

Early medieval iron bloomery centre at Zamárdi (Hungary) Complex archaeometrical examinations of the slags

Raně středověké hutnické centrum v Zamárdi (Maďarsko)
Komplexní archeometrický průzkum strusek

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Archaeological excavations at Zamárdi (Hungary) revealed one of the largest early medieval iron smelting centres in Central Europe with about a hundred ore-roasting pits, twenty bloomery furnaces, reheating furnaces and a forge. In addition, a related Avar settlement dating from the 7th to 9th centuries was also unearthed, with remains of carriage roads, about twenty houses with stone furnaces and a number of open-air furnaces. The bloomery remains fit into the series of furnaces of the 7th and 8th centuries found previously on other sites in former Pannonia. As a part of a complex research project, more than a hundred slag samples from Zamárdi were examined by XRF, ICP, XRD and SEM-EDS. Different slag types and their metallurgical roles were identified. We concluded that the nature of archaeometallurgical sites can be confidently determined by the typological examination of several kinds of slag.

Avars – iron smelting – bloomery – slag – archaeometry

Během archeologických výzkumů v Zamárdi (Maďarsko) bylo odkryto jedno z největších středověkých středisek hutnictví železa ve střední Evropě s asi sto jámami na pražení rudy, dvaceti železářskými pecemi, vyhřívacími pecemi a kovárnou. Kromě toho bylo objeveno související avarské sídliště z 7.–9. století s pozůstatky vozových cest, asi dvaceti domy s kamennými pecemi a řadou venkovních pecí. Pozůstatky železářské výroby zapadají do série nálezů pecí ze 7. a 8. století, které byly objeveny na jiných místech někdejší Panonie. V rámci komplexního výzkumného projektu bylo analyzováno více než sto struskových vzorků ze Zamárdi, a to pomocí XRF, ICP, XRD a SEM-EDS. Identifikovány byly různé druhy strusky a jejich vztah k hutnímu pochodu. Dospěli jsme k závěru, že základní rysy archeometalurgických lokalit mohou být spolehlivě stanoveny typologickou klasifikací několika druhů strusky.

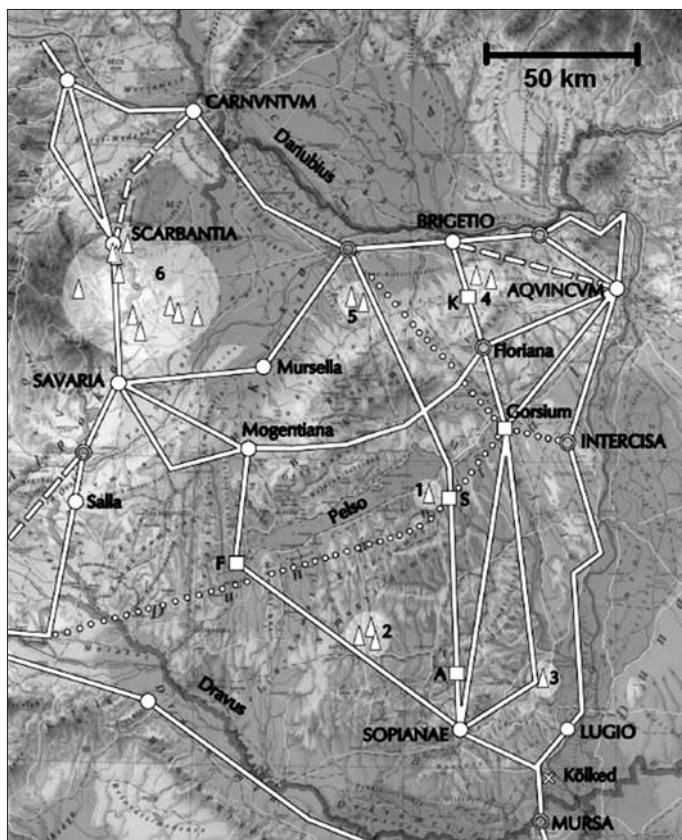
Avaři – hutnictví železa – železářská pec – struska – archeometrie

1. Introduction – historical background

There is no evidence for siderurgy on a vast scale in Roman Pannonia. Currently, there is no archaeological evidence of furnaces associated with iron reduction and as few as one and a half dozen of smithy workshops are known from this period (*Gömöri 2000a*, 220; *Rupnik 2014*, 273). The smithy workshops in Pannonia might have been supplied with raw material from the metallurgical centres of Noricum, Dalmatia and Siscia (*Gömöri 2000b*, 220). The iron metallurgical centres in Dacia Ripensis province (East Serbia) were founded at the end of the 3rd century, and were abandoned due to the attack of the Huns in 411. These centres were reorganized by Imperial orders in the 5th and 6th centuries and might have operated until the end of the 6th century or the beginning of the 7th century (*Gömöri*

Fig. 1. Roman routes and Avarian iron working sites in Pannonia – 1 Zamárdi, 2 Kaposvár, 3 Bátaszék, 4 Tatabánya (Avarian smithy?), 5 Tarjánpuszta, 6 Surroundings of Nemeskér and Zillingtal, K, S, F, A Roman fortresses (Gömöri 2012, 28).

Obr. 1. Římské komunikace a avarské železářské lokality v Panonii – 1 Zamárdi, 2 Kaposvár, 3 Bátaszék, 4 Tatabánya (avarská kovárna?), 5 Tarjánpuszta, 6 okolí Nemeskéru a Zillingtalu, K, S, F, A římské pevnosti (Gömöri 2012, 28).



2012, 26–27). Nevertheless, in the relevant iron reduction sites near Pannonia, the volume of iron production was not consistent from the Late Antiquity through the Middle Ages. It is notable, however, that the Avarian iron smelting sites commonly were established in the areas of Roman settlements (*vici, villae*), which raises the possibility of continuity (fig. 1; Szentpéteri 2009, 237; Gömöri 2000a, 223; Gömöri 2012).

Beyond the borders of the Roman Empire in the Carpathian Basin, in the territories of the Sarmatians and Imperial Period Germans, archaeological data concerning iron smelting is meagre. However, remains of smithy workshops have been recovered from Sarmatian and German sites (Kulcsár – Jakab 2009, 59; Lönhardt 2012).

After the fall of the Roman Empire, an identical situation seems to have occurred regarding iron production; that is, evidence of iron reduction is poor while iron working evidence is common. Although fairly numerous iron objects are known from the 5–6th-century burials of the Migration Period Germans in the Carpathian Basin (primarily Gepids and Langobards), German bloomery furnaces have not been found in Hungary. As a result, it is ambiguous whether the iron smelting technology of the Avars, who took over former Pannonia succeeding the emigration of the Langobards in 568, is related to previous local or western influence to any extent.

A common feature of the iron and metal production culture of the Gepids and the Avars, who moved to the Carpathian Basin during the final decades of the 6th century, is the presence of smith burials. The artefact inventories from these graves are very similar in relation to the shape and amount of tools as well as for their weapons (*Beninger 1966*, 177–178; *Tejral 2008*, 71; *Rácz 2009*, 75–80). A certain degree of correlation may be assumed about iron working between the Germans and Avars, but the same cannot be proposed for iron reduction. Additionally, some of the tools of the Avarian iron smiths, including anvils of truncated pyramidal shape, hammers and flat pliers (*Rácz 2009*, 79, fig. 13), follow German types that had widely been used since the Roman Period (*Rácz 2009*, 75, 79–80).

By tracking down the migration of the Avarians from the eastern steppe region to the Carpathian Basin, as well as the movement of their various ethnic components over time, it becomes clear that for several hundred years they could have been in contact with peoples and empires having a sophisticated iron metallurgy, such as the Juan-juan Empire in the 4th–6th centuries and the succeeding Turkic Empire (552–745) (*Gömöri 2008*, 65–68; *Vásáry 2009*, 21, 34–37). The antecedents and analogies of the Avarian iron smelting furnaces (*Semykin 2015*, 13, fig. 31) are evident at Volga Bulgarian sites (*Fjodorov-Davidov 1996*, 15) and in villages and iron reducing centres dating to the 6th and 7th centuries in the Podolian Upland, located to the East of the north-eastern Carpathians (*Gömöri 2000b*, 179). Extensive iron metallurgy, indicated by the regular occurrence of smithy workshops and iron reduction furnaces, also was pursued in the settlements of the Khazar Empire (7th–10th centuries; *Fodor 2009*, 52). Their characteristic underground furnaces, supplied with two subsurface tunnel-like bellows, do not occur either on Avarian or on later, Hungarian Conquest Period sites in the Carpathian Basin (*Pleiner 2000*, 188, 190, fig. 51).

The population of the Avarian Kaganate became even more heterogeneous in the second part of the 7th century. It was the Onogur group, settled around 670, who started exploiting the bog iron deposits of the Carpathian Basin for the first time. The culture of the newcomers presumably led to important changes in the lifestyle of the already heterogeneous local Avarian population. During the second half of the 7th century, they might have established iron working settlements exclusively on the territory of the Avarian *tudun* (*Princeps Pannoniae*, western proconsul), in former Pannonia, in the territories of Roman *villae* and *vici*, and, for easier transport, along Roman roads (fig. 1). The development of these iron working settlements reached a peak in the 8th century and, as the available data indicate, they survived the fall of the Avarian Empire. Their technological heritage lasted up to the end of the 9th century, with influences extending even to the Hungarian Conquest period (*Gömöri 2000a*, 221–239). Their iron working activities were centred in two main regions, in northern Transdanubia of today's western Hungary (mainly the Prealpine region) and in southern Transdanubia, mainly of the territory on today's Somogy County (*Gömöri 2012*, 29). In some workshops south of Lake Balaton, e.g. Zamárdi and Kaposvár, iron workers and smelters might have lived and worked together. Although Avarian iron production decreased if compared to the Roman period, it was still significant, since they succeeded in reducing iron import dependency (*Gömöri 2000a*, 221–239).

The Avarian iron working technology stemmed from territories to the east of the Carpathian Basin. In addition to their ancient eastern roots, the influence of the Onogurs in the Carpathian Basin is important as well and interactions with the Bavarians and the Moravi-

ans also may have played a part too (*Pleiner 2000*, 276–277, figs. 13, 49). After the fall of the Avar Kaganate, lasting about 250 years, the territories north of the Rába River were annexed by the Carolingians to the Frank-Bavarian zone of influence under the name of Pannonia Superior in the 820s. The local Avarian smelters were divided in several *comitates* by the Bavarians, and were forced to pay their taxes in iron (*Gömöri 2008*, 74).

2. Archaeology of the Avarian Age ironmaking in the Carpathian Basin

The highly developed ironworking skills of the Avarians are indicated by the burial inventories and by the vast amount, great complexity and wide variety of Avarian Age iron artefacts. *Gömöri (2000a, 222–223)* listed 33 archaeological sites related to Avarian iron working, among which 26 are located in Transdanubia; their amount has increased during the past twenty years. As a result of the significant earlier excavations of Avarian bloomery workshops in Hungary (*Gömöri 2000a*, 102–126, 210–216, 185–196,) and of the archaeo-metallurgical studies, the historical background and main operating stages of the bloomery process in the period were successfully outlined (*Gömöri 2000a*, 221–256).

Among the early medieval iron working sites in Central Europe discovered in the past few decades, the workshops at Kaposvár, Zamárdi and Bátaszék are most important. In 2001, the excavation at Kaposvár-Fészerlak unearthed more than 400 Avarian Age features associated with iron working across a total of 17,500 m² area (*Gallina 2002*). This is the second largest known Avarian ironmaking sites in Europe, featuring the most characteristic structures recorded on iron reduction sites of the same period. The peculiarities of the site include wells with well-preserved wooden constructions; the source of water for iron working (*Gallina 2002*, 80–82). The adjacent late Avarian Age cemeteries and settlements and the sizeable bloomery workshops, presumably owned through special rights, shows that the site was a regional centre. The recovered bloomery workshops, found in a single archaeological layer, might have operated over the course of a surprisingly short period, between the end of the 7th century and the mid-8th century (*Gallina 2002*).

At Bátaszék-Nagyorros, Avarian bloomeries (a total of 25 features in an area of 1,000 m²) were better preserved than those at Kaposvár, thus their structures could be easily reconstructed. Several types of furnaces of the 8th and 9th centuries were found in this site. They forecast important changes in the previously somewhat rigid typology (*Gömöri 2000a*, 242) and also show transitions to the furnace types of the Hungarians (*Czövek 2010*, 213–241). Traces of a furnace type were found that is structurally transitional between the so-called ‘Avarian type’ (*Gömöri 2000a*, 242, fig. 157: 1: more or less free-standing bloomery, with a subsurface base) and the 10th-century Hungarian ‘Fajsz-type’ furnace (*Gömöri 2000a*, 240, 242, fig. 157: 4: fully built in the wall of the workshop). A 3D theoretical reconstruction of this transitional type is shown in *fig. 2*.

Two Avarian bloomery furnaces and their related workshop pits were unearthed recently at Zillingtal (Austria), near the Hungarian border. According to *Mehofer (2010, 229)* these features also represent a transitional type between the free-standing and the built-in types. Based on the recovered tuyere fragments and the amount of slag, the workshop served the local iron market only.

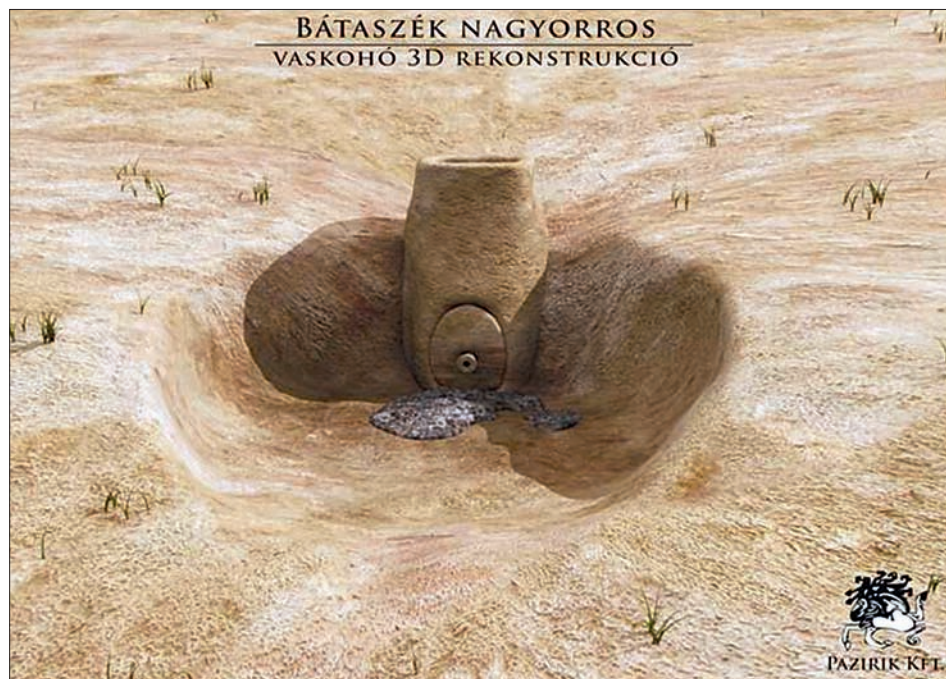


Fig. 2. Theoretical reconstruction of a transitional type bloomery at Bátaszék (Czövek 2010, 239).

Obr. 2. Teoretická rekonstrukce přechodného typu železářské pece v Bátaszéku (Czövek 2010, 239).

At Zamárdi, on the southern bank of Lake Balaton, four sites were excavated in 2005 and 2012. The nearly 1,500 archaeological features recovered from a total area of 27,700 m² date to six periods. The Avarian Age is represented by 580 features, including nearly 100 ore roasting pits, around 20 bloomery furnaces, as well as additional traces of a half-dozen demolished bloomeries. Two reheating fireplaces and a smithy workshop also were unearthed. Beyond smelting-related features, 20 houses with built-in fireplaces and over 100 outdoor fireplaces were found too. The excavations revealed an iron working centre and settlements of outstanding importance in the Avarian Age that stretched more than 1 km in length (fig. 3).

The various workshops and settlements at Zamárdi occurred sequentially; since more workshops were added southward, all the finds and features related to iron metallurgy found in the southernmost area date exclusively to the late Avarian period. The settlement features are only partially associated with the smelters' centre, and were partly found in younger archaeological layers. The complex of bloomery workshops and settlement, 1,100 m in length and 150–200 m in width, was in use from the middle of the 6th century to the end of the 9th century (much more longer period than that of Kaposvár), ranging from the Langobard era to the Hungarian conquest (Gallina – Hornok – Somogyi 2007a, 153–168; 2007b, 71–81; Gallina 2011, 179–198).

The importance of the excavation at Zamárdi is highlighted by the 2,500 graves found just 400–500 m away from the settlement. They form one of the largest known early and



Fig. 3. Aerial photograph of the excavation sites at Zamárdi and 3D-reconstruction (made by Pazirik Kft based on Zs. Gallina's instructions) of the southern part of site 89. Photos in figs. 3–5 by Zs. Gallina.
 Obr. 3. Letecká fotografie výzkumu v Zamárdi a 3D rekonstrukce jižní části lokality 89.

late Avarian Age cemeteries in the Carpathian Basin (*Bárdos 1992, 55; 1996, 48*). In this cemetery, Germanic influences may be recognized, such as the characteristic sealed pottery. Some researchers suppose that the seat of an Avar *kagan* was located at Zamárdi



Fig. 4. Traces of a bloomery workshop covered by a roof.
Obr. 4. Stopy zastřešené železářské dílny.

(*Szentpéteri 1995*, 242–243) or at least the capital (*ordu*) of a high-status individual from the closest entourage of the kagan (*Bóna 1986*, 14), while others do not share this opinion (about this subject see *Gömöri 2000a*, 221–223).

The remains of operational processes preceding the smelting at Zamárdi are the round hollows (workshops) with a diameter of 2–3 m and a depth of 20–35 cm. They can be found in a relatively small area in a great number in groups. The bloomeries in the workshops, with circular, oval or horseshoe-shaped bottom, were built with thick walls. Their hearths had a foundation of finely polished clay that was mixed with sand. The diameters of the hearths vary largely between 30 and 95 cm. The outer arc of the hearths reddened for 10–20 cm in thickness and their inner part turned into grey by the heat 5–10 cm in thickness. On some occasions, larger slag blocks were found inside the furnaces. It was possible to reconstruct their form which was cone-shaped or bottle-shaped, i.e. larger at the base with a narrow upper section. It might reach a height of 70–80 cm. Large variations are evident in the shape and position of their slag holes and breast-wall holes. The air blowing was performed by using probably one bellows through a clay tuyere embedded in the middle of the breast-wall. Sometimes these furnaces were restored and restructured. Among iron working features, superpositions also occurred (*Gallina – Hornok – Somogyi 2007a*, 164). The bloomeries are often found in groups of various size. At Site 89, two complex workshops covered by a roof with the ore roasting pits under it were unearthed (*fig. 4; Gallina – Hornok – Somogyi 2007a*, 160).

Semi-subterranean bloomeries with only their hearths dug in the ground, classified as ‘Avarian type’, were found at Magyaratád (*Gömöri 2000a*, 109–110), Zamárdi (*Gömöri 2000a*, 211–213) and Tarjánpuszta (*Gömöri 2000a*, 187–193; *Pleiner 2000*, 171, fig. 44: 1). These sites date to the late Avarian Age. The Avarian furnaces at Zamárdi, Kaposvár and Bátaszék were sunk into the ground, a substantial part of their height was built into the wall of the workshop, equipped with breast-wall and tuyere (*Czövek 2010*, 213–224; *Gallina 2011*, 179–198). Thus, these features were somewhat similar to the 10th-century Hungarian furnaces found at Somogyfajsz, 50 km from Zamárdi (*Pleiner 2000*, 173, fig. 45).

The outcrops of near-surface bog iron ore with limonite concretions used for smelting were probably along the neighbouring stream at Zamárdi (*Gömöri 2000a*, 258, fig. 159: a). In the fill of some features large amounts of roasted iron ore were found. On the basis of the investigation of related finds and the smelting experiments it can be presumed that ore and charcoal were broken to a grain-size of 1–2 cm. The furnace was dried before processing with wood and charcoal, then it was heated to a constant high-temperature-profile. The quantity of ore for one smelting process reached 10–15 kg. During the continuous air blowing, the charcoal was further added in order to maintain the furnace temperature (1150–1350 °C in the hearth) and reducing atmosphere. The use of slag forming materials could not be detected but it cannot be excluded. The relatively high quantity of slag is a characteristic feature of the bloomeries at Zamárdi. A great number of large pieces of tapped slags flowing into the slag-pit in front of the open tap hole on the bottom of breast-wall and of furnace slags taken out of the furnace at the end of smelting were found. After completing the metallurgical process, the bloom of a weight of 1–3 kg drawn through the opened breast-wall was heated on the round mildly dished reheating fireplaces near the furnaces and compacted and purified by hammering out the slag inclusions and gathering ups by using a wooden hammer (*Török – Kovács – Gallina 2015*, 236).

Surprisingly only one forge was unambiguously identified at Zamárdi (fig. 5). The reason could be, according to *Gömöri (2000a, 278)*, that these structures were timber-framed constructions that tend to decay relatively quickly. Nevertheless, semi-subterranean forges had been built at Tarjánpuszta already in this period and remained in use until the 12th century.

Zamárdi was both a settlement and an iron working site. The volume of iron production was considerably larger on this site, with significantly larger furnaces and workshop pits as well as many ore roasting pits, than at the shorter lived Kaposvár smelters settlement. However, if compared to the amount of furnaces only, a small number of breast-walls and tuyeres were recovered. The approximately 100 outdoor ovens for baking and meat smoking, renewed several times, indicate daily activities connected with the smelters centre. Large numbers of millstones were also found (*Gallina – Hornok – Somogyi 2007a*, 160). The long period of continuous site use may imply the vicinity of a strong power centre; this assumption seems to be supported by the above mentioned large cemetery. By contrast, at Kaposvár the scale of production was lower as indicated by smaller furnaces and fewer roasting pits but aided with relatively high numbers of tuyeres and breast-walls. Additionally, only a few residential buildings were unearthed on the smelters’ settlement or in its vicinity at Kaposvár. Thus, it may be assumed that this site was specialized in iron production. This also gives a hint about the different work management strategies in the period (*Gallina 2002*, 75–86).



Fig. 5. Smithy workshop of site 56 at Zamárdi and its theoretical reconstruction (made by Pazirik Kft based on Zs. Gallina's instructions).

Obr. 5. Kovářská dílna v lokalitě 56 v Zamárdi a její hypotetická rekonstrukce.

3. Archaeometrical examinations of slag samples

3.1. Methods and materials

A complex research project coordinated by the Archaeometallurgical Research Group of the University of Miskolc (ARGUM) has been running for a number of years. The general goal of this research is to gain deep insight into the technical, technological and environmental knowledge of Avarian Age ironworking in the Carpathian Basin. As one of the main objectives of this research project, about 100 slag samples were analysed from Zamárdi and other Avarian Age sites related to iron metallurgy. Different slag types and their chemical and mineralogical compositions, microstructures as well as their metallurgical roles were identified. By studying the properties of slag finds, the results can offer useful information to determine the technological level of local methods and the quality of raw materials and products.

The main analytical techniques include chemical analysis with ICP-OES (Varian 710-ES), supplemented by using titration for separating the Fe^{2+} and Fe^{3+} (the importance of the relative proportions of Fe^{2+} and Fe^{3+} was demonstrated by *Bachmann 1982, 8*), textural-chemical investigations with SEM-EDS microanalysis performed on both polished and fracture surfaces (Zeiss EVO MA10 equipped with EDAX EDS, Amray 1830 I and Jeol 8600 JXA Superprobe) and mineralogical analysis (XRD Bruker D8 Advance diffractometer with Bragg-Brentano and Göbel mirror for parallel beam, Cu-K_α source) performed predominantly on powder specimens. In some cases chemical investigations can be supplemented by WD-XRF (Rigaku Supermini 200) analysis on powder pellets or fused beads as well as by portable ED-XRF (XMET8000 Expert) on the sample surface.

In one of our previous studies related to the Zamárdi sites (*Török – Kovács – Gallina 2015, 229, 232*), two different groups of slag were identified: tap-slags flowing out of the furnace and furnace slags (cinder); *Pleiner (2000, 257)* used this term only with regard to the unreduced ore grains embedded in this slag remaining in the bloomery up to the end of smelting. However, in many cases significant difficulties may arise in distinguishing the different kinds of slag from different steps of the bloomery process. Considering other kinds of residues (purification slag, reheating and forging slags), which often have similar chemical and mineralogical compositions, their investigation is even more difficult. There are numerous scientific papers dealing with the analyses of late Antiquity and Medieval iron smelting slags. Referring to those studies, *Pleiner (2000, 252–253)* provided a comprehensive explanation for the relatively wide ranges of chemical components and the typical mineralogical constituents of bloomery slags. *Pleiner's (2000, 258)* extensive survey has a schematic representation of the different slag types and of the furnace zones of their occurrence inside and outside the two kinds of bloomeries (slag-pit and flat-hearth tapped furnaces). Similarly to the majority of previous related works (e.g. *Oelsen – Schürmann 1954, 599*), *Pleiner (2000, 259–264)* classifies the bloomery slags into two groups (tapped slags and furnace slags) and distinguishes the slag-pit blocks formed inside the bottom of the hearth or gathered in a subterranean slag-pit. However, *Pleiner (2000, 257)* underlines that the different slag classifications are usually based on the authors' archaeological, investigational and/or experimental experiences acquired by exploring finds of a given period and site(s) as well as by using specific techniques.

Buchwald's (2005, 92, 96) comprehensive work gives also detailed descriptions of the different types of iron smelting slags, as “production slags”. In addition to these materials, the characteristics of the so-called purification and manufacturing (forging) slags, formed typically in oxidizing atmosphere, are discussed as well (*Buchwald* 2005, 92, 97, 100, 138, 196).

3.2. Discussion and conclusions

As a preliminary step of the complex examination, the slag samples from Zamárdi and the other Avarian Age sites were divided into several groups. Based on their external features, a part of the studied slag assemblage was classified as tapped-slag or furnace slags from the smelting. Numerous furnace slags and slag-pit blocks were discovered *in situ* on the sites and some slag pieces were found in specific, well-definable contexts, e.g. were stuck to a fragment of furnace lining or to a tuyere. A few examined samples were classified as purification slags or were considered as forging slags. The remaining slag pieces had unclear or transitional characteristics.

A relatively low weight ratio (~10 %) of the unearthed slag finds can clearly be identified as tapped-slag. This kind of slag, heavy, compact and completely melted, usually has a shiny black surface and sometimes bizarre forms due to their flowing. Minor gas bubbles are found in their dark-grey fractures otherwise their inner structure is relatively homogeneous. The chemical composition of the analysed tapped-slag samples shows that the two dominant components are SiO₂ (on average 27–30 wt%, however, in some cases it may reach 60–65 wt%) and FeO (iron-oxide with Fe²⁺) generally 40–45 wt% (*Török – Kovács – Gallina* 2015, 232) but in numerous cases only 4–5 wt% FeO could be detected. In general, the CaO-content was low (2–5 wt%). Based on their chemical composition, a typical SEM-image of a tap-slag displays three phases: fayalite laths often having a distinctive pattern in the middle, iron-oxide (wüstite) dendrites and pyroxene network (or glassy parts) around them. In some cases, wüstite dendrites were not observed or just in the form of very small crystals. Very similar micrographs of this kind of microstructure are presented by *Buchwald* (2005, 97, 127, 136)

In our tapped-slag samples (*tab. 1*), most of the crystalline phases formed around 750–800 °C as indicated by the pyroxenes. The smelting point of these slags is about 1100–1150 °C. The amount of amorphous material is directly related to their high SiO₂, silicate or quartz content, and with their low Fe and Mg content points to highly viscous and quickly cooled slags. The higher the amorphous content, the faster was the cooling (i.e., within a few minutes). Sample Z89-662 in *table 1* represents the characteristic tapped-slag material: silica rich thus highly viscous. This kind of slag forms relatively quickly, outflows and cools rapidly. Even if Z58b-227 has similar physical characteristics to the previous one, the strongly dissimilar mineralogy would suggest a different classification. The high amounts of fayalite and wüstite indicate a moderately slow cooling in the 1200–900 °C range, under oxidizing conditions. The textures of the examined tapped-slugs often contain glassy parts in great proportion, which is confirmed by the relative high amount of amorphous phase (sometimes 55–60 %) calculated based on the XRD results.

Some SEM micrographs of the tapped-slag samples show an almost pure glassy structure with the characteristic conchoidal fracture with sharp edges. Tapped-slag forms during the early period of the smelting process. However its flowing outside the furnace depends

Phase type	Phase Name	Z89-662 T	Z58b-227 T	Z89-645 F	Z89-466 F	Z58a-156 F	Z89-468 P	Z58b-48 P, S(?)	Z56-160 S	Z58b-46	Z58a-74
main silicate	Fayalite (Ca,Mn) (Ca,Mn,Fe ²⁺)SiO ⁴	36,0			69,0		52,0		2,9		
	Fayalite (Mg) (Mg,Fe ²⁺)SiO ⁴			55,5		67,4					
	Forsterite (Fe) (Mg,Fe ²⁺)SiO ⁴			8,6							
K-solids	Leucite KAlSi ₂ O ₆	3,8	8,5	8,0	2,9						0,7
	Sanidine (Na,K)AlSi ₃ O ₈			11,0							
	Kalsilite KAlSiO ₄		1,0			0,6		1,5	2,8		
	Wuestite FeO		18,9				21,1	21,8	21,5		0,1
Spinel	Titanomagnetite Fe ²⁺ (Fe ³⁺ ,Ti) ₂ O ₄					1,7					
	Magnetite Fe ²⁺ F ³⁺ ₂ O ₄		2,0	4,4	1,5		1,6		6,1	1,1	0,5
	Spinel (Fe) (Mg,Fe)Al ₂ O ₄				7,5						
High T slag	Monticellite (CaMg)SiO ₄		9,9			4,5			29,0		
	Kirschsteinite (CaFe ²⁺)SiO ₄							44,5			
	Srebrodolskite Ca ₂ Fe ³⁺ ₂ O ₅									2,9	
High T klinker	Cristobalite low SiO ₂	2,1						0,6			1,4
	Mullite Al ₆ Si ₂ O ₁₃	0,4									1,7
	Cordierite Mg ₂ Al ₄ Si ₅ O ₁₈										0,3
	Anorthite CaAl ₂ Si ₂ O ₈	4,2									
	Diopside CaMgSi ₂ O ₆	10,1									
	Quartz SiO ₂	27,1	2,3	1,1		1,8	0,7	6,5	4,7	15,5	32,8
	Gehlenite Ca ₂ Al(AlSi)O ₇	0,3									
	Zoisite Ca ₂ Al ₃ (SiO ₄) ₃ OH					2,1					
	Sillimanite Al ₂ SiO ₅		4,1					2,5			
alteration	Calcite (Mg) (Ca,Mg)CO ₃	0,8								5,4	
	Dolomite CaMg(CO ₃) ₂			0,9						6,4	
	Siderite FeCO ₃									4,3	
oxida- tion	Hematite Fe ₂ O ₃						0,3	0,2		11,7	0,4
	Goethite FeOOH						9,3	4,4	10,0	8,2	0,9
soil conta- mination	Muscovite KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂									3,7	
	Kaolinite Al ₂ Si ₂ O ₅ (OH) ₄									5,5	
	Albite NaAlSi ₃ O ₈									4,3	0,2
	amorphous	55,0	22,0	10,0	14,0	19,0	15,0	18,0	23,0	31,0	61,0

Tab. 1. Results of the XRD examinations of some typical slag samples (T – tapped slag, F – furnace slag, P – purification slag, S – smelting slag).

Tab. 1. Výsledky XRD analýz některých typických vzorků strusky (T – struska z předpecních jam, F – pecní struska, P – struska z procesu kovářského zhutňování železné houby, S – kovářská struska).

on the slag's viscosity and temperature. Moreover, the shape of the furnace hearth, the breast-wall and the tap-hole are also influential. Although some papers reported that pure tapped-slag may contain up to 70 wt% FeO (*Tylecote 1986*, 176), numerous samples of the Zamárdi tapped-slugs contain less (e.g. Z58b-227), in fact, sometimes insignificant FeO. In a case study on iron smelting slags from Merovingian workshops, the slag samples were distinguished according to their macroscopic aspect: compact material or porous slags, moreover, slags formed by a single flowing or by a succession of so-called corded flowing. The proportion of early wüstite facies was commonly high in compact slags, however, it was very low in the single corded slags which were denoted as a special category of the compact slags (*Le Carlier – Leroy – Merluzzo 2007*). The viscosity of the bloomery slag is inversely proportional to its FeO-content (*Buchwald 2005*, 96–97), however in general, given the thermal conditions of the early Medieval bloomery process in the hearth, a fayalite-rich slag may have been liquid enough to flow out of the furnace. Fast cooling of the silica-rich slag in the open air can cause an increased proportion of glassy parts in its texture. Because of the lack of tapped-slag, *Mehofer (2010, 228)* supposed that in the furnaces of the Avars at Zillingtal the temperature achieved was not high enough to form a sufficiently liquid slag. Based on the mineralogical analyses of the furnace slag samples from Zamárdi, it seems that the shape and the dimensions of the furnace were important to achieve this goal.

The furnace slags (*Pleiner 2000*, 262–263) belong to the other group of bloomery slags. These materials do not flow out of the furnace, but remain inside it until the end of the process. They are generally large, strongly indented, sponge-like slag-blocks with a lot of gas holes, having a lower density and usually a very heterogeneous structure. Embedded pieces of charcoal and furnace wall-fragment can be observed often. Most of the slags (~ 80 %) found at the sites of Zamárdi belong to this type. Some slag pieces coalesced with a fragment of furnace lining also were unearthed at these sites. A significant difference between the average chemical compositions of tapped-slugs and furnace slags was not observed, however, furnace slags usually have a lower iron(II)/iron(III) oxide ratio. Numerous samples of furnace slags have 20–35 wt% FeO with 20–30 wt% calculated Fe_2O_3 (*Török – Kovács – Gallina 2015*, 232). While XRD (and SEM-EDS) does not provide information regarding Fe valence in amorphous components, we can identify crystalline phases of Fe^{2+} and Fe^{3+} . The source of Fe^{3+} denotes oxidation, which may be related to the smelting process (e.g. unreduced ore grains or contact of incandescent slag with air), but it may also be a late oxidation effect that occurred in the soil over the course of centuries.

The overwhelming majority of the examined slag (and ore) samples from Zamárdi, in particular the furnace slags, have a relatively high MnO-content (6–9 wt%). This may be considered as a regional feature as compared to the MnO-content of other examined early medieval slags found in other parts of the Carpathian Basin (*Török 1999*, 218; *Gömöri – Török 2002*). In the SEM-images of the examined furnace slags, a great degree of variations in the three-phase microstructure, mentioned above, can be observed. If the fayalite crystallized in blocks, it implies relatively slow cooling, while fayalite laths denote a faster cooling (*Török – Kovács 2010*, 457).

In some cases the composition of furnace slags has a significant phosphorous content (0.3–0.6 wt% by EDS point analysis) in the moderate amount of amorphous content (by XRD). Phosphorous associated with K and Na gives the slag a high liquidity even at 850–900 °C. According to *Selskiené (2007, 23)* P_2O_5 content is associated to tapped-slag

Fig. 6. SEM-micrograph of sample Z89-468. Photo in figs. 6–7 by Á. Kovács.

Obr. 6. Mikrosnímek vzorku Z89-468 pořízený pomocí SEM.

1 – O:12.68, Mg:0.32, Al:0.76, Si:0.15, P:0.06, K:0.15, Mn:4.70, Fe:81.06; 2 – O:19.57, Na:0.26, Mg:3.04, Al:0.23, Si:18.67, P:0.22, Ca:1.79, Mn:10.72, Fe:45.41; 3 – O:19.62, Na:0.10, Mg:2.71, Al:0.18, Si:18.40, P:0.16, K:0.11, Ca:2.16, Mn:10.79, Fe:45.78; 4 – O:23.41, Na:0.53, Mg:0.35, Al:9.56, Si:21.34, P:0.88, K:3.27, Ca:11.71, Mn:4.67, Fe:24.30.

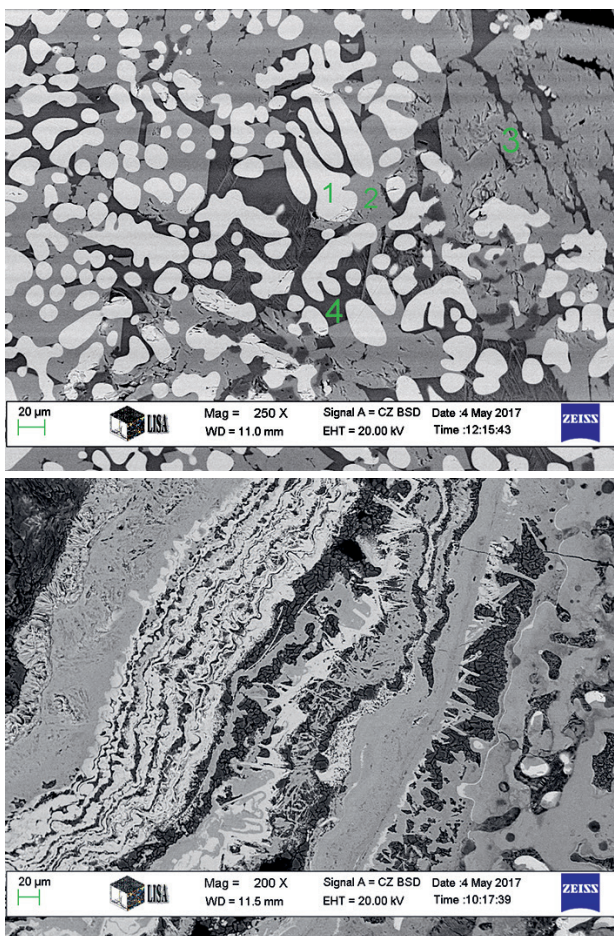


Fig. 7. Layered structure of the sample Z58b-48.

Obr. 7. Vrstevnatá struktura vzorku Z58b-48.

and furnace (bottom) slag, and smithy slags always contained much lower concentration of phosphorous as compared to the smelting slags. According to our results, furnace slags and smithy slags can be distinguished by their wüstite content, since wüstite will not appear in furnace slags. The occurrence of fayalite with Mg, Mn and/or Ca substitution indicates a temperature of ca. 1200 °C (*Deer – Howie – Zussman 1997*, 132); high enough to separate the silicate slag from the bloom.

During the hammering of the hot and raw bloom, relatively small pieces of purification slag are squeezed out of the bloom, which commonly have a plano-convex shape and a heterogeneous, frequently layered structure (*Buchwald 2005*, 97–99). This kind of slag may occur in shallow bowls that are very similar to the burning pits, about a hundred of which were unearthed at the Zamárdi sites. It is feasible that both the purification of the bloom and ore pre-roasting were carried out in the same feature. A common chemical composition was not observed in the identified purification slag samples, however, a typical SEM-micrograph of a purification slag sample can be seen in *fig. 6*.

Since only one clearly identifiable forge was unearthed at Zamárdi, the occurrence of smithy slag was not really expected in large numbers. Smithy slags are characterized by the presence of significant wüstite, a low amount of quartz and glassy phase as well as the absence or very small amount of fayalite. Instead of fayalite, monticellite and kirschsteinite can be found, these phases crystallize <900 °C. *Fig. 7* shows a layered structure which can often be observed by the examinations of smithing or purification slags.

4. Summary

The workshops at Zamárdi and Kaposvár are among the largest Central European archaeo-metallurgical sites and the largest early medieval so far discovered in the Carpathian Basin. The Avarian type workshop commonly shows several specific features, such as associated work-stage features close to the bloomeries including: roasting pits, storage pits, wells, very low number of smithies, and traditional settlement features. This overall picture, however, is coloured by variations in work management practices (*Gömöri 2000a*, 223; *2000b*, 163–164, 184, 190–193; *Gallina 2002*, 77–80).

Based on the so called barbarian servant population model (*Györfy 1972*, 269; *Gömöri 2000a*, 221), the large area of smelters workshops suggests that they were craftsmen settlements founded in close proximity to the central localities of important leaders and bog iron ore deposits. It also implies that iron production and iron smelting were controlled by a centralized authority. After the distribution of blooms from the centres, iron forging were conducted in the smaller settlements where the final products were utilized, lacking further centralized coordination.

Chemical and mineralogical analyses carried out on slag samples provide us useful information for determining the nature of the metallurgical workshops and of the technologies used. Our investigations can reveal the main characteristics which connect a slag to a particular phase of the iron working process.

Fayalite, wüstite and leucite could be additional reference phases for slag classification:

1. High SiO₂ mineral and glassy phase content, without most of the minerals of 2 and 3 types: **tapped-slag** characterized by high viscosity, solidified with fast cooling of high crystallization rate in the 800–500 °C range.
2. Fayalite with leucite, without a high amount of wüstite and low amorphous content: **furnace slag** slowly cooled in the 1200–1000 °C range. Leucite is the solidus phase of K-content introduced by hard wood ash. It should be noted that according to *Selskiené (2007, 24)* many smithing slags, examined by them, had a larger quantity of leucite and wüstite than smelting slags had.
3. Wüstite in significant amount with fayalite, low amorphous content: **purification slag**, oxidizing cooling of an incandescent bloom in the 1100–900 °C range.
4. Wüstite with high (900–1000 °C) Ca-Mg-Fe silicates and moderate amorphous content: **smithy slag**.

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