arenillas to recover silver as evidenced by the abundant finds of speiss, lead, litharge and the slags from the excavated slag heap, although exactly how this was done is still far from clear. Percy (1870, p. 313) describes the process carried out at Freiburg in Germany where silver and lead were smelted from pyrites. The speiss formed was broken off the *matte* (Percy uses the term *regulus*) and roasted, then smelted with lead, or lead products such as litharge from the cupellation process. The smelt produced speiss, matte and lead. The last two contained the silver and they were returned to the main smelters, and the speiss was treated to recover the nickel and cobalt which it contained before being discarded.

The Rio Tinto speiss is somewhat different, being the product of a different ore. The jarosites are low in both nickel and cobalt, so these elements do not figure in the speiss, and the ore is, of course, a sulphate and not a sulphide as was the case at Freiburg, so there is no *matte* with the Rio Tinto speiss. We assume therefore that the silver-rich speiss at Rio Tinto was routinely collected from the furnaces where jarosites were smelted and taken to centres such as Las Arenillas for further processing. The few small fragments of speiss which were left behind and/or entrapped in the slag of the main slag heaps, show that the speiss often contained several thousand ppm of silver.

We suggest the following process model (Fig. 4): First, the speiss would have been roasted in crucibles to that found in the heaps on North Lode. This would have oxidised a substantial portion of the iron arsenide, driving off the arsenic as arsenious oxide and leaving behind oxides of iron. Analyses of the speiss from Las Arenillas do indeed show that the arsenic content is much reduced. Silica in the form of crushed quartz would then be added to the molten speiss to form a slag with the iron oxides. Inevitably some speiss would get incorporated into the slag, as happened with the slag found on Las Arenillas. This slag reflects the material treated, and is thus much lower than the main smelting slag in the alkaline earths such as barium, which are quite prominent in the jarosite ore, but of course, absent in the speiss. The small percentage which is present probably derives from the fuel, flux and furnace linings.

The now concentrated speiss would then be treated with lead or litharge in such quantity that the bulk of the silver transferred from the speiss to the lead. Because the quantities of speiss were very low compared with the original ore, the Romans could afford to use a large excess of lead ensuring that the amount of silver left in the speiss was minimal. The lead itself, run off from the furnace, would also have quite a low concentration of silver (several hundred ppm), but it was not necessary to recover this by cupellation at this stage. At Freiburg the still relatively small volume of lead could be returned to the main ore smelting furnaces to be further enriched with silver before tapping and cupellation, and this could have been done at Rio Tinto.

The ores at Rio Tinto are unusual and their successful treatment required sophisticated and complex processes. As more work is done on the Rio Tinto material the greater becomes our appreciation of the technical skills of the ancient metallurgists and our respect for their craft.

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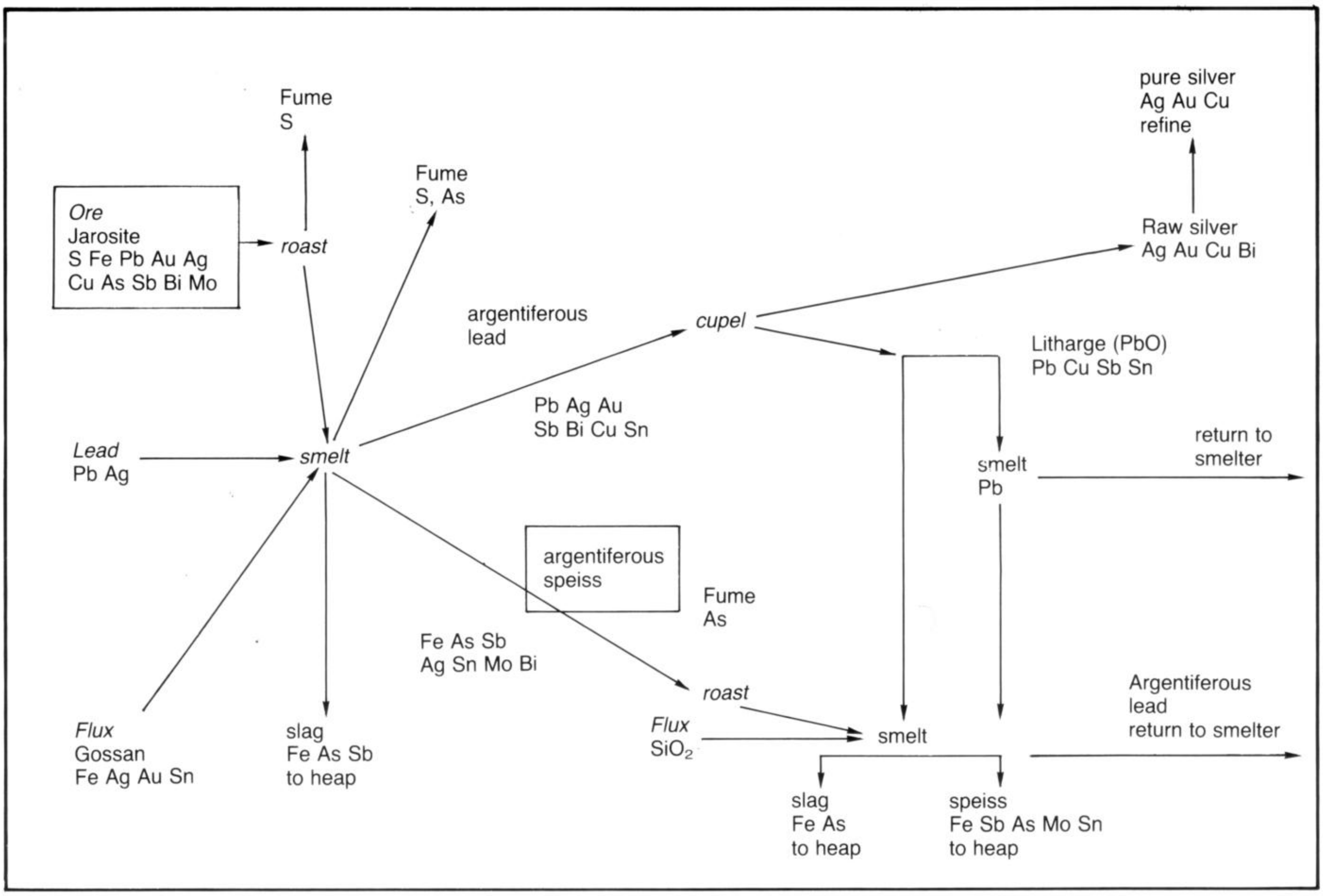

Fig. 4. Smelt process model.

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Clay Moulds for Copper Ingots — a first discovery

For a long time metallurgists and archaeologists assumed that bun-shaped and similar copper ingots often found in ancient hoards and shipwrecks are the primary product of the copper smelting process, i.e. the plano-convex shaped ingot was assumed to be a 'replica' of the furnace bottom. The smelting process model was thus presented: after pre-heating the bowl-shaped smelting hearth, the ore mixture was charged into it and there reduced to metallic copper prills; these sank through the liquid gangue material, the 'slag', to form a plano-convex copper ingot on the concave furnace bottom. In advanced process models the slag was then tapped out of the furnace and the copper ingot, remaining at the bottom, could then be simply recovered.

Experimental and theoretical research into copper smelting carried out during the last few years by IAMS's metallurgical research group and its students established that this model was an over-simplification. Most of the copper ingots were, in fact, secondary products, i.e. cast into shape after the conclusion of the primary smelting process in an additional operation and from raw copper, not necessarily from one and the same smelting operation. In other words: most of the common ingots and, of course, ingots of more elaborate shapes like the 'ox-hide' ingots of the Mediterranean, are the product of a casting operation not directly connected with the primary smelting of copper. However, the essential piece of missing evidence was a casting mould for ingots.

In the collection of our Arabah and Sinai research unit (The Institute of Mining and Metallurgy in the Biblical World, Tel Aviv) are a large number of furnace fragments, lining parts, clay tuyères and other refractories which were uncovered in the excavations of the Timna smelting camps in 1962–83. As part of the current preparations for the definitive publication of