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# Extracting phosphoric iron under laboratorial conditions smelting bog iron ores

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## Abstract

In recent years it has been indicated by archaeometric investigations that phosphoric-iron (P-iron, low carbon steel with 0,5-1,5wt% P), which is an unknown and unused kind of steel in the modern industry, was widely used in different parts of the world in medieval times. In this study we try to explore the role of phosphorus in the arhaeometallurgy of iron and answer some questions regarding the smelting bog iron ores with high P-content. XRF analyses were performed on bog iron ores collected in Somogy county. Smelting experiments were carried out on bog iron ores using a laboratory model built on the basis of previously conducted reconstructed smelting experiments in copies of excavated furnaces. The effect of technological parameters on P-content of the resulted iron bloom was studied. OM and SEM-EDS analyses were carried out on the extracted iron and slag samples. On the basis of the material analyses it can be stated that P-iron is usually extracted but the P-content is highly affected by technological parameters. Typical microstructures of P-iron and of slag could also be identified. It could also be established that arsenic usually solved in high content in iron as well.

## 1. Introduction

In recent years it has been indicated by archaeometric investigations that phosphoric iron (P-iron, low carbon steel with 0,5-1,5wt% P) was widely used in different parts of the world in medieval times [1, 2, 3, 4]. In the modern steel industry P is an element to be avoided. Its detrimental effects includes various forms of embrittlement which reduce the toughness and ductility, however P has positive effects as well. P-iron was used for decorative purposes in case of pattern-welded swords or knife blades in medieval times because P increases corrosion resistance, which is why the pattern will be more contrastive [5, 6]. Increasing the hardness is another positive effect of P, which has been properly examined [7]. This effect was also utilized in the cutting edge of knife blades [8].

In this study we tried to explore the role of phosphorus in the arhaeometallurgy of iron in the Carpathian basin. Based on the industrial archaeological work of recent decades in Somogy county [9] and on archaeometric investigations of local archaeometallurgical remains (in which P in high content was established) [10, 11], we focused on this region. We tried to answer the following questions regarding the smelting of bog iron ores from Somogy county:

- 1. Is P-iron generally extracted in smelting these iron ores?
- 2. Is it possible to identify typical microstructures of extracted P-iron and of slag?
- 3. Is it possible to control the P-content of the extracted iron bloom?

## 2. Methods

2kg of 10 different P-rich bog iron ore samples was collected, 9 from Somogy county and 1 from Nyírség. XRF bulk analysis was carried out on samples from homogenized, roasted or unroasted bog iron ores (Table 1). It can be established that each of the bog iron ores has a high P- and As-content but they also usually have a high CaO-content comparing examined archaeological iron ores from other parts of Hungary [12, 13, 14].



ID	Location	EOV			Chata									
				MgO	$As_2O_3$	$AI_2O_3$	SiO <sub>2</sub>	$P_2O_5$	K <sub>2</sub> O	CaO	MnO	$Fe_2O_3$	Sidle	
1	Somogyszob	515.132	106.650	0,76	0,36	3,59	14,8	3,32	0,66	4,60	0,74	69,9	Roasted	
2	Petesmalom	530.807	099.280	0,33	0,13	0,4	3,85	4,70	0,04	3,30	3,19	83,4	Roasted	
3	Libickozma	532.949	130.562	0,51	0,20	0,63	7,00	3,11	0,14	15,3	6,80	63,8	Roasted	
4	Somogyfajsz	536.065	130.005	0,36	0,13	0,88	4,90	4,24	0,15	13,4	0,94	68,9	Unroasted	
5	Somogyfajsz	536.065 130.005		0,52	0,39	0,35	3,50	3,60	0,07	14,4	2,15	71,6	Unroasted	
6	Somogyfajsz	536.074 130.036		0,70	0,05	1,28	11,4	4,33	0,27	22,9	0,64	52,3	Unroasted	
7	Somogyfajsz	534.660	130.896	0,64	0,16	1,54	14,4	3,06	0,26	11,0	2,01	64,1	Unroasted	
8	Libickozma	532.902	130.885	0,39	0,09	0,92	22,8	2,76	0,35	14,4	2,70	50,8	Unroasted	
9	Libickozma	534.218	131.321	0,86	0,15	2,39	26,9	2,70	0,50	12,9	3,33	46,3	Unroasted	
10	Nyírség	n.a.		0,27	0,15	1,06	39,0	3,61	0,45	5,80	2,16	43,1	Unroasted	
11	Limestone	n.a.		1,04	0	0,09	0,02	0	0	97,2	0	0	Roasted	

Table1: Chemical composition based on XRF spectroscopy of the bog iron ores

Smelting experiments were carried out under laboratory conditions using an open system laboratory model (detailed in [15]), which was built on the basis of previously conducted reconstructed smelting experiments in copies of excavated medieval furnaces [16]. The open system model was a 450mm high, 100mm inner diameter shaft furnace (Fig1). A S235 structural steel tube (twyer) was set in the middle of a prismatic fireclay tube covered with a ceramic fibre thermal insulation blanket. The air supply was assured by a centrifugal ventilator. The volumetric flow rate was regulated by choking the ventilator and measured with a single-ball rotameter placed between the ventilator and the twyer. A Pt-PtRh10% thermocouple was inserted 100mm above the twyer to measure the temperature. In case of 10dm<sup>3</sup>/min air flow the temperature was 900±50°C and in 20dm<sup>3</sup>/min 1050±50°C.



Figure 1: Structure of the open system model

In each experiment 250g of roasted bog iron ore fractionized to 1-3mm grains with charcoal also fractionized to 3-15mm grains was charged into the preheated furnace from above in five portions. There were different amounts of iron obtained depending on the technological parameters. The iron was hammered out of the obtained spongy bloom in a cold state, its weight was measured and the

iron yield was calculated ( $m_{ore}/m_{iron}$ ). In case of the first five experiments the effect of charcoal/ore ratio (exp2, 6), the effect of air flow (exp4, 5, 6) and the effect of lime (exp3, 4, 5, in which lime was charged in five portions mixed with the iron ore), while in the other experiments the effect of the chemical composition of the ores on the iron yield and P-content of the iron bloom was studied. The parameters of the experiments and their results are summarized in the Table 3.

Metallographic section was made on the small iron blooms and slag samples. The microstructure of the iron bloom samples were studied under Optical Microscope (OM). The microstructure of the slag samples were studied using Scanning Electron Microscope (SEM). The chemical composition of the different phases was measured by Energy Dispersive X-ray Spectroscopy (EDS).

# 3. Results and discussion

Based on the OM and SEM+EDS analysis of the iron blooms it was found that in exp1, 6, 8, 12, 14 and 15 P-iron was obtained. 2 typical microstructures could be identified in the non P-iron blooms and 5 microstructures in the P-iron blooms (Table 2). The typical P-iron microstructures under OM and their chemical compositions after EDS can be seen in Figure 2.

Table 2: Typical microstructures in non P-iron and P-iron obtained in experiments, [P] means P is in solid solution

Non P-iron		P-iron					
#	Microstructure	#	Microstructure				
1	Pure ferrite (Fe)		Ferrite+[P], Fe-Fe <sub>3</sub> P eutectic (Fe[P], Fe-Fe <sub>3</sub> P)				
2	Ferrite, pearlite (Fe, Pe)		Pearlite+[P], Fe-Fe <sub>3</sub> P eutectic (Pe[P], Fe-Fe <sub>3</sub> P)				
		С	Pearlite+[P], ferrite+[P], Fe-Fe <sub>3</sub> P eutectic (Pe[P], Fe[P], Fe-Fe <sub>3</sub> P)				
		d	Pearlite+[P], Fe-Fe <sub>3</sub> P eutectic, secondary cementite (Pe[P], Fe-Fe <sub>3</sub> P, Fe <sub>3</sub> C)				
		е	Ferrite+[P] (Fe[P])				



Figure 2: Metallographic pictures under OM of P-iron microstructures and the chemical compositions after EDS; a - Ferrite+[P], Fe-Fe<sub>3</sub>P eutectic (exp15), b - Pearlite+[P], Fe-Fe<sub>3</sub>P eutectic (exp6), c- Pearlite+[P], ferrite+[P], Fe-Fe<sub>3</sub>P eutectic (exp1), d - Pearlite+[P], Fe-Fe<sub>3</sub>P eutectic, secondary cementite (exp8).

In case of low P-content pure ferritic microstructure without pearlite was typical, P is solved in ferrite. If the P is solved over 2,8wt% in the ferrite, Fe-Fe<sub>3</sub>P-eutectic with a melting point of 1050°C appeared on the grain boundaries [17]. Smelting bog iron ores with high P- and SiO<sub>2</sub>-content 2-10mm diameter iron spheres were obtained (epx14, 15) in which the ferrite grains were in a Fe-Fe<sub>3</sub>P eutectic matrix (Fig2a), that was in molten state during the smelting. Fe-Fe<sub>3</sub>P eutectic could be identified on pearlite grain boundaries (Fig2b) and inside ferrite grains as well (Fig2c). In hypereutectic steel Fe-Fe<sub>3</sub>P eutectic usually appeared on the pearlite grain boundaries with secondary cementite nails (Fig2d). These microstructures are well paralleled with observations on a medieval P-iron bloom [18]. Besides the P, arsenic has usually solved in the iron from the iron ore, e.g. in exp2, 7, As-iron was obtained without P.

During SEM-EDS analysis of the slag samples we found that P appeared in the glass phase (Fig3a) or in  $Ca_3PO_4$  (C3P) nails (Fig3b). It could also be observed that smelting bog iron ores with a high CaO content the Fe is substituted by Ca in fayalit (see Fig3b, analysis 2) and so the iron yield increases. The summarized OM and SEM+EDX results can be seen in Table 3.



Figure 3: SEM pictures of slags and the chemical compositions of the phases (C3P – calcium-phosphate, Fay – fayalite, Wu – wustite, Av – average) after EDS; a – P in glass phase (slag from exp7), b – P in C3P phase (slag from exp8).

From a metallurgical and physico-chemical point of view, the  $P_2O_5$  content of the slag and the C content of the solid iron bloom take part in an exchange reaction which results forming of P- and CO-bubbles dissolved in the iron bloom. In the solid bloom the carbon diffuses outward quickly, meanwhile the P diffuses inward more slowly. When the P content of the surface has reached a certain volume, liquid Fe-P-C phase appears between the molten slag and solid Fe-P-C phases. The speed of P-diffusion can be accelerated through that liquid phase.

The higher the basicity  $(CaO/SiO_2)$  of the slag (which is affected by the chemical composition of the iron ore, adding limestone, and the charcoal:ore ratio), the lower the activity factor of  $P_2O_5$  in the slag, because of the forming of a complex compound of  $3CaO \cdot P_2O_5$ , thus the lower P-content dissolved in the iron (see fig 4). In case of slag with relatively high basicity the P-content is low, and the C-content is relatively high in the bloom without the formation of Fe-Fe<sub>3</sub>P eutectic phases.

On the basis of the results it can be stated that charging lime (conf.: exp1 and exp3, 4, 5), increasing the charcoal: ore ratio (conf.: exp1 and exp2, 6), and increasing the air flow (conf.: exp1 and exp4, 5, 6) increased the iron yield. If the  $SiO_2$ -content was high in the smelted bog iron ore (exp13, 14, 15),

the iron yield was low by forming fayalite (2FeO.SiO<sub>2</sub>). It can also be seen that increasing the air flow by this the temperature in the furnace increases the P content of the iron.

Table 3: Parameters of smelting experiments, weight of the extracted iron blooms, calculated iron yield, summarized OM and SEM+EDX analysis results, calculated basicity of the slag.

	Parameters					Viold	Microstructure	Main elements in the			slag in	P in	Basicity
ID	Ore Air flow			m <sub>iron</sub> (σ)	(%)	of the iron		average (wt%)			iron in average	of the	
	ID	dm <sup>3</sup> /min)	Charcoal/ore	(g)	(6/	(70)	Table 2)	Si	Р	Ca	Fe	(wt%)	(Ca/Si
1	1	10	1:1	0	24	9,6	Pe[P], Fe-Fe <sub>3</sub> P (b) Fe[P], Pe[P], Fe-Fe <sub>3</sub> P (c)	15,03	1,55	6,69	32,43	0,73 (As!)	0,45
2	1	10	2:1	0	32	12,8	Fe, Pe (2)	12,21	1,26	8,13	22,01	0,00 (As!)	0,67
3	1	10	1:1	50	34	13,6	Fe (1)	14,40	2,15	15,85	27,59	0,00	1,10
4	1	20	1:1	50	42	16,8	Fe (1)	16,72	2,43	17,81	15,01	0,00	1,07
5	1	20	1:1	100	61	24,4	Fe, Pe (2)	12,28	3,23	27,93	12,39	0,00	2,27
6	1	20	1:2	0	18	7,2	Pe[P], Fe-Fe <sub>3</sub> P (b) Fe[P], Pe[P], Fe-Fe <sub>3</sub> P (c)	13,15	1,86	7,53	37,68	1,09	0,57
7	2	10	1:1	0	28	11,2	Fe, Pe (2)	6,71	6,85	6,21	43,65	0,00 (As!)	0,93
8	3	10	1:1	0	20	8	Pe[P], Fe-Fe <sub>3</sub> P, Fe <sub>3</sub> C (d)	7,75	2,99	8,47	45,33	1,48	1,09
9	4	10	1:1	0	8	3,2	Fe, Pe (2)	10,37	4,04	23,63	25,71	0,00	2,48
10	5	10	1:1	0	17	6,8	Fe (1)	7,48	2,16	15,76	40,82	0,00	2,11
11	6	10	1:1	0	9	3,6	Fe, Pe (2)	12,35	1,16	16,51	34,23	0,00	1,33
12	7	10	1:1	0	13	5,2	Fe[P] (e)	19,13	1,00	14,61	25,29	0,8 (As!)	0,76
13	8	10	1:1	0	7	2,8	Fe, Pe (2)	12,19	0,68	11,79	40,00	0,00	0,97
14	9	10	1:1	0	4	1,6	Fe[P], Fe-Fe₃P (a)	25,91	0,84	7,45	25,50	4,72 (As!)	0,29
15	10	10	1:1	0	4	1,6	Fe[P], Fe-Fe₃P (a)	27,35	0,97	3,63	19,55	4,81 (As!)	0,13





## 4. Conclusions

1. The smelted bog iron ores collected in Somogy county have a high P- and CaO-content, which seems a common property in case of this region. As-content is also usually high.

- 2. Smelting P-rich, acidic bog iron ores collected in Somogy county, resulted in P-iron, and iron with high As content was also usually observed.
- 3. 5 typical microstructures in P-iron could be identified:
  - Ferrite + [P] in solid solution, Fe-Fe<sub>3</sub>P eutectic
  - Pearlite + [P] in solid solution, Fe-Fe<sub>3</sub>P eutectic
  - Pearlite + [P] in solid solution, ferrite + [P] in solid solution, Fe-Fe<sub>3</sub>P eutectic
  - Pearlite + [P] in solid solution, Fe-Fe<sub>3</sub>P eutectic, secondary cementite
  - Ferrite + [P] in solid solution
- 4. It is possible to control the P-content of the iron bloom:
  - Increasing the basicity of the slag decreased the P-content of the bloom
  - Increasing the air supply increased the P-content of the bloom
- 5. Smelting with basic slag decreases not only the P-content of the iron, but also increases iron yield, because Fe is substituted by Ca in fayalit.

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