# MATERIAL ENGINEERING, STRUCTURAL STUDIES, DIAGNOSTICS

## APPLICATION OF BULK ANALYTICAL TECHNIQUE – PGAA FOR STUDYING IRON METALLURGY SLAGS, ORE AND ARTEFACTS

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In the course of the archaeological research (excavations) in Mazovia, to the west of Warsaw, a vast ironmaking region was discovered in 1967. It is estimated that the total number of furnaces in the region (area of 300 km² – Brwinów, Pruszków, Pęcice) probably numbered 100 000 – 150 000. Maximum production was achieved in the Roman-Barbarian Period (1st to 2nd centuries AD). The slag-pit furnaces were fed with local bog ores.

The smelting of ores is almost invariably related to the formation of slags, because slags act as collectors for impurities introduced into the smelting process. Slag analysis thus has the potential for revealing important information about the metallurgical technology. This technological information is important for establishing the context and scale of production of iron artefacts in ancient Poland [1].

The art and technique of ancient iron smelting in slag-pit furnaces, man's original method for winning metallic iron from its ore, has been largely lost in recent centuries. Many reconstructions of this technique have been attempted by archaeologists in the last 50 years [2]. These experimental smelts have tended to be rather disappointing in terms of the production of usable iron; nonetheless, many conclusions have been drawn from this work.

Our primary goal was to smelt iron of sufficient quantity and quality, and to explore the process for a deeper understanding of iron production and distribution in antiquity.

Table 1. Chemical composition of bog iron in Poland – analytical method PGAA.

| Element | Ore, product and slag – Rakszawa | | | | Ore and product – Chorzele | |
|---|---|---|---|---|---|---|
| | ORE2 | Roasted | IRON1 | SLA3 | Roasted | IRON7 |
| | c% el/el | | | | | |
| B | 0.002845 | 0.004593 | | 0.00235 | 0.001218 | 3.25E-05 |
| Na | 0.62644 | | | 0.59496 | | |
| Al | 2.481618 | 1.593409 | | 2.376294 | 0.592094 | |
| Si | 40.01055 | 22.5588 | | 33.74277 | 8.719373 | |
| P | | | 3.691281 | 2.28363 | 3.169151 | 3.545599 |
| S | | | | | 0.298987 | 0.10196 |
| Cl | | | | | 0.014419 | 0.006505 |
| K | 1.184573 | 1.846757 | | 0.859582 | 0.171358 | 0.038389 |
| Ca | 4.013675 | 9.100188 | | 0.688826 | 3.317972 | 0.148829 |
| Ti | 0.435308 | 0.144684 | | 0.178788 | 0.032388 | 0.010794 |
| Mn | 14.24406 | 4.74582 | 15.71211 | 1.137574 | 0.372215 | 0.031574 |
| Fe | 36.99927 | 60.00548 | 80.53422 | 58.13245 | 83.31082 | 96.11632 |
| Co | | | 0.062397 | | | |
| Sm | 0.000759 | | | 0.000661 | | |
| Gd | 0.000897 | 0.000271 | | 0.000761 | | |

Table 2. Chemical composition of bog iron ore after sieving.

| Element | Size of grain [mm] | ORE11 >0.75 | ORE12 >1.2 | ORE13 >=0.75 | ORE14 >0.6 | ORE15 >0.49 | ORE16 >0.38 | ORE17 >0.3 | ORE18 >0.25 | ORE19 >0.2 | ORE20 >0.15 | ORE21 >0.1 | ORE22 >0.075 | ORE23 >0.06 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $c\%$ el/el | | | | | | |
| B | | 0.00412 | 0.003649 | 0.003578 | 0.003848 | 0.003781 | 0.003994 | 0.004078 | 0.004521 | 0.004813 | 0.005298 | 0.006761 | 0.007096 | 0.007716 |
| Na | | 1.071196 | | | | 0.744947 | 1.145441 | 1.004881 | 1.560014 | 0.927536 | 2.813669 | | | |
| Al | | 3.451308 | 3.736447 | 2.978499 | 5.767298 | 3.305274 | | 4.012555 | 3.924189 | | 4.066451 | 3.775672 | 3.1979 | 5.007714 |
| Si | | 36.58437 | 33.3871 | 34.15583 | 35.8034 | 39.16056 | 42.41622 | 38.92991 | 43.91736 | 47.08168 | 49.78298 | 53.2189 | 53.267 | 50.99586 |
| P | | | 2.546826 | 2.710617 | 3.153743 | 2.578096 | | 2.850344 | | | | | | |
| S | | | | | | | | | | | | | | |
| Cl | | 0.822174 | 0.778042 | 0.676454 | 0.383306 | 0.242882 | 1.057682 | 0.711069 | 0.794459 | 0.655766 | 2.754597 | 0.941897 | 0.63368 | 0.53434 |
| K | | 1.730395 | 1.304292 | 1.3365 | 1.394623 | 1.527534 | 1.383803 | 1.414027 | 1.562759 | 1.686705 | 1.784989 | 1.95491 | 2.150665 | 2.93739 |
| Ca | | 2.933783 | 3.18085 | 3.125266 | 2.865877 | 2.974287 | 3.229209 | 4.419429 | 2.940707 | 3.222527 | 2.886085 | 3.261043 | 3.368803 | 3.161832 |
| Ti | | 0.335858 | 0.404028 | 0.305729 | 0.304979 | 0.380223 | 0.638205 | 0.460639 | 0.545933 | 0.641261 | 0.385993 | 0.530718 | 0.699364 | 0.90925 |
| Mn | | 6.363666 | 6.135541 | 6.453772 | 6.767827 | 6.506394 | 7.228881 | 7.303549 | 8.083364 | 8.248981 | 8.304647 | 9.473336 | 9.358181 | 9.46609 |
| Fe | | 46.70227 | 48.52248 | 48.25301 | 43.55438 | 42.57532 | 42.89586 | 38.88882 | 36.66631 | 37.53034 | 27.21457 | 26.83595 | 27.31644 | 26.97888 |
| Co | | | | | | | | | | | | | | |
| Sm | | 0.000378 | 0.000341 | 0.000323 | 0.000313 | 0.0003 | 0.000286 | 0.00029 | | | 0.000308 | 0.000338 | 0.000383 | 0.00041 |
| Gd | | 0.000479 | 0.000399 | 0.000427 | 0.000411 | 0.000402 | 0.000411 | 0.000411 | 0.00039 | 0.000389 | 0.000415 | 0.000472 | 0.000484 | 0.000514 |

The evidence from the mines suggests that all available bog iron ore was taken and used. First, it would be beneficiated (crushed an concentrated) by removing as much as possible of the gangue (waste rock). This could be done either by washing swirling the crushed material in water and letting the denser ore separate out or by simply picking out the richest mineral manually. To smelt the metal, the ore would be first have been roasted within the temperature range of 500-800°C to make it more friable and to convert any minerals (carbonates, sulphides or chlorides) to oxides. The enriched ore would then have been smelted in a bloomery furnace.

Iron was obtained directly from its ore within a single metallurgical process in a heart by reduction of the ore with charcoal which simultaneously served as a fuel.

The melting point of pure iron is 1540°C. Even by Roman times bloomery furnaces were not producing heat much over 1200°C. Bloomery iron did not involve the iron turning to the liquid state. Instead, it was a solid state conversion requiring chemical reduction of the ore. Ore was placed in a pit and mixed in a hot charcoal fire. Air was forced into the dome covered structure *via* bellows through a fireproof clay nozzle called a tuyere. After a sustained temperature of 1100-1200°C, liquid slag (oxidised non-metallics) penetrated the pores down and fell to the bottom leaving the spongy mass containing the iron. Holes forming the sponge texture were a result of the removal of the non-metallics impurities when the slag melted out.

The bloomery furnaces were always necessarily quite small: typical dimensions would be about 1.5 m tall with an internal diameter of about 50 cm.

There are good technical reasons for such a small size of the individual furnaces. Air supply was one of the major constraints; if the furnace volume was larger then it was impossible to supply manually enough air to maintain the necessary temperatures.

Thus the early historical production process differed from the blast-furnace process in use nowadays, as iron was produced in direct process in the solid state and the slag liquified.

Slag fulfills two physical functions in a furnace: protection and transportation. Molten slag coats and protects reduced iron particles from reoxidation and carbonisation. Both protection and transportation require a liquid, free-running slag. The fluidity of the slag is a function both of its chemistry and temperature. Although the slags appear amorphous and uninformative, they are in fact a complex interacting systems of various crystalline minerals and glassy phases. Many of the minerals only form under quite specific conditions, and their identification and analysis, principally by scanning electron microscopy (SEM) and X-ray diffraction (XRD), can reveal much of the temperature and reducing conditions within the furnace. The bulk analysis of the slags, together with the identification of the minerals present, enable the chemistry, thermodynamics and efficiency of the process to be reconstructed.

Our first trials provided us with a valuable experience, but produced only the most pitiable examples of iron lumps. We attempted to deal with these problems by reducing both the fuel:ore ratio, and lowering the airflow and temperature, with disappointing results. The ore in this trial was our local bog ore with different iron contents from bog

Table 3. Chemical composition of bog iron ore after washing and sieving.

| | ORE111 | ORE112 | ORE113 | ORE114 | ORE115 | ORE116 |
|---|---|---|---|---|---|---|
| Size of grain [mm] | 0.06 | 0.102 | 0.075 | <0.06 | >0.075 | 0.15 |
| Element | c% el/el | | | | | |
| B | 0.008922 | 0.008509 | 0.008862 | 0.009034 | 0.006255 | 0.008802 |
| Na | 2.302044 | 1.121506 | 1.050139 | 1.511068 | 0.976348 | |
| Al | | 5.357504 | 4.923862 | 4.95099 | 3.816995 | 5.488688 |
| Si | 52.9562 | 50.00307 | 50.40772 | 53.14214 | 69.10386 | 46.07704 |
| P | | | | | | |
| S | | | | | | |
| Cl | 0.63751 | 0.70355 | 0.664487 | 0.486551 | 0.284543 | 1.678677 |
| K | 2.653438 | 2.413196 | 2.423075 | 2.659867 | 2.359763 | 2.340581 |
| Ca | 4.042358 | 3.845684 | 3.918397 | 3.367239 | 1.733573 | 4.14504 |
| Ti | 0.561439 | 0.593748 | 0.517069 | 0.700938 | 0.470382 | 0.889727 |
| Mn | 10.1036 | 9.691022 | 9.68697 | 8.797393 | 5.15977 | 11.48238 |
| Fe | 26.73344 | 26.26169 | 26.39887 | 24.37363 | 16.08783 | 27.8882 |
| Co | | | | | | |
| Sm | 0.000467 | | | 0.000507 | 0.000296 | 0.000362 |
| Gd | 0.000581 | 0.000515 | 0.000544 | 0.000643 | 0.000388 | 0.0005 |

Table 4. Composition of experimental slags – method PGAA.

| Element | SLA1 | SLA2 | SLA33 | SLA6 | SLA7 | SLA8 | SLA9 | SLA10 |
|---|---|---|---|---|---|---|---|---|
| | c%<br>el/el | | | | | | | |
| B | 0.004997 | 0.004623 | 0.004832 | 0.002615 | 0.004103 | 0.001997 | 0.002339 | 0.00372 |
| Na | 0.064408 | | | | | | | |
| Al | | | 1.178934 | | | | | 0.469964 |
| Si | 19.4961 | 17.26569 | 16.88526 | 13.81824 | 17.68517 | 9.266886 | 12.56741 | 13.52937 |
| P | 2.707275 | 3.288353 | 2.980674 | 2.328626 | 2.818836 | 2.041433 | 2.219448 | 3.024368 |
| S | | | | 0.142482 | 0.127723 | | | |
| Cl | | | | | | | | 0.096596 |
| K | 1.264562 | 1.258678 | 1.307747 | 0.587635 | 1.152863 | 0.488882 | 0.453708 | 0.732912 |
| Ca | 4.647395 | 4.506834 | 4.636327 | 2.862201 | 4.196719 | 2.529265 | 2.87418 | 4.396486 |
| Ti | 0.133941 | 0.113901 | 0.128258 | 0.056435 | 0.099742 | 0.048548 | 0.045808 | 0.047322 |
| Mn | 1.625203 | 1.552447 | 1.500036 | 1.443747 | 1.78702 | 1.470789 | 1.41719 | 1.708313 |
| Fe | 70.05579 | 72.00915 | 71.37761 | 78.75785 | 72.12752 | 84.15206 | 80.41977 | 75.99077 |
| Co | | | | | | | | |
| Sm | 0.00014 | 0.000139 | 0.000129 | 6.15E-05 | 0.000121 | 5.21E-05 | 6.28E-05 | 7.17E-05 |
| Gd | 0.000192 | 0.000177 | 0.000196 | 0.000101 | 0.00018 | 8.28E-05 | 8.52E-05 | 0.000113 |

ore: Brwinów (28.6% Fe), Chorzele (43.7% Fe) and Rakszawa (about 38% Fe).

The ore must be dressed carefully by hand-picking and washing, leaving less iron – rich pieces aside. It was roasted in a fire, and then broken up until the pieces ranged from 1-2 cm to fines. The next steps of dressing ore were sieving and flotation. After all these operations the results of smelting process were still disappointing. The question is about ancient methods of enriched bog iron ore.

The relationship between the chemical composition (especially at trace levels) of elements present in metal finding and the period and the ore where these findings belong, would enable us to work out chronological groupings.

The site provided enough material for an extensive analysis such as bog iron ore, slag, slagblocks and fragments of furnace. We carried out elemental analysis by means of a PGAA (prompt gamma activation analysis) analytical method. PGAA is a multicomponent analytical method, *i.e.* all the chemical elements can be detected with different sensitivities. In principle, it is possible to determine both the major and the trace elements simultaneously, though the detection limits are matrix-dependent. The measurements do not require sample preparation; they give prompt results. It allows for determining such elements as: H, B, N, Si, Ca, Cd, Gd, Pb and Bi, the analysis of which with the instrumental neutron activation analysis (INAA) method is difficult or almost impossible. On the other hand, the sensitivity of the PGAA method is lower than the INAA method by a few orders of magnitude. Moreover, usually after some days of cooling (*i.e.* decay of radioactive products) the same identical sample can be returned to the user.

PGAA is based on the detection of gamma-ray photons, which are emitted after the capture of thermal or subthermal neutrons into the atomic nuclei,

Table 5. Composition of ancient slags – method PGAA (Brwinów).

| Element | SLA41 | SLA43 | SLA44 | SLA48 |
|---|---|---|---|---|
| | c%<br>el/el | | | |
| B | 0.004028 | 0.002702 | 0.004309 | 0.002099 |
| Na | | | | |
| Al | | | | 0.773157 |
| Si | 19.45592 | 16.34909 | 13.74093 | 13.49859 |
| P | 3.839959 | 4.37883 | | 1.161344 |
| S | | | 0.110485 | |
| Cl | 0.003045 | | | 0.004855 |
| K | 0.974574 | 0.65318 | 1.217156 | 0.455521 |
| Ca | 3.533646 | 2.451395 | 4.184282 | 2.501455 |
| Ti | 0.094488 | 0.054389 | 0.068296 | 0.148695 |
| Mn | 1.983828 | 2.236292 | 2.307618 | 2.196033 |
| Fe | 70.11031 | 73.87398 | 78.36678 | 79.25794 |
| Co | | | | |
| Sm | 8.86E-05 | 5.82E-05 | 6.65E-05 | 0.000136 |
| Gd | 0.000111 | 8.19E-05 | 8.37E-05 | 0.000176 |

*i.e.* the (n,γ) reaction. The photons energies range between 50 keV and 11 MeV and are characteristic of a given element. The element identification

is based on the precise determination of gamma photon energies and intensities.

The PGAA measurements were performed at the Institute of Isotope and Surface Chemistry, Chemical Research Center (Budapest, Hungary). For PGAA analysis purposes, a guided cold neutron beam, obtained from the 10 MW Budapest Research Reactor, was used [3]. The thermal neutrons, which exit the reactor core, are cooled by a liquid hydrogen cell down to 16 K. Consequently, the achieved thermal equivalent neutron flux was $5 \cdot 10^7$ cm$^{-2}$s$^{-1}$. The size of the neutron beam was restricted to $1 \times 1$ cm$^2$ area. The investigated samples ore, slags and iron artefacts were packed in thin teflon (FEP) films, and were placed in a well-defined position of the sample holder chamber. The mass of the investigated samples varied between 0.12-12 g.

The emitted gamma photons were detected with a complex HPGe-BGO detector system in Compton-suppression mode; the signals were processed with a multichannel analyser. The spectra were evaluated with Hypermet-PC software; the element identification was performed on the basis of our prompt-gamma element library [4].

The peaks of interest were fitted by Hypermet-PC and mass ratios were calculated. The combined standard uncertainties of the mass ratios depend on the uncertainty of the counting statistics, the uncertainty of efficiency function and the uncertainty of $k_0$ factors. The most dominating of them is the uncertainty of counting statistics. The measurement time for one individual coin varied between 460 s-24 h.

Chemical composition of bog iron ore, ancient iron products, and slags from Chorzele and Rakszawa are listed in Table 1. The results of the chemical analysis of the ore after sieving and washing are presented in Tables 2 and 3. Composition of the ancient slags and from our experiments is shown in Tables 4 and 5.

The Mn content of Chorzele and Rakszawa ores varies from 0.37 to 14.2%, respectively.

The Ca content is mainly below 10%. Si and Al are comparable in the ores and the slags and range from 40 to 8.7% and 2.5 to 0.6%, respectively. The slags contain up to 80% Fe and up to 2% Mn. The percentage of Fe present in the slags is still quite high, as could be expected from the mineralogical composition of the main component. The Fe content of the ore found in the settlement is, however, lower than of the slags (Tables 2-5). Because of the low Fe content in the ore, the analysed pieces cannot be characteristic of the ore used for the ancient production. The main problem connected with methods of enriching ores in ancient times still is unresolved. The main focus of our work is to continue to obtain iron as thoroughly as possible. We also hope to achieve more specific experiments in enriched ore and to apply our experience to other types of ore, including goethite and hematite.

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# TITANIUM DIOXIDE AND OTHER MATERIALS COATED WITH SILICA-QUATERNARY ALKYLAMMONIUM COMPOUNDS FOR USING IN BUILDING INDUSTRY AND ENVIRONMENT PROTECTION

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Silica biocides based on water glass and quaternary N-alkylammonium salts (SiO$_2$-QAC) were elaborated previously [1,2], by precipitation them with H$_2$SO$_4$ from water glass (WG) and QAC. These water-insoluble biocides show fungicidal, bactericidal and algae destroying activity when added to water, or mixed with paints or building mortars. Biocides can contain structurally bonded carriers such as, *e.g.* TiO$_2$ or dolomite. Titanium dioxide is of special interest because of its properties useful for the building industry and environmental protection. Its ability to kill bacteria by absorbed UV light is known.

We have found that SiO$_2$-QAC materials absorb UV light similarly to TiO$_2$. Combined with TiO$_2$ they can show a synergism of UV effects.

Unfortunately, SiO$_2$-QAC biocides, with and without a carrier show a weak ability to disperse in commercial resins. This distinctly limits their practical use.

We elaborated, therefore, a modified technology for obtaining SiO$_2$-QAC biocides, especially containing TiO$_2$ and other materials with good ability to disperse in resins and building mortars. The technology is based on the observed ability of WG-QAC salts to coate under suitable conditions TiO$_2$, dolomite and other materials. The salt is formed by exchange of Na$^+$ cation in Si(ONa)$_n$ salt by QAC$^+$ cation:

$$Si(ONa)_n + QAC + Cl^- \rightarrow Si(ONa)_{n-1}QAC \ (+NaCl)$$
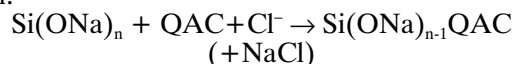
Coated material is stabilised by adding H$_2$SO$_4$.