

PHASE COMPOSITION OF METALLURGICAL ZINC AND LEAD SLAGS

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Slags formed in the “Miasteczko Śląskie” Zinc Smelting Plant process contain substantial amounts of heavy metals such as Pb, Zn, Cd, Cu. In hypergenic environment this elements may occur in stable or unstable phase. Environmental conditions and the forms of occurrence of elements decide about metals stability and mobility. On the basis of laboratory, microscopic and modeling studies it was found that the main phase present in slags from the current production of the shaft furnace is fayalite, which is unstable in Eh-pH wide range in water and soil environment of the surroundings of HC “Miasteczko Śląskie”.

Keywords: lags, Zinc Smelting Plant, metals, hypergenic environment, Eh-pH diagrams

1. INTRODUCTION

The “Miasteczko Śląskie” Zinc Smelting Plant (HC Miasteczko Śląskie) is the only zinc and lead manufacturer in Europe that uses the ISP (Imperial Smelting Process) pyrometallurgical process. The process is carried out in a shaft furnace in a manner enabling simultaneous production of Zn and Pb. The charge for this process comprises raw materials, i.e. sphalerite and galena concentrates from zinc and lead ore flotation, raw zinc oxide and recycled material, i.e. undersize particles of Zn-Pb sinter, dust, slurries, dross, steel-making dust [4, 5, 11].

Slags formed in the ISP process in an amount of 60,000 t·y⁻¹ are the only waste at Zinc Smelting Plant Miasteczko Śląskie that is disposed at the Hazardous Waste Landfill. All other waste (dust, slurries, dross) is recycled within the process.

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Tests performed in the past [2] have shown that slags deposited in the landfill contain substantial amounts of heavy metals (such as Zn, Pb, Cu, Cd) and can therefore have a strong impact on the environment.

Identification of the forms of occurrence of selected metals in the slags will help determine the mobility thereof based on Eh and pH diagrams, and will thereby enable the prediction of environmental impact of the deposited slags.

2. SAMPLING AND TESTING METHODS

Slag samples from the Shaft Furnace Unit were taken in 1-2-monthly intervals (7 series in all), each sample weighing ca. 0.5 kg [7]. Average chemical composition was determined for the adequately prepared slag samples, while the content of Zn, Pb, Fe, Cu, Cd in each sample was determined by means of a JY 2000 inductively coupled plasma atomic emission (ICP-AES) spectrometer. Phase identification was based on microscope observations and X-ray diffraction method. Microscopic observations were conducted in transmitted light using a ZEISS microscope, whereas an HZG-4 diffractometer was used for the X-ray method (analysis conditions: $\text{Cu}_{\text{K}\alpha}$ lamp, 2 theta angle range – 4-64°, measuring increment – 0.05°, voltage – 35 kV, current – 16 mA). The Eh-pH diagrams were drawn on the basis of “Development and Interpretation of Computer-Generated Potential –pH Diagrams” by Tayer L. [8].

3. RESULTS

3.1. Chemical composition of slags from the Shaft Furnace Unit

The major constituents (> 10 wt.%) in the average chemical composition of the slags include iron (determined as FeO), silica (SiO_2) and calcium (CaO) (Table 1). These three constituents jointly comprise more than 76 wt.%, with FeO content (ca. 34 wt.%) much higher than that of SiO_2 (ca. 25 wt.%) and CaO (ca. 17 wt.%).

Table 1. Chemical composition of the from the Shaft Furnace Unit

Chemical component	Average content [wt. %]
SiO_2	24,82
Al_2O_3	8,29
FeO	33,95
MgO	2,68
CaO	17,43

PbO	2,13
ZnO	7,86
SO ₃	2,84
Sum	100,00

Apart from these chemical constituents, the other significant constituents include aluminium (Al₂O₃) and zinc (ZnO), the content of which amounts to ca. 8 wt.%. The content of MgO, PbO and SO₃ ranges from ca. 2 to ca. 3 wt.%. Therefore the chemical composition indicates that mineral constituents of the slag comprise mainly iron and calcium silicates and aluminosilicates.

Metal content was determined in a number of samples of slags of various deposition duration times (Table 2). Slags from the Shaft Furnace Unit are characterized by varying concentrations of the studied metals: 5.5%-9.5% Zn; 1.1%-3.9% Pb; 15.3%-27.8% Fe; 2.1%-3.8% Cu and 0.001%-0.019% Cd.

Differences in the content of these metals in the slags result from the varying chemical compositions of the charge material and from the changing conditions of the smelting process. The highest mean concentration (20.9 %) among the metals determined is that of Fe, which is the consequence of the fact that this element, along with SiO₂, the average content of which is ca. 25 %, is the main slag-forming constituent.

3.2. Phase composition of slags from the Shaft Furnace Unit

The only components identifiable under the microscope were glaze and crystals, most probably olivine crystals. The other constituents formed opaque grains.

The glaze showed characteristic optical isotropy and often contained opaque inclusions. Olivine crystals are idiomorphic, have a high relief, show dark yellowish pleochroism and high interference colours, which suggests that the olivines are rich in fayalite (Fig. 1 and 2).

By means of X-ray diffraction phase identification it was found that the main phase of slags from the Shaft Furnace Unit was fayalite. This is indicated in the diffraction pattern by the presence of reflections, which are characteristic of this phase (Table 2). In addition to fayalite, the slags contain oxides of iron, calcium, magnesium doped with Cu, Cd, Sb [5], wherein the content of these constituents is probably much lower than that of fayalite. The diffraction pattern also shows a stronger background within the 2-theta angle range, which indicates the presence of an amorphous substance (e.g. glaze observed under the microscope).



Fig. 1. Idiomorphic olivine crystals with characteristic high relief, one nicol, magnification 400x.

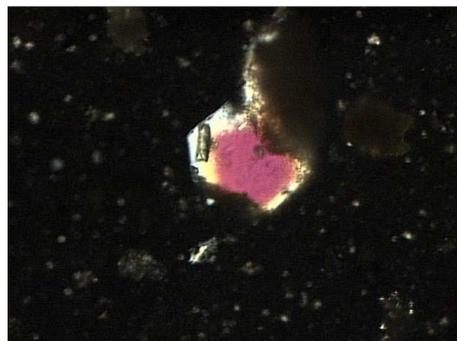


Fig. 2. Idiomorphic olivine crystals with characteristic interference colours, crossed nicoles, magnification 200x.

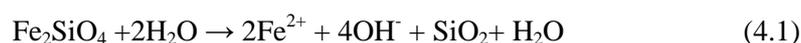
Table 2. Interpretation of averaged slag sample diffraction pattern

Diffraction Reflex No.	d_{hkl}	θ [°]	I	Mineral
1	3,56	10,15	7,0	fayalite
2	3,06	11,16	6,5	fayalite
3	3,05	11,72	5,0	fayalite
4	2,82	12,50	10,0	fayalite
5	2,63	14,58	4,0	fayalite
6	2,55	14,63	7,0	fayalite
7	2,49	15,85	9,0	fayalite
8	2,45	15,93	1,0	fayalite
9	1,78	16,13	5,0	fayalite

4. DISCUSSION OF RESULTS

Interpretation of the results of phase examination of landfilled slags in the context of the environmental impact thereof should mainly apply to the basic phase, that is to fayalite. Based on the chemical composition of the slag (Table 1), considering the stoichiometric ratios of fayalite (chemical formula Fe_2SiO_4), the content of this phase was estimated at ca. 50 wt.%. Fayalite may contain admixtures of MgO and CaO.

In the surface region fayalite is decomposed by dissociated H_2O molecules in the following reaction:



Products of this reaction comprise: stable phase of SiO_2 and unstable Fe ions or hydroxides thereof [3, 9].

The slag, and fayalite particularly, will be subject to hypergenic processes occurring under the influence of such factors as: seasonal temperature

variability, atmospheric precipitation, insolation and Eh and pH conditions of soil-water environment. The Eh and pH conditions, in turn, depend on many other factors, principally on chemical interactions with precipitation water and soil. For this reason the following values were adopted when evaluating the environmental impact of slag: mean precipitation: 700 mm/year, mean temperature in winter season: -3°C , mean temperature in summer season: $+18^{\circ}\text{C}$ (maximum $+25^{\circ}\text{C}$), mean annual temperature: 8°C . Studies were performed within the water stability field (Eh range: $-1.0 + 1.4\text{V}$ and pH range of $0\div 14$ were adopted) [3]. Within these value ranges Eh-pH diagrams were plotted to show the stability fields of the main chemical constituents of fayalite (silicon and iron) under adopted temperatures (Fig. 3a-3d).

As shown in Eh-pH diagram for the temperature of -3°C (Fig. 3a), the fayalite stability field at pH=6.8 spans from Eh equal to -0.33 up to -0.30V , and at pH=14 it spans from Eh = -0.75 up to -0.70V . With increasing temperature the stability field of fayalite is shifted towards lower pH values, to 6 at the temperature of 25°C , with insignificant changes of Eh values. On the other hand, a distinct decline of Eh value down to -0.85V is observed with temperature increase to 25°C at the extreme pH value of stability field.

Changes of Eh and pH that determine the stability field of fayalite in aqueous environment cause its decomposition. One of the products of this decomposition is always SiO_2 , whereas iron, depending on the conditions, adopts the following forms: Fe_3O_4 , $\text{FeO}\cdot\text{OH}$, Fe^{2+} or Fe^{3+} . It may therefore be presumed that stable forms among these products will include SiO_2 and Fe_3O_4 , while Fe^{2+} and Fe^{3+} , being ions, will be present in aqueous solution.

In an aqueous environment, within pH range of $14.0 - 7.8$ and at the temperature of -3°C (Fig. 3a), where fayalite is stable at Eh values indicated by lines 1 and 7, this constituent decomposes to:

- Fe_3O_4 and silica (SiO_2), in the area defined by lines 2, 6 and 7,
- $\text{FeO}\cdot\text{OH}$ and silica (SiO_2), in the area bounded by line 6.

If pH change of the aqueous environment in the range of $7.0 - 7.9$ and at the temperature of -3°C is considered (Fig. 3a), fayalite decomposition will be observed, depending on Eh value, in areas bounded by:

- lines 1 and 2, into Fe^{2+} ion and silica (SiO_2),
- lines 2 and 6, into Fe_3O_4 and silica (SiO_2),
- lines 3 and 6, into $\text{FeO}\cdot\text{OH}$ and silica (SiO_2).

If pH change of the aqueous environment in the range of $1.3 - 7.0$ is considered, fayalite decomposition products, depending on Eh value in areas bounded by the lines specified, will include:

- lines 3 and 4 - Fe^{2+} ion and silica (SiO_2);
- lines 3 and 5 - $\text{FeO}\cdot\text{OH}$ and silica (SiO_2).

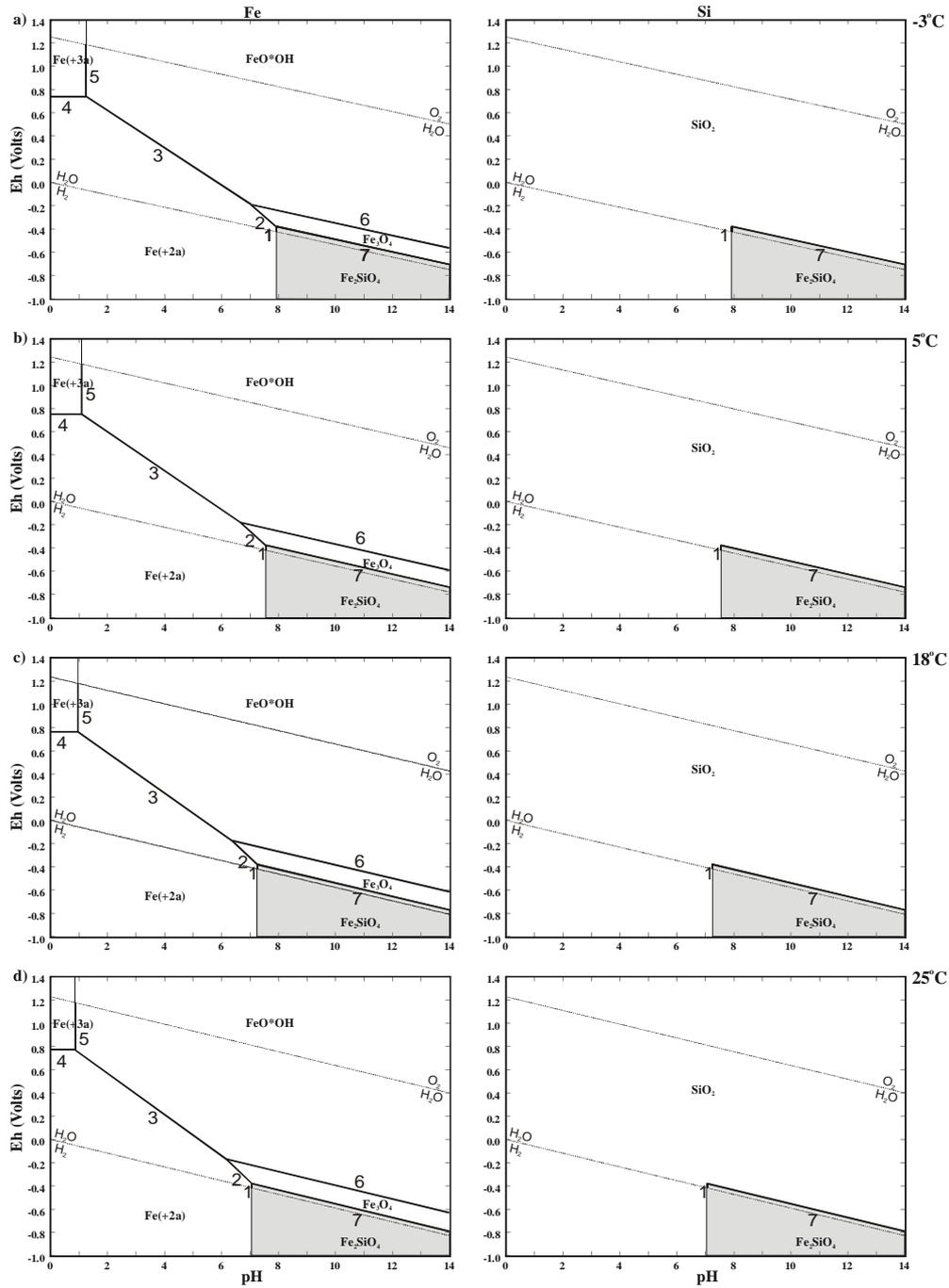


Fig. 3. Eh-pH diagrams of fayalite stability in temperatures: -3°C (a), 8°C (b), 18°C (c) and 25°C (d).

The last case considered is pH range of 1.3 – 0.0, wherein fayalite decomposes, depending on Eh value in areas bounded by the lines specified, into:

- lines 3 and 4, Fe^{3+} ion and silica (SiO_2);
- lines 4 and 5, Fe^{3+} ion and silica (SiO_2).

The water and soil environment under investigation (Miasteczko Śląskie) has a pH range of 4.5 to 7.5 [10]. This range falls generally outside of the stability field of fayalite, with a partial overlap only at the temperature of -3°C . Fayalite will therefore undergo decomposition. It may be presumed that, depending on Eh of this environment, the products of fayalite decomposition at -3°C will always include silica, and additionally Fe^{2+} ion or $\text{FeO}\cdot\text{OH}$ compound.

At temperatures of $+8$, $+18$ and $+28^\circ\text{C}$ the stability field of fayalite is gradually shifted towards $\text{pH}=7$, with insignificant changes of Eh value. In the extreme case, at the temperature of 25°C , there is also a slight shift of the stability field of the Fe^{3+} ion towards lower pH values.

It should be noted that temperature increase within the pH range of the water and soil environment under consideration (4.5 – 7.5) results in fayalite being stable only in the pH range of 7.0 – 7.5 (Fig. 3).

Account should also be taken of the possibility of the presence of various metals in olivines, e.g. Mn, Ni, Zn, Co [1, 6] which will be released into the water and soil environment during fayalite decomposition.

5. CONCLUSIONS

In the course of investigations it was found that fayalite is the main phase present in slags from the current production of the shaft furnace at Zinc Smelting Plant Miasteczko Śląskie. The mineral composition of the slag is complemented with glaze and opaque constituents, which have not been identified.

Interpretation of pH-Eh diagrams has shown that fayalite will undergo decomposition at the temperatures of -3°C and $+8^\circ\text{C}$ in the hypergenic environment of the surroundings of Zinc Smelting Plant Miasteczko Śląskie. At higher temperatures of $+18^\circ\text{C}$ and $+25^\circ\text{C}$ the stability field of Fe_2SiO_4 is shifted towards lower pH values, the effect being that fayalite remains stable only within a narrow pH range of 7.0 to 7.5. Therefore, slags deposited in the landfill may constitute a potential source of contamination of the water and soil environment of Zinc Smelting Plant Miasteczko Śląskie. Potential contaminants include not only iron compounds, but also other metals geochemically bound in olivines.

In order to maintain fayalite stability in the water and soil environment, the pH value in the latter should be kept above 7.

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SKŁAD FAZOWY ŻUZLI POCHODZĄCYCH Z HUTNICTWA CYNKU
I OŁOWIU

Streszczenie

Huta Cynku „Miasteczko Śląskie” jest jedynym w Europie producentem cynku i ołowiu wytapianych metodą ogniową w procesie Imperial Smelting Process (ISP). Proces prowadzony jest w piecu szybowym w sposób umożliwiający jednoczesne uzyskiwanie Zn i Pb. Wsad do procesu technologicznego stanowią surowce, tj. koncentraty blendowo-

galenowe z flotacji rud cynkowo- ołowiowych, surowy tlenek cynku oraz materiały zwrotne, tj. podziarno spieku Zn- Pb, pyły, szlamy, zgary, pyły stalownicze. Żużle powstające w procesie technologicznym Huty, zawierają w swym składzie ilości metali ciężkich (m.in. Zn, Pb, Cu, Cd). Identyfikacja form występowania wybranych metali w żużlach pozwoliła na określenie ich mobilności w środowisku hipergenicznym, w oparciu o diagramy Eh i pH. Na podstawie przeprowadzonych badań mikroskopowych i modelowych stwierdzono, że główną fazą występującą w żużlach z bieżącej produkcji pieca szybowego Huty jest fajalit, który w środowisku gruntowo-wodnym rejonu Zinc Smelting Plant „Miasteczko Śląskie”, jest niestabilny w szerokim zakresie Eh-pH.