GeoArch

Report 2015/01

Assessment of archaeometallurgical residues from Greenpark Residential Site, Port Talbot

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15th January 2015

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Abstract

A small group of samples of archaeometallurgical residues and associated deposits were investigated. Because the area was formerly rich in non-ferrous metal works, with their attendant contamination issues, a triage was conducted to check the safety of the samples. This was undertaken through portable (hand-held) X-Ray Fluorescence (pXRF), in most cases with the samples still inside their plastic bags. The results from this triage are not fully calibrated, but do indeed suggest significant contamination of some of the deposits.

The submitted materials included three samples of dense, grey, vesicular slags in this sheets, one with pronounced flow lobes. These are interpreted as residues from puddling (a family of conversion processes involved in the fining of pig iron to wrought iron between the late 18th and mid-twentieth centuries).

A second group of samples were dominantly fuel residues, including coal dust, coke and other materials. These samples appear to be contaminated with copper, zinc, lead, arsenic and tin. The source of the contamination may be both the fuel ash itself, as well as from metallurgical residues.

A brightly ochreous sample of finely sandy deposit was probably particularly highly contaminated with arsenic. This may have been a water-lain sediment.

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Methods

All materials were examined visually with a low-powered binocular microscope where required. As an evaluation, the materials were not subjected to any high-magnification optical inspection, not to any form of instrumental analysis except semi-quantitative investigation by portable (hand-held) X-Ray fluorescence (pXRF). The identifications of materials in this report are therefore necessarily limited and must be regarded as provisional. The summary catalogue of examined material is given in Table 1.

Because of the former prevalence of the non-ferrous metal industries in the coastal fringe of Swansea Bay, the risk of dangerous contamination of the samples by various elements was considered sufficiently acute that most of the samples were analysed by pXRF before examination (Tables 2 and 3). The specimens were analysed on a semi-quantitative basis using a Bruker Tracer III-SD portable X-Ray fluorescence spectrometer. The instrument was operated with the Bruker 'yellow' filter (300µm Al + 25µm Ti), at 40kV and 9.60 µA, with a filament current of 189 µA, for 100s.

The instrument was controlled by a PC running Bruker's S1PXRF with spectra stored as pdz files and csv files. The images presented in Figure 1 are produced from the csv output. The output was converted for measurement of net peak areas in Bruker's Spectra (Artax) software.

Since the irregular and corroded surface of the pieces precluded meaningful quantitative analysis, a crude calibration of the results was obtained through comparison of the net peak areas with those recorded by Nicholas and Manti (2014) on a series of copper alloy standards, using exactly the same instrument and settings. The potential errors associated with this procedure are large, particularly given the large difference in sample matrix, but a more thorough calibration would not be justified at this stage. The results (Table 3) are sufficient to provide a broad classification of the materials, but should not be taken as any more than indicative.

This project was commissioned by Sophie Lewis, of the Glamorgan-Gwent Archaeological Trust.

Results

Puddling slags

Context 217, sample 16
This sample comprised three blocks of grey, dense slag with a total weight of 1.81kg. Where the slag was freshly broken it showed a lead-grey colour and was finely crystalline. In areas where it was coarsely vesicular, the large vesicles commonly showed convex internal sub-spheroidal blebs, suggesting molten slag broke through the chilled margin of the vesicle.

Context 219, sample15
This sample was a block of weathered grey dense slag weighing 4.85kg. Internally, the block showed three separate sheets (flows?) of slag, each approximately 40mm thick. The slag showed moderate vesicularity and in places appeared to be brecciated.

Context 233, sample 17
This sample was part of a flow of dense tapped slag with a shiny surface. The flow had encountered steep-sided obstacles, giving the piece and overall 'T'-shape. The low was 40mm thick and was partially coated in a rusty accretion. The sample comprised one large piece plus some small fragments, with a total weight of 512g.

pXRF Analysis
These samples showed only very low levels of non-ferrous metals. Manganese was richer in the strongly lobed 'tapped slag than in the more massive varieties.

Fuel-dominated deposits

Context 317, sample 7
This sample comprised five fragments ranging up to a few centimetres in length and a quantity of fine debris, with a total weight of 74g. The material was formed of compacted sediment, largely composed of coke and coal dust.

Context 318, sample 8
This sample (496g) was composed of small fragments of a compacted deposit formed largely of coal dust. There were small inclusions of slag, coke and possibly brick of up to 5mm.

pXRF Analysis
These samples showed high levels of several non-ferrous metals and metalloids (copper, zinc, arsenic, lead and tin).

Bulk sediment samples

Context 309, sample 9
A 194g bulk sample was a dark brown, almost black, deposit with fine coal particles. The matrix was clayey.

Context 324, sample 10
This sample (94g) was a dark brick red in bulk, but appearing browner when spread. There were some grey inclusions, probably weathered slag, up to a few mm in size.

pXRF Analysis
These samples showed high levels of several non-ferrous metals and metalloids (copper, zinc, arsenic, lead and tin).

Discussion

The larger iron-rich slag blocks showed many features in common, being lead grey slags, mostly with a fine microstructure and large vesicles, forming approximately 40mm thick flowed sheets. Some samples showed the development of flow lobes, and one showed a texture derived from tapping against a steep-sided obstacle. These features all suggest these slags are conversion slags, deriving from one of the late 18th to early 20th century processes of conversion of pig iron into wrought iron.

From the late 18th century the conversion process gradually evolved from a refining stage followed by dry puddling, firstly with the introduction of wet puddling and subsequently by the abandonment of the refining stage and the use of a variant of puddling known as 'pig boiling' (Overman 1851; Percy 1864). The residues from these processes are not as well-known as widely believed. The refining process was particularly poorly known until recent investigations by GGAT at Ynysfach Ironworks, Merthyr Tydfil (Young 2014). There are a few modern analyses of puddling slags, but mostly of early variations, of which that by Killick & Gordon (1987) is the most notable. The present material shows broad textural similarities with puddling slags, but cannot be allocated to a variant of the process with certainty.

The fuel waste deposits (317, 318) show a degree of compaction and would be compatible with an origin associated with a floor or other surface. Bulk sample #9 from (309) is broadly similar, but unconsolidated. These materials are dominated by fuel wastes (coal, coke…) in small particles and also contain some millimetric clasts of other industrial materials (slag, brick…).

The screening of the materials by pXRF for safety purposes has shown that there may be high levels of contaminant elements associated with the fuel waste deposits. Although the pXRF technique was not adequately calibrated for these classes of material, the levels of arsenic and lead in particular are likely to be well above background levels. The net peak areas and their approximate calibration are given in table 3.

The soil guideline values (SGV) for arsenic on land with commercial use is 640mg kg-1 and 32 mg kg-1 for residential use (Environment Agency, 2009). There is no current SGV for lead, pending publication of new toxicity data. The previous SGV (Defra and the Environment Agency, 2002) for lead was 450 mg.kg-1 for residential with/without plant uptake; and 750 mg.kg-1 for commercial/industrial use.

Lead contamination is defined as that exceeding the normal background concentration, which for Urban Domain 1 (the industrial area which had a strong non-ferrous metals industry, centred on Swansea, with the Swansea and Neath valleys) is 1300 mg/kg (Defra 2013c). The TGS for arsenic gives a NBC of 250mg/kg for Urban Domain 1 (Defra 2103a) and 550 mg/kg for copper (Defra 2013b). The values derived from the pXRF suggest that the fuel waste-dominated deposits (309, 318, and therefore probably the similar deposit 317) are likely to exceed these levels (Table 4).

The bulk sample #10 from context (324) appears to comprise a finely sandy sediment with iron oxides. The origin of the deposit is not certain, but may be water-lain. The pXRF data show a much lower content of lead, but a higher content of arsenic than the samples of fuel debris. Arsenic is adsorbed from groundwater onto iron oxide substrates and that may have occurred here.

Contamination by tin is also present, suggesting an influence from the tinplate process, rather than purely from the fuel itself.

Evaluation of potential

Further investigation of the present material is not warranted. Puddling slags are poorly known and in need of additional research, but investigation of these residues should be undertaken on sites where the residues can be tightly constrained to a particular variant of the process. The deposits of fuel residues do appear worthy of further investigation unless specific archaeological questions arise about the deposits.

It is recommended that any further work on the site, or on artefacts/samples from the site, should take cognisance of the contamination. Although the present study does not prove the high levels of contamination suspected (because of the poorly calibrated nature of the analyses undertaken as the triage), the values do suggest that further testing would be appropriate and appropriate risk assessment/amelioration undertaken as necessary.

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Table 1: Submitted samples

Context	Sample	Wt (kg)	Pieces	Notes
217	16	1.810	3	dense grey vesicular slag, lead grey where freshest, finely crystalline, many large vesicles with internal blebs
219	15	4.845	1	weathered grey vesicular slag in 40mm sheets, rusty crust, some brecciation, very dense
233	17	0.512	1 bits	rust coated grey lobed dense tapped slag, apparently moulded against steep sides to give 'T'-shaped piece, 40mm thick, shiny surface.
309	9	0.194	sample	dark brown, almost black, deposit with abundant fine coal particles, in a clayey matrix
317	7	0.074	5 + dust	compacted coke and coal dust
318	8	0.496	fragments	dark grey sheets of compacted deposit dominated by coal dust. Has small inclusions of slag, coke, and possible brick
324	10	0.094	sample	dark brick red soil ample, silty, brownish when spread, some grey, weathered slag? inclusions

Table 2: notes on samples analysed by pXRF

Analysis	Notes
217-16-1	tabular piece of pale grey slag - point on fresh slag
217-16-2	coarsely crystalline grey slag in a flow with a lobate base
217-16-3	dense grey slag in slightly lobate flow
233-17	grey slag encased in red secondary oxides
309-09	dark brown bulk sample
318-8-1	larger flat tabular piece
318-8-2	small pieces
324-10	reddish bulk sample

Table 3: pXRF results

a) peak net areas

Element	K	Ca	Ti	V	Rb	Sr	Zr	Cr	Mn	Fe	Cu	Zn	As	Sn	Sn	Pb	Pb
Line	K12	K12	K12	K12	K12	K12	K12	K12	K12	K12	K12	K12	K12	K12	L1	L1	M1
Puddling slags																	
217-16-1	307	6182	3323	241	1999	1002	658	285	22544	2677773	12087	343	85	689	215	812	265
217-16-2	233	6094	3636	968	1406	2265	1266	767	17288	1622102	1697	332	290	1237	181	955	148
217-16-3	1	1284	2984	315	2246	420	363	574	8156	2919270	1105	322	25	781	94	477	161
233-17	746	4618	5284	2288	2099	3248	1781	1187	29126	2146610	2175	2453	574	1046	220	4582	90
Fuel rich materials																	
318-8-1	342	11005	2995	609	2446	18151	7472	40	14393	545568	13806	17102	3224	31626	892	51274	249
318-8-2	737	4072	3465	502	3383	12016	7844	568	5154	815841	14506	58926	3887	17795	234	50577	295
Bulk samples																	
309-09	102	1785	2343	249	1017	3520	1960	395	5526	1867227	30219	3295	6072	6311	101	89455	355
324-10	1144	2393	3694	587	4430	24964	7756	544	5473	1067681	16086	25267	11216	12489	263	18737	253

b) key elements with semi-quantitatively calibrated analyses in elemental wt%

	Mn	Fe	Cu	Zn	As	Pb	Sn	total
Puddling slags								
217-16-1	0.8	47.5	0.2	<	<	<	<	48.5
217-16-2	0.6	28.8	<	<	<	<	0.1	29.5
217-16-3	0.3	51.8	<	<	<	<	0.1	52.1
233-17	1.0	38.1	<	<	<	0.2	0.1	39.4
Fuel rich materials								
318-8-1	0.5	9.7	0.2	0.2	0.1	2.2	2.2	15.0
318-8-2	0.2	14.5	0.3	0.7	0.1	2.1	1.2	19.1
Bulk samples								
309-09	0.2	33.1	0.5	<	0.1	3.8	0.4	38.2
324-10	0.2	18.9	0.3	0.3	0.2	0.8	0.9	21.6

Table 4: Contaminant elements with semi-quantitatively calibrated analyses and statutory concentrations. All values in ppm (mg kg^{-1}).
Statuatory values are dry weight. pXRF samples were not dried.
SGV – soil guideline value, published by the Environment Agency
TGS – Part 2a Technical guidance sheets, Environmental Protection Act 1990, for Wales
* - Value no longer used
n/d – not determined

	Cu	As	Pb
SGV residential	n/d	32	450*
TGS: NBC Urban 1	550	250	1300
Tentative pXRF estimates:			
Fuel rich materials			
318-8-1	2400	650	22000
318-8-2	2600	790	21000
Bulk samples			
309-09	5300	1200	38000
324-10	2800	2300	8000

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