Abstract

The processing of waste powders from steel production in electric arc furnaces is a world problem. The presence of Fe, Zn, Cd, Pb, etc. in the powders makes them a valuable source for these metals. Zinc is the metal that is most often utilized, which leads to reduction of environmental pollution.

The greatest problem in this connection is the presence of chlorine and fluorine in the powders, which influences the electroextraction of zinc in a significantly negative way.

The presented paper shows the results from the study of the possibilities for zinc leaching from powders obtained in the steel production in Bulgaria. A detailed characterization of the powders was made using chemical analysis, XRD, DTA and TGA and Mössbauer spectroscopy. The results from the powder leaching with different solvents give the reason to recommend a technological scheme for the complete and total processing of the waste powders from steel production.

Keywords: Gamzigrad - Romuliana - Romulianum; Early Byzantine period; Mettalurgy; Iron ore; Smelting furnace; Workshop

The most important find from the archaeological excavations conducted in 2004 – 2005 was large metallurgical workshop, situated in the southeastern corner of the fortified Galerius’ Palace. The workshop was discovered in the area defined on the north by Galerius’ baths, from the east and west by ramparts of younger fortification (fig. 1). Metallurgical object spread to the west to the western wall of square tower of older fortifications, tower V. The facilities was held area of about 250 m² and was a true metallurgical plant in which the melted iron, as well as iron objects were made by casting and minting (fig. 2). Based on the archaeological findings, one could say that the building dates from the end of V and the first half of VI century.
Fig. 1. General plan of Romuliana

Fig. 2. Metallurgical workshop in SE corner of Romuliana (sector of Galerius’ baths)
Furnace in the metallurgical object, marked as furnace 7/2004, was used for melting iron ore (fig. 3). It’s basis was of horseshoe-plan, 5.00 x 2.50 m in size, on the foundation made of broken stone bounded with clay. The interior of the furnace was lined with clay, which was due to high temperature burnt. According to this, furnace lining varies in color from white through orange and light red to red. Upper furnace construction was most probably domed, built with bricks bounded with clay, by system of dropping square stones (fig. 4). Calotte (dome) collapsed into the interior of the furnace, while the opening for discharging slag was in its north-eastern corner (fig. 5). In the central part, the basis of furnace was entrenched, and the ellipsoidal trench was filled with ash, soot and charred wood (fig. 6). In order to determine layers in the interior of the furnace, a cross-section of it was made, in the east - west direction (fig. 7). On
the cross-section, three layers was clearly defined, of which the first consisted of slag, the second of iron slag mixed with coal, ash and soot, while the third layer consisted of ash and soot mixed with minute sand and gravel.

It is interesting that in the furnace a lot of different parts of deer horns with traces of working were found. The most probably is that the cuttings of deer horn, ensue during the process of making of various items from the raw materials in the workshop on Romuliana, were put into the furnace with coal and iron ore made for melting. Deer horn contains a high percentage of oxygen, so it is, in the process of melting iron, probably used as a means of binding carbon. In this way, the iron was made more elastic and much more convenient for further processing by coinage.

On the floor level of metallurgical object, in the vicinity of the furnace, two pits were entrenched, about 2, 50 m in diameter, used for depositing slag (fig. 8). Since the intense melting of the iron, these pits had been filled up and the slag discharged from the furnace was running further to the north-east, where its solified remains, in a length of about 12 m, were found. Slag layer thickness was periodically up to 1 m. In the cross-section of this layer, various lenses were established (fig. 9): 1 – slag; 2 - iron slag; 3 - charcoal, soot and ash mixed with sand, and 4 - sand and gravel with ash and soot.

In the western part of the building, two
rectangular furnace bases were discovered, marked as furnace 1 and furnace 2/2005 (fig. 10). Furnace 1/2005, 1. 25 x 1. 00 m in size, with dug out bottom, was most probably smelting furnace. Its wall in the lower zone was built of broken bricks and stone laid in clay. Firebox, as is confirmed by the zone of burned earth and ash, was in the east. Upper structure of this furnace was not preserved. Furnace 2/2005, 0. 90 x 0. 60 m in size, with floor paved with tegulae, could have been the blacksmith’s furnace. This furnace had been restored and between the floors was encountered the lense of soot, ash and burned earth. Its upper structure was not preserved, but it was most probably similar to upper constructions of blacksmith’s furnaces discovered in the southwestern tower of younger fortification of Romuliana (tower 19) in 2002, as well as structures of furnaces found in the sector of Galerius’ baths in previous campaigns. In both furnaces a large number of iron objects was found, as well as an iron anvil, and a large quantity of iron slag. These two furnaces were most probably part of the blacksmith workshop, which was, in the most intense period of activity in the metallurgical furnace (furnace 7), its indivisible part, forming together real plant for the processing of iron ore.

Without incomplete chemical - physical analysis of slag, iron slag and iron objects from the furnaces, one could not with certainty discuss about their function. Malachite findings from the layer directly above the furnace 7, could perhaps indicates the processing of non-ferrous metals (copper) in the explored metallurgy facilities, along with the obvious black metallurgy.

At the end of V and the first half of VI century, in the time of the rule of Zeno, Anastasius and Justinus the 1st [1], performed a new epoch for Coastal Dacia and other northern provinces of Illyricum, marked by consolidating of Byzantine power. In this very period Romuliana was restored. The first horizon of early-byzantine fortified settlement was characterized by intensive handicraft, the testimony of which was metallurgical object investigated from 2004 to 2005. Melting and casting of iron in this workshop were very intense and larger scaled. This could be primarily seen by the
dimensions of metallurgical furnace (furnace 7), as well as the amount of slag removed. Also, according to the dimensions of the pits envisaged for outpouring of slag, it seems that, at the beginning, small-scale work was planned, but melting, for some reason, continued, the pits were completely filled and that the slag from them was running further to the North East. The workshop was a time abandoned, its interior nivelated with send above which the horizon of the second half of VI century was formed, with the corresponding layer, which was formed by the beginning of VII century. The layer, illustrated, among other things, with poor architecture, clearly speeks about the process of penetration of the population from the vicinity into the city, established during the seventieths of the VI century.

Activities of metallurgical workshop, where smaller iron objects were cast according to the findings of moulds (fig. 11), probably started at the time of Emperor Anastasius (491 - 518), when a restoration of life was intense in Coastal Dacia, derelicted after invasion of Huns and constant irritusions of Barbarians during the second half of V century. Its peak the workshop experienced in the time of Iustinianus’ restoration, crowned by establishing a new Archbishopric in new-built city Iustiniana Prima. Production of Gamzigrad’s workshop could, therefore, been associated with the renewal of the border on the Danube, when weapons for the purpose of Danubian castella could be make and mend in it. For such a function could indicate arrow-peaks found in layer above the floor of metallurgical object, as well as moulds for military belt-buckles, previously found in the area of Galerius’ baths. But, that is to say with certainty is that the production of the
workshop was intense throughout the fifth and sixth century, which testify to different objects of various materials (fig. 13 - 22).

Fig. 13. Golden tremesis (1/3 of solidus) of Emperor Iustinus I (518 - 527)

Fig. 14. Combs of dear horns

Fig. 15. Comb case, lining and whorl of dear horns

Fig. 16. Bronze fibulae

Fig. 17. Bronze linings from different objects and handle of a bronze spoon
The fact is that the processing of iron in the Byzantine Empire had a huge significance. Blacksmith was an integral part of economy, and very often was shown in the ivory cases. As the main actors of these scenes there were Adam and Eve: Eve was usually shown kneeling or sitting, managing cylindrical bellows to fire, while Adam was
standing towards the firebox, dressed in peasant suit, holding with pencers some object in one hand, while with the other hand was hammering at anvil.

Expert archaeometallurgical and chemical - physical analysis of slag, iron slag and iron objects from the furnaces, as well as of the objects found on the same levels in tower 19 and metallurgical objects built by south façade and southeast corner of Galerius’ baths, will give more informations about character of metallurgical activities in Late Roman Romuliana, as well as about the applied technological process.

All data collected so far clearly indicates that iron ore was melted in the furnace 7 / 2004 [2]. Most probably is that intermediate reductional process was applied, and the iron, by openning the furnace, cast in the fluid or liquid state. Such a technological process, which requires a very high temperature, was first documented in Germany and Scandinavia in the XIII - XIV century.[3] Before the discovery of metallurgical workshop in Gamzigrad, this way of melting iron ore was not confirmed in any Late Antique or Early Byzantine archaeological site on our territory. The most similar to metallurgical furnace in Romuliana are double furnaces, discovered on the site Bellaire III, as well as the furnace from the site Boécourt in Jura, Switzerland, dated from the AD 500 to AD 650.[4]

Romuliana, with its many handicraft workshops, is a perfect model for the reconstruction of the death of one early byzantine city. This unstoppable process of ruralisation of cities, started even in the V century, Justinianus’ restoration was only delay, leading to the same time to disintegration of once urban tissue in less economic groups. Perfect illustration of this phenomenon is the metallurgical workshop in Gamzigrad, as well as numerous other trade workshops discovered here. Ruralized and impoverished Balkan cities sunken in isolation, resulted from an illusion of possible self-subsistence based on the coexistence of its economic microregions. Thus made them easy prey for the Avars and joined Slavs, who conquered last byzantine strongholds in the interior of the Balkans in 614/615. Romulianum and other fortifications in the hinterland of Danube succeeded to postponed their death until the middle of VII century, when they finally succumbed barbaric attacks.

References

1. After the short and successful war with Vandals in Africa 534, and before the beginning of war with Gots 535, Iustinianus fortified Danubian coast with new fortifications in the district of Katarakta – Đerdap as well as in Coastal Dacia. At the time new ramparts of Aquis were built and all the belonging castellan, among them Romulianum, has
been restored (about restoration of Danubian frontier: Procopii, De aedificiis, IV, 4). At the time, Gamzigrad already had church with baptistery (Basilica III) and could be centre of church municipalities (ecclesia) for neighbouring fortifications.


4. Ibidem, 182 – 183, fig. 20, fig. 46, Pl. XIII