Research Department Report 54/2007

Warmley Brassworks, Siston, Bristol Analysis of some Eighteenth-Century Brassworking Debris

Harriet White and David Dungworth

© English Heritage 2007

ISSN 1749-8775

The Research Department Report Series, incorporates reports from all the specialist teams within the English Heritage Research Department: Archaeological Science; Archaeological Archives; Historic Interiors Research and Conservation; Archaeological Projects; Aerial Survey and Investigation; Archaeological Survey and Investigation; Architectural Investigation; Imaging, Graphics and survey, and the Survey of London. It replaces the former centre for Archaeology Report Series, the Archaeological Investigation Series, and the Architectural Investigation Report Series.

Many of these reports are interim reports which make available the results of specialist investigations in advance of full publication. They are not subject to external refereeing, and their conclusions may sometimes have to be modified in the light of archaeological information that was not available at the time of the investigation. Where no final project report is available, readers are advised to consult the author before citing these reports in any publication. Opinions expressed in Research Department reports are those of the author(s) and are not necessarily those of English Heritage.

Warmley Brassworks, Siston, Bristol Analysis of some Eighteenth-Century Brassworking Debris

Harriet White and David Dungworth

Summary

William Champion established the brassworks at Warmley in the 1740s as the first integrated production plant of its kind for non-ferrous metal goods. Production included copper smelting, brass manufacture by cementation, and zinc distillation. A variety of residues thought to derive from the industrial processes carried out at Warmley were recovered from the site during archaeological interventions. These were examined using SEM-EDS to investigate their origin or use. A fragment of refractory was from a zinc retort, a zinc-rich deposit was the spent charge from zinc distillation, and slag samples were shown to be from copper smelting. Analysis of a fragment of clay-graphite crucible revealed that it had been exposed to high temperatures and strongly reducing conditions, however, it could not be linked with any certainty to Champion's industrial processes.

Keywords

Metal Working – non Fe Technology Post Medieval

Authors' address

Harriet White: English Heritage, Fort Cumberland, Fort Cumberland Road, Portsmouth, PO4 9LD Telephone: 02392 856700

David Dungworth: English Heritage, Fort Cumberland, Fort Cumberland Road, Portsmouth, PO4 9LD Telephone: 02392 856783

Introduction

The production of brass in the post-medieval period is well documented in the historical record and this resource has been utilized to discuss the development of the industry during this period (for example Day 1973, 1991 and 1998). There has, however, been little in the way of scientific analysis of archaeological remains or debris from the manufacturing processes at brassworking sites of this period, so these remains are poorly understood. Recent archaeological excavations undertaken by English Heritage at the late 18th century brassworks at Warmley, Bristol (Fig. 1, NGR ST6691672833) revealed a number of residues thought to derive from the metalworking processes carried out at the site. The opportunity was taken to carry out a program of scientific analysis to shed light on the details of industrial activities that took place at Warmley, in addition to providing a body of knowledge that may be used to aid in the interpretation of remains at other similar metal production sites in Britain.



Figure 1. Showing location of Warmley Brassworks.

Historical Background

William Champion established the brassworks at Warmley in the 1740s as the first integrated production plant of its kind for non-ferrous metal goods. All processes were carried out at the site from the smelting of ores to the manufacture of finished wares for sale (Day 1998). Production included copper smelting, brass manufacture using the traditional cementation method and zinc distillation for the production of specialist high-zinc brasses (Champion patented a method for the production of metallic zinc in 1738), as well as the manufacture of brass sheets and wire, and objects such as pins and kettles (Day 1998). To give an indication of the scale of operations of this important site one can refer to the

diaries of the Swede, Angerstein, who visited the works in 1754 and recorded 15 copper smelting furnaces, 12 brass furnaces and four zinc furnaces, in addition to a number of rolling and battery mills for the manufacture of various goods (Berg and Berg 2001), while seven years later, in 1761, an inventory lists 22 copper furnaces, 15 brass furnaces and five zinc furnaces, with one wire mill, three rolling mills and five battery mills (Day 1973). Champion continued to expand the business by building new furnaces one mile away at Kingswood, battery mills in the village of Bitton two miles away and at Kelston five miles away, and a brass foundry at St Augustine's Back in the centre of Bristol. Overexpansion caused financial problems leading to the collapse of the Warmley Company in 1767. The company was bought by Champion's rival, the Bristol Brass Company, in 1769 (Day 1973) and limited operations continued at the Warmley site (possibly only zinc smelting) into the early 19th century.

According to Angerstein (Berg and Berg 2001), copper smelting was carried out at Warmley in rectangular reverberatory furnaces, approximately 2.6m by 1.2m (external dimensions), that had two chambers separated by a low wall. The fuel (coal) was burnt in the smaller chamber while the ore was placed in the second chamber. The hot gases from the burning coal reduced the copper ore and allowed the extraction of the metal it contained in a multistage process. The smelting process was helped by a chimney situated at the far end of the chamber and by the low ceiling of the ore chamber which reflected heat down onto the ore. Most of the ores used were copper-sulphides or copper-iron-sulphides and so were smelted together with silica (e.g. sand). The silica would react with the iron to form a slag which would be tapped from the furnace as a runny liquid. Since the fuel and ore were kept separate, the vitrified ash of the coal would not be absorbed by the smelting slag and would form a separate residue: clinker. The initial product of smelting was copper sulphide, which would be further roasted to remove the sulphur and other impurities (such as arsenic and antimony). Copper smelting in the Bristol area went into decline in the 1780s, and probably ceased by the end of the 18th century (Day 1991, 154).

Producing metallic zinc from its ore is more problematic since it vapourizes at 907°C. Champion's patented method relied on the zinc vapour formed in one crucible being condensed in a second. Zinc ore and charcoal (Angerstein refers to the use of coal (Berg and Berg 2001, 143)) were sealed into large crucibles (more correctly retorts) 1.2m high and arranged around coal fuel in the combustion chamber of the furnace (Day 1991, 180). Percy (1861, 551-3) describes zinc retorts as 1.0m high with a diameter of 0.9m and wall thickness from 40 to 65mm. An iron pipe was inserted into a hole in the base of each retort, the other end of which would protrude through the furnace base into a vessel of water in the condensation chamber below. During firing, the zinc vapour condensed in the iron pipes and collected in the water-filled vessels below (Day 1991; 1998). Percy (1861, 557) records that 20cwt of calcined zinc ore would give 6 to 8cwt of zinc, suggesting that approximately half the charge would remain in the retort as 'residuum' which would be scraped out at the end of the firing. Large quantities of coal were required for the production of zinc, making the resultant metal extremely expensive, thus it was used only for the manufacture of specialist high-zinc brasses.

Ordinarily brass was produced in furnaces at Warmley using the cementation process. Layers of calcined zinc ore, copper pieces and charcoal (Angerstein notes the use of small amounts of coal in the bottom of the crucibles (Berg and Berg 2001, 38)) were sealed in crucibles and heated in a circular furnace. At temperatures above 907°C the zinc ore was reduced to metallic zinc in the form of vapour, which diffused into the copper pieces to form the brass. The practical upper limit to the amount of zinc absorbed by the copper in the cementation process is widely reported at 28-32% (for example Day 1991 and Bayley 1998). This figure represents the final equilibrium state between the zinc vapour and the zinc dissolved in the copper (Newbury *et al.* 2005). Angerstein's 1754 description of brass cementation crucibles from Birmingham indicates they were much smaller than the retorts used for zinc distillation, being 0.4m high with a diameter of 0.2m at the mouth (Berg and Berg 2001, 38). Percy records similar dimensions for brass cementation crucibles from the same town a century later, with their height given as 0.3m, diameter as 0.2m at the mouth (and walls 25mm thick at the rim and 50mm thick at the base) (Percy 1861, 614). There appears, therefore, to be a size distinction between vessels used for zinc distillation and those used for brass cementation in the 18th and 19th centuries.

In literature describing the zinc production process at Warmley, calamine (zinc carbonate) is traditionally named as the ore utilized (for example Day 1973, 75; 1998, 147 and Spry 2003, 39). The use of this term derives from a description of the process by Watson (1786, 38) written twenty years after he witnessed the furnace in operation in 1766, in which he states: 'the pots were filled with a mixture of calamine and charcoal, and the mouth of each was then close stopped with clay'. Champion's brother, John Champion, obtained British patent no. 726 in 1758 for producing brass and zinc from zinc sulphide by converting the sulphide ore (blende) to zinc oxide in a coal-fired furnace (Champion 1758). This allowed zinc sulphide, common in North and Mid-Wales to be used as a substitute for calamine. It is interesting to note that William Champion's own patent titled 'A method of Invention for the Reducing of Sulphureous British Minerals into a Body of Metallik Sulphur' refers to the use of 'calamy or other sulphureous British mineral or minerals' (Champion 1738, 2). Calamy (calamine) was used to describe non-sulphide zinc ores and so perhaps the term 'sulphureous' was employed deliberately to obscure the nature of his process.

Archaeological Background

A number of archaeological excavations have been carried out at Warmley over the past two decades which have produced direct evidence of Champion's metal working processes. For example, 1986 construction work adjacent to the Clocktower building of the Warmley industrial complex exposed a series of features. Emergency archaeological investigations revealed them to be consistent with the remains of cementation furnaces. Described by Day (1988, 28), they comprised sections of three vertical, cylindrical, brick constructions, each divided at half its height by a wide ledge which would have supported firebars or a pierced cast-iron furnace bedplate, upon which the charged crucibles would have sat. The estimated diameter of the structures below the ledge was approximately 1.05m, while the diameter above the ledge was larger at approximately 1.25m. The upper sections of the furnace walls survived to a height of around 0.6m above the ledges. It was thought the walls would have continued upwards to form a domed top with an opening covered by a round brick lid. A large number of fragments of a blue-coloured stoney material were intermixed with rubble infill near the furnace area. Analysis of a single sample revealed it to be a ceramic containing common sub-angular quartz grains (approximately 0.1mm in diameter) and coarse grog temper or mudstone inclusions. Compositional analysis demonstrated a high concentration of zinc oxide (approximately 40 wt%) in addition to 49 wt% silica, 10 wt% alumina and minor amounts of iron, magnesium, calcium and potassium oxides (<1wt %). Detailed investigation of the ceramic matrix showed that zinc spinel ($ZnAl_2O_4$), often enclosed by zinc silicate (Zn_2SiO_4) had formed around cracks and voids (Freestone 1988). The results indicate the ceramic is likely to be a fragment of a zinc distillation retort or brass cementation crucible (though some copper contamination might be expected on a cementation crucible).

A number of clay-graphite vessel fragments were also recovered from Warmley during the 1980s archaeological interventions. Graphitic crucibles were introduced into Britain around 1750 from South Germany or Austria but by the beginning of the 19th century were made in Cornwall (Cotter 1992, 268; Blinkhorn 2003). Blinkhorn reports that on a macroscopic level the English crucibles are indistinguishable from the imported ones.

The dimensions of a well preserved fragment found at Warmley (internal diameter: 0.43m, wall thickness: 38mm) show it to be larger than expected for brass cementation crucibles though smaller than zinc retorts (see above). A second large fragment from a base is described as having a diameter of 0.25m at the base, and increasing to 0.40m 0.12m higher up. Three small square holes arranged in a triangle 11 cm apart and 4 cm from the edge occur in the bottom (Bayley 1988). The presence of holes in the bottom of the base fragment would suggest this vessel to be a retort rather than a crucible.

A number of other archaeological evaluations and excavations have been undertaken at the Warmley site in the past two decades by Avon Archaeological Unit in which industrial debris were recovered but to date the findings are to date unpublished. More recently, in October 2006, English Heritage carried out emergency excavations and recording of a number of archaeological features that had been exposed by digging activities at the site. A variety of remains associated with industrial activities were recovered including slag bricks, clinker, refractory material and zinc-rich deposits. It is these remains recovered from the English Heritage excavation in addition to one graphite crucible fragment recovered from previous excavations at Warmely in the 1980s that were investigated (Table I).

Sample No.	Context*	Description
01	[001]	Slag brick used to cap culvert
02	[002]	Copper slag brick fragment
04	[002]	Copper slag brick fragment
05	us	Refractory
09	[012]	Zinc-rich deposit (friable)
12	us	Graphite crucible

Table 1. Details of samples selected for analysis. Samples 01 to 09 excavated by English Heritage, Sample 12 excavated during the 1980s.

* See Stabler 2006 for context descriptions

Methodology

Polished sections of each sample were examined using a scanning electron microscope with an attached energy-dispersive X-ray spectrometer (SEM-EDS). The instrument used was a Zeiss-Stereoscan 440 SEM with a tungsten filament, and an Oxford Instruments germanium EDX detector. The germanium detector allows for the simultaneous detection of all elements from boron to uranium, providing they are present in concentrations above the detection limits of the system. The operating conditions of the SEM were 25 kV accelerating potential with a probe current of 2.5 nA, and each spectrum was collected for 100s livetime. The spectra were calibrated using a cobalt standard, and deconvoluted with the phi-rho-z correction procedure using the Oxford Instruments SEMQuant software. This utilizes element profiles derived from single element or simple compound standards (eg pure iron,

jadite, wollastonite). EDX spectrometry provides no direct information on the valence states of the elements present in the analysed material. Therefore the appropriate valence states were selected and the oxide weight percents (wt%) of each element were calculated stochiometrically where necessary. The minimum detection levels for each element, determined by previous analyses, are presented in Appendix 1.

The slags (samples 01, 02 and 04) were analysed by collecting spectra from areas typically $300 \times 500 \mu m$ in size and included the glassy matrix and inclusions. Exploratory scans revealed compositions to be homogenous thus the results presented represent those from one analysis only. The remainder of the materials were analysed using area scans (typically $15 \times 20 \mu m$ in size) or spot analysis, and the results presented reflect the mean of two or more analyses. In general analytical totals were between 98 to 102%. However, in a number cases the porous nature of the materials or phases analysed meant that analytical totals were much lower, in the range of 60 to 90%. All totals were therefore normalized to 100% for consistency.

Results

Slags

The three samples of copper slag had very similar characteristics and so are treated together. They were iron-calcium-aluminium-silicate slags (Table 2). Their compositions are broadly similar to that of a previously analysed sample of copper slag from Warmley (Spry 2003) (Table 2). The sulphur content of the three samples suggests sulphide ores were being smelted. This is supported by documentary evidence which records that the Bristol copper smelting industry principally used sulphide ores from Cornwall, and Champion is listed as a buyer of Cornish copper ores from 1746 (Percy 1861; Day 1973). Quartz and some lime were commonly added to Cornish copper ores during the smelting process to help produce the slag. The presence of zinc in the slag is unexpected as zinc is not usually found in copper ores from this region. However, copper ore from North America was also used at Warmley (see Berg and Berg 2001; Day 1973) and it may be that ores from different sources were blended.

The copper smelting process was very complex with multiple stages including ore calcination, ore smelting and metal refining (for example Percy 1861, 322-27). The majority of stages produced a slag. Percy lists ore furnace slag, metal slag, refinery slag and roaster slag and these would undoubtedly show compositional and microstructural variances. The silica polymorphs (quartz) identified in the slags analysed (Fig. 2) provide some clue to the process producing them as Percy identified only one (the ore furnace slag) that contained silica inclusions. It is therefore probable that the samples derive from the initial ore smelt. This is supported by the fact that this slag was a waste product and was disposed of, while the remaining slags were re-introduced as part of the charge in the remaining stages of the smelting process (Day 1991, 163). While some residues of the metal, refinery and roaster slags would survive in the archaeological record, it is the ore furnace slag that is most likely to predominate.

		Sample No.			
	01	02	04	Spry 2003	
Na ₂ O	<0.5	<0.5	0.8		
MgO	0.6	0.6	0.4		
	7.1	6.7	4.9		
SiO ₂	46.0	44.2	44.3	65.7	
P_2O_5	<0.2	<0.2	<0.2		
SO ₃	1.9	2.2	<0.2		
K ₂ O	0.9	0.5	0.3		
CaO	8.7	10.3	15.3		
TiO ₂	0.2	0.2	0.2		
MnO	0.2	<0.1	0.2		
Fe ₂ O ₃	26.8	30. I	28.5	24.I	
CuO	0.3	0.7	0.4	1.0	
ZnO	5.8	4.6	4.9	0.8	
As_2O_3	1.1	<0.5	<0.5		
SnO ₂	0.4	<0.5	<0.5		

Table 2. Results of SEM-EDS analysis of copper slags (wt%).



Figure 2. SEM-EDS micrograph (in backscatter mode) of Sample 01 (slag block from culvert [0001]), showing copper-iron-zinc-sulphide and silica polymorph inclusions in an iron-calcium-aluminium-silicate matrix.

Zinc rich deposit

Sample 09 consists of a slightly porous and moderately friable blue zinc-rich material (Figs 3 and 4a to e) and is interpreted as a residue from zinc distillation. SEM examination shows that this material is highly heterogeneous (Fig 4a) with metallic zinc (Fig 4b), metallic lead (Fig 4c), a number of zinc compounds (Figs 4b and 4d), fragments of refractory materials (Fig 4e), charcoal and coal cemented together in a zinc-rich 'earthy' matrix. The metallic zinc is mainly present as discrete droplets ranging in size from 20microns to 2mm. SEM-EDS analysis only detected zinc; no iron, lead or cadmium were detected in the metal. The SEM images (Figure 4b) show the presence of small (<2microns), discrete droplets within the metallic zinc which were determined to be lead. Image analysis suggests that these droplets make up 0.34% of the volume of the zinc droplets, which equates to 0.2wt%. The outer regions of the metallic zinc droplets usually have a coating of zinc oxide which has probably formed after the material was discarded. The metallic zinc and zinc oxide are present in a matrix of zinc sulphate which has also probably formed after deposition. Zinc is present in one region as a zinc silicate (Fig 4d, Table 3) with a composition approximating hemimorphite $(Zn_4Si_2O_7(OH)_2,H_2O)$. Hemimorphite would be unlikely to survive the zinc distillation process (typically 1200°C) and it has probably formed post deposition. Droplets of metallic lead (up to 1mm across; Fig 4c) are occasionally found throughout the sample. No droplets of metallic iron were detected in the sample. Fragments of two sorts of refractory material can be seen throughout the sample. In most cases the refractory has a microstructure which resembles most post-medieval refractory ceramic: grains of silica in a vitrified clay matrix. The refractory usually contains some zinc oxide and cadmium oxide suggesting a link with zinc working (Table 3, Refractory 1). The concentrations of cadmium are in places relatively high compared to those seen in the zinc distillation retorts from Zawar (Freestone et al 1991, Table 3). Cadmium has lower melting and boiling points than zinc and it is expected that most cadmium would be removed from retorts during smelting. Some fragments of refractory (Fig 4e) have a microstructure resembling the refractory vessel (Sample 05) described below, ie grains of silica and small crystals of zinc-aluminium spinels (Table 3, Refractory 2 and 3, cf. Figs 4e and 4f). The various inclusions and phases of Sample 09 are present in a zinc-rich 'earthy' matrix (Table 3).

The presence of metallic zinc, a possible zinc ore, refractory materials, coal and charcoal suggest that this material derives from the smelting by distillation of zinc. Percy's description of the Champion zinc distillation process says that it was carried out for 67 hours until no more zinc could be profitably be extracted (Percy 1864, 557-8). Once the retorts had cooled the exhausted charge 'residuum' (Percy 1861, 558) or retort residue (Almond 1998, 209) was scraped out. Almond (1977) notes that the large numbers of 19th-century zinc retorts at Tindale Fell, Cumbria have remains of the charge adhering to them. This is described as lumps of coal or coke in a matrix of carbonaceous matter and zinc calcine. Developments in the 19th and 20th centuries enabled the re-processing and smelting of retort residues (Almond 1998) so it is likely to be rather scare on those sites which were readily accessible to later zinc works. The residue analysed here shows significant differences compared to those from Zawar, India (Freestone et al 1985; 1991). The presence of two different sorts of refractory and the relatively high levels of cadmium in some regions may indicate that the material derives from more than one source. One source is likely to be retort residue but other waste materials associated with zinc manufacture may also have been incorporated.



Figure 3. Sample of zinc-rich deposit (left), with a view of a polished section (right). Width of Field of polished section is 7cm.

Table 3. Mean composition (n=3) of select phases present in the zinc rich deposit

	Zinc	Matrix	Refractory	Refractory	Refractory
	silicate		I İ	2	3
Na ₂ O	<0.5	<0.5	<0.5	0.9	1.0
MgO	<0.3	0.6	0.6	<0.3	1.2
Al_2O_3	0.3	12.7	20.5	8.2	29.3
SiO ₂	29.I	43.5	71.0	77.8	60.3
P_2O_5	<0.2	0.5	<0.2	0.2	<0.2
SO₃	<0.2	1.4	<0.2	<0.2	<0.2
K ₂ O	<0. I	0.4	0.8	0.3	5.3
CaO	<0.1	2.6	0.5	0.3	0.2
TiO ₂	<0. I	0.7	0.9	0.9	1.2
MnO	<0. I	<0.1	<0.1	<0.I	<0.1
FeO	0.2	3.7	1.7	1.7	1.0
ZnO	70.4	33.I	3.5	9.7	0.5
CdO	<0.3	0.3	0.5	<0.3	<0.3
BaO	<0.3	<0.3	<0.3	<0.3	<0.3
PbO	<0.5	0.5	<0.5	<0.5	<0.5



(a) Zinc rich deposit



(b) Droplets of metallic zinc (pale grey) surrounded by zinc oxide (mid grey) and zinc sulphate (dark grey). Very small white droplets are visible in the metallic zinc and these are metallic lead.



(c) Droplet of metallic lead (white)



(d) Zinc silicate (hemimorphite)



(e) Refreactory particle showing silica grains (dark grey) and small zinc spinel crystals (white). (cf. figure 4f)



(f) Zinc retort fragment (Sample 5, see below) showing grains of silica (dark grey) and small zinc spinel crystals (white)

Figure 4(a to e). SEM-EDS micrographs (in backscatter mode) showing the range of phases present in the zinc rich deposit. The areas highlighted are those analysed by SEM-EDS (Table 3). Figure 4f shows the zinc retort fragment (Sample 05).

Refractory

The unstratified refractory material (Sample 05) is approximately 48mm thick with vitrified layers on both surfaces, indicating it is a crucible or retort fragment (Fig. 5). Examination of the refractory core shows a similar microstructure to the blue stoney material analysed by Freestone (1988, see above), with large argillaceous inclusions (up to 3mm) and small subangular quartz grains in a ceramic matrix. Compositional analysis of the matrix showed it contained significant concentrations of silica, alumina and zinc oxide, and minor amounts of iron and sodium oxides (Table 4). Subtracting the zinc oxide content and normalizing the remaining element oxide concentrations to 100% provides a clearer picture of the ceramic composition (see Table 4). Like fireclays, it is rich in silica and poor in fluxing elements such as iron, calcium and potassium oxides. Both vitrified surfaces have similar compositions. The most notable difference between the vitrified surfaces and the refractory core are the increased potassium, iron and calcium oxide concentrations which indicate they formed through interaction of the surfaces with coal ash (Dungworth 2003). Small, angular crystals of zinc-aluminium spinel ($ZnAl_2O_4$) were found to be dispersed throughout the ceramic core and vitrified surfaces (Fig. 6), while droplets of metallic iron were noted on the inner vitrified suface. Freestone et al (1985, 238) noted the presence of metallic iron droplets in the vitrified interior surfaces of zinc distillations vessels from Zawar, India. The reduction of iron oxides to metallic iron is to be expected given the highly reducing conditions required to smelt zinc oxide (Freestone et al 1985, Fig 3). Copper was not detected in any area of the sample.

As with the refractory from Warmley analysed by Freestone (1988) the presence of zinc compounds within the ceramic matrix and vitrified outer layers demonstrate it has been permeated by zinc vapour during use. This and the absence of traces of copper in the core indicate that it is a fragment of a zinc distillation retort rather than a brass cementation crucible. The thickness of the wall (48mm) falls in the range for retort dimensions noted by Percy (1861), (see above).



Figure 5. Unstratified refractory material approximately 48mm thick, with vitrified interior and exterior surfaces.



Figure 6. SEM-EDS micrograph (in backscatter mode) of refractory material showing quartz grains (grey) and crystals of zinc-aluminium spinel (white) dispersed throughout ceramic matrix.

	Fabric	Fabric exc. Zn	Vitrified exterior surface	Vitrified interior surface
Na ₂ O	1.7	2.1	1.0	<0.5
MgO	0.3	0.4	0.4	0.7
	22.8	27.2	16.8	15.0
SiO ₂	54.9	65.6	67.4	71.8
P ₂ O ₅	<0.3	<0.3	<0.3	<0.3
K ₂ O	0.7	0.8	6.6	3.9
CaO	0.6	0.3	1.5	1.7
TiO ₂	1.2	1.4	1.2	0.9
MnO	<0.1	<0.1	<0.1	0.2
Fe ₂ O ₃	1.7	2.1	3.3	3.2
CuO	<0.1	<0.1	<0.1	<0.1
ZnO	16.3		1.4	1.2

Table 4. Mean compositions (n=3) of the refractory fabric and vitrified surfaces.

nd = not detected

Clay-graphite crucible

The large fragment of clay-graphite crucible (Sample 12) recovered during the 1986 excavations falls in between the dimensions of cementation crucibles and zinc distillation retorts provided by Angerstein (Berg and Berg 2001) and Percy (1861), (Table 5 and above).

Table 5. Comparison of dimensions between Sample 12 and cementation crucible and retort dimensions provided by Angerstein and Percy.

	Sample 12	Cementation Crucible ¹	Cementation Crucible ²	Zinc Retort ²
Height		0.4m	0.3m	1.0m
Diameter	0.4m	0.2m	0.2m	0.9m
Wall thickness	38mm		25mm	40 to 65mm

¹ Dimensions provided by Angerstein (Berg and Berg 2001)

² Dimensions provided by Percy (1861)

The crucible shows evidence of having been used. The inner and outer surfaces have a vitrified layer approximately 1mm thick, while the lower part of the inner surface is covered with a white deposit. Above the white layer the fabric of the crucible is oxidized, with the graphite flakes burnt out (Fig. 7). A second small fragment of a graphitic vessel (not sampled for this research) was also recovered from Warmley. The fragment is too small to give indication of the vessel dimensions and only one vitrified surface is preserved. Copper corrosion products are present on the fractured surfaces and their location suggests they are post depositional deposits. Similar copper corrosion products were not noted on the surface of Sample 12.

Little analytical work has been carried out on archaeological finds of graphitic crucibles, with the most comprehensive research being that undertaken on post-medieval Bavarian dark crucibles (Martinón-Torres *et al.* 2003; Martinón-Torres and Rehren 2006). Analysis of the Warmley example was therefore carried out to add to the limited knowledge of graphitic

crucibles in general and to investigate whether it could be linked to a specific process carried out at Warmley, such as zinc distillation or brass cementation.

The fabric of the vessel was found to contain approximately 45 vol% graphite (Fig. 8) in a ceramic matrix rich in silica and alumina with minor amounts sodium, potassium, calcium and iron oxides (Table 6). Notably, zinc and copper were not detected in the analyses. The internal and external vitrified surfaces were similar. Both contained iron-silicon compounds and silicon in a homogenous silica- and alumina-rich matrix (Table 6, Fig. 8). The same silicon and iron-silicon compounds were identified dispersed throughout the fabric core. The detection of these phases was unexpected as high temperatures and a strongly reducing atmosphere is required to reduce silica to silicon. Nevertheless, the high concentration of graphite in the fabric would produce strongly reducing conditions during firing which may account for the formation of silicon according to the reaction:

 $SiO_2 + C \rightarrow Si + CO_2$

Silicon is comercially prepared today using the carbon reduction method whereby high purity silica is heated with charcoal, coal or coke to 1900°C in an electric arc furnace. The presence of the silicon and iron-silicon compound inclusions within the fabric itself suggests that the reaction was internally derived. Analysis of the white layer covering the lower part of the inner surface of the vessel showed it was alumina with minor amounts of silica (Table 6). A possible explanation for the presence of the alumina-rich layer is that as the silica from the alumino-silicate matrix reduced to form silicon and iron-silicon compounds free alumina disassociated and was deposited on the surface.



Figure 7. Fragment of clay graphite crucible showing white layer on internal surface and oxidised fabric (reddish colour) above the white layer. The crucible dimensions are internal diameter: 0.43m, wall thickness: 38mm



Figure 8. SEM-EDS image (in back scatter mode) of clay-graphite crucible, showing graphite flakes (black) in the fabric (left), and iron-silicon (white) and silicon compounds (light grey) in the vitrified surface (right). The very small white spots between the graphite flakes are iron-silicon compounds.

	Fabric	Vitrified	White Layer		Phases iden Vitrified S	tified in ourface
	Tabric	Surface	(inner surface)		Iron-Silicon Compound	Silicon
Na ₂ O	5.9	nd	nd	Na	nd	nd
MgO	0.6	0.6	0.8	Mg	nd	nd
	29.8	27.5	97.I	ΑΙ	0.2	nd
SiO ₂	58.7	68.6	1.6	Si	52.5	99.3
P_2O_5	0.3	<0.2	<0.2	Ρ	nd	<0.2
K ₂ O	1.6	0.3	<0.I	К	nd	nd
CaO	0.4	1.0	0.2	Ca	<0.1	nd
TiO ₂	1.1	0.6	<0.I	Ti	nd	<0.1
MnO	<0.1	<0.1	<0.I	Mn	0.5	nd
Fe ₂ O ₃	1.4	0.9	<0.1	Fe	43.6	0.2
CuO	<0.1	<0.1	0.1	Cu	0.2	<0.1
ZnO	nd	<0.1	nd	Zn	<0. I	0.1

Table 6. Mean compositions (n=3) of the various phases identified in the clay-graphite crucible.

If this vessel had been used as a brass cementation crucible or zinc distillation retort, zinc compounds might be expected to be present in the fabric or vitrified surfaces. The analyses

of the refractory material from Warmley (see above) demonstrate the aggressive penetration of zinc vapour into the vessel fabric during firing, which reacts with the ceramic to form a range of zinc compounds. Their absence from the fabric in this case, and especially from the oxidized area of the vessel, suggests it has not been exposed to zinc vapour during firing. The lack of zinc may, however, result from the nature of the graphitic fabric. As noted by Martinón-Torres and Rehren (2006, 520) the presence of graphite in a crucible greatly enhances its technical qualities: in addition to increasing toughness, thermal shock resistance, refractoriness and tensile strength, it promotes corrosion resistance. It may therefore be the case that even if exposed to zinc vapour the graphite fabric does not react with it in the same way as conventional ceramic vessels.

From the analytical data in Table 6 there is no evidence to link the vessel to Champion's zinc distillation or brass cementation processes. However, the work did highlight the need for more analytical work to be carried out on vessels of this fabric type to understand the formation mechanisms of the various phases identified, and also raised the question of how reactive clay-graphite fabrics might be when in contact with metal vapours at high temperatures.

Discussion and Conclusions

Historical archives have been used in the past to describe the development of Champion's brassworks at Warmley (Day1973, 1991 and 1998). However, total reliance on this resource can lead to a simplified view of past activities. It is often the case that the surviving records relate more to finances, standing structures or designs of large pieces of machinery rather than to the details of specific processes themselves (Payne 2004). Moreover, industrial practices were often shrouded in secrecy. This is certainly the case with Champion's zinc distillation process. The title of his 1738 patent, and the specifications contained within it reveal little detail of his methods (Day 1973), and he protected particulars of his production process from visitors to the works. The scientific analysis of archaeological residues from the site therefore provides a powerful tool for reconstructing his processes and adding to the information derived from historical documentation. However, this avenue of research has been largely neglected, with Freestone's (1988) analysis of the refractory material and the slag sample presented by Spry (2003) being the only published examples to date. The work reported above provides a necessary step in further clarifying the metallurgical processes undertaken at this site.

The results of the study are revealing. The analysis of the copper slag, in the main, supported the historically documented use of sulphurous Cornish copper ores at Warmley. However, the presence of zinc in the slag was unexpected and may indicate ores from different sources were blended. The silica polymorphs present in the slags suggest they derive from the initial ore smelting stage rather than the later metal refining and roasting steps of the copper production process.

The zinc rich deposit proved to be a very complex material containing numerous phases. These include metallic zinc, lead, zinc compounds, coal charcoal and refractory material. This range in materials indicates the deposit is likely to be composed of waste from Champion's zinc distillation process. One source is likely to be retort residue but other waste materials associated with zinc manufacture may also have been incorporated. The analysis of the refractory material corresponds well with the results obtained by Freestone (1988). The presence of zinc compounds formed within the ceramic matrix demonstrates the aggressive penetration of zinc vapour into the ceramic wall during firing and indicates the refractory is a fragment of zinc distillation retort.

Interpretation of the unstratified clay-graphite crucible fragment was more problematic. The analytical data from the clay-graphite vessel were unable to provide an answer regarding its use. Macroscopic and microscopic features, especially the oxidation of the fabric and the burning out of the graphite component from the upper inner surface, the formation of silicon and iron-silicon compounds within the fabric, and the vitrified outer surfaces, all show it had been heated to very high temperatures. Nevertheless, the absence of metal residues (zinc or copper compounds) mean it cannot be positively linked to Champion's zinc distillation or brass cementation processes. While graphitic crucibles are known to be less easily corroded than ordinary refractory ceramic crucibles, it might be expected that if the vessel had been exposed to zinc vapour some would have penetrated the fabric. The investigation of this vessel highlights the need for further work to be undertaken on crucibles of this type.

Recommendations for Further Work

This scientific investigation of a variety of physical remains from Warmely provided important new information, but it demonstrated there is still much to learn about the residues of industrial activities carried out at the site during the second half of the 18th century. A number of recommendations for future work can therefore be made. These are:

- 1. Copper smelting was a complex process involving many stages which produced a variety of slags (Percy 1861, 322-27). It is therefore desirable to extend the sampling of slag from Warmley to investigate the range of materials present and so unravel the details of the copper smelting process.
- 2. Remains from the zinc distillation process (an example of zinc retort and the residues from zinc distillation itself) have been identified analytically. It would be beneficial to analyse more samples in order to confirm the conclusions drawn above.
- 3. Future analytical work should focus on material derived from well stratified contexts in order to link the remains more precisely to activities relating to the different phases of use of the site. It would then be potentially possible to investigate possible changes in production processes during Champion's own time and compare them to later activities carried out at the site by the Bristol Brass Company.

- Almond, J K 1977 'Zinc production at Tindale Fell, Cumbria'. *Historical Metallurgy* 11(1), 30-38
- Bayley, J 1988 'Preliminary Notes on Crucible Fragments thought to be from the Warmley Brass Works'. English Heritage (unpublished internal report)
- Bayley, J 1998 'The production of brass in antiquity with particular reference to Roman Britain century', *in* Craddock, PT (ed) 2000 Years of Zinc and Brass (revised edition) BM Occasional Paper 50, 7-26
- Blinkhorn, P 2003 'The finds' in Hull, G 'The excavation and analysis of an 18th century deposit of anatomical remains and chemical apparatus from the rear of the first Ashmolean Museum (now The Museum of the History of Science), Broad Street, Oxford'. Post-Medieval Archaeology 31(1), 1-28
- Berg, T and Berg, P 2001 RR Angerstein's Illustrated Travel Diary, 1753-1755: Industry in England and Wales from a Swedish Perspective. London: Science Museum
- Champion, J 1758 'Manufacture of Spelter and Brass', Patent No. 726. Cardiff: UK Intellectual Property Office
- Champion, W 1738 'Treating Sulphureous Minerals to Obtain Metallic Sulphur', Patent No. 564. Cardiff: UK Intellectual Property Office
- Cotter, J P 1992 "The mystery of the Hessian Wares" post-medieval triangular crucibles', in Gaimster D and Redknap M (eds.) Everyday and Exotic Pottery from Europe c.650-1900: Studies in Honour of John G. Hurst. Oxford: Oxbow Books, 256-272
- Day, J 1973 Bristol Brass: A History of the Industry. Newton Abbot: David and Charles
- Day, J 1988 'The Bristol brass industry: Furnace structures and their associated remains'. Historical Metallurgy 22, 24-38
- Day, J 1991 'Copper, zinc and brass production', in J Day and R F Tylecote (eds) The Industrial Revolution in Metals. London: Institute of Metals, 131-199
- Day, J 1998 'Brass and zinc in Europe from the Middle Ages until the mid-nineteenth century', *in* Craddock, PT (ed) 2000 Years of Zinc and Brass. (revised edition) BM Occasional Paper 50, 133-158
- Dungworth, D 2003 Scientific examination of glass and glassworking materials from Silkstone, Yorkshire. Centre for Archaeology Report 90/2003 London: English Heritage
- Freestone, I 1988 'Appendix I. Report on the examination of blue material from industrial remains at Warmley', *in* Day J1988, 37-38
- Freestone, I C, Craddock, P T, Hedge, K T M, Hughes, M J and Paliwal, H V 1985, 'Zinc production at Zawar, Rajasthan', in P T Craddock and M J Hughes (eds) *Furnaces and Smelting technology in Antiquity* London: The British Museum, 229–244.
- Freestone, I C, Middleton, A P, Craddock, P T, Gurjar, L K and Hook, D R 1990, 'Role of materials analysis in the reconstruction of early metal extraction technology: zinc and silver-lead smelting at Zawar, Rajasthan', in P B Vandiver, J Druzik and G S Wheeler (eds) Materials Issues in Art and Archaeology II Materials Research Society Symposium Proceedings, Vol.185 Pittsburgh: Pennsylvania, 617–627.
- Martinón-Torres, M, Rehren, Th, and von Osten, S 2003 'A 16th-century lab in a 21stcentury lab: archaeometric study of the laboratory remains from Oberstockstall, Austria'. Antiquity **77(298)** [http://antiquity.ac.uk/ProjGall/martinon/index.html]
- Martinón-Torres, M and Rehren, Th 2006. 'The 'mystery' of the post-medieval triangular crucibles reconsidered – a global perspective', in J Pérez-Arantegui (ed), Proceedings of the 34th International Symposium on Archaeometry, Zaragoza, 3-7 May 2004. Zaragoza: Institución Fernando el Católico, 515-524
- Newbury, B D, Notis, M R and Newbury, D E 2005 'Revisiting the zinc composition limit of cementation brass'. *Historical Metallurgy* **39(2)**, 75-81
- Payne, S 2004 'Contaminated land or human history?'. British Archaeology 79, 32
- Percy, J 1861 Metallurgy. Fuel; Fire-clays; Copper; Zinc; Brass; Etc. London: John Murray

Spry, N 2003 'Eighteenth century slag construction blocks in Gloucestershire – a survey'. Gloucestershire Society for Industrial Archaeology Annual Journal for 2003, 36-58

Stabler, K 2006 Warmley Brassworks, Siston, Bristol NGR 366972 172821, SAM no. 28518, Archaeological Recording Exercise Report, Project No. 5176. English Heritage: Unpublished Internal Report

Watson, R 1786 Chemical Essays, Volume 4. Cambridge: J Archdeacon

Appendix I: Minimum Detection Limits (MDL) for the SEM-EDS system

	MDL	Error (I sdev)
Na ₂ O	0.5	0.5
MgO	0.3	0.3
Al_2O_3	0.3	0.3
SiO ₂	0.3	0.7
P_2O_5	0.2	0.1
SO ₃	0.2	0.1
K₂O	0.1	0.4
CaO	0.1	0.3
TiO ₂	0.1	0.1
MnO ₂	0.1	0.1
Fe_2O_3	0.1	0.1
CoO	0.1	0.1
CuO	0.1	0.1
ZnO	0.1	0.1
As_2O_3	0.5	0.3
SnO ₂	0.3	0.3
PbO	0.3	0.3

Table 1. Minimum detection limits and error for analytical results (wt%)