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**MINERALOGICAL AND CHEMICAL CHARACTERISTICS OF SLAG  
FROM FORMER Ni – SMELTER IN SZKLARY (LOWER SILESIA, SW  
POLAND)**

**Abstract:** Pyrometallurgical slags were produced during over 100 years of silicate nickel ores exploitation in Szklary (Lower Silesia, SW Poland). The slags consist mainly of glass but other phases like silicates, oxides, sulfides and alloys of various metals such as Ni, Fe, Cu, Sn also occur. Metallic trace elements which are hazardous for the environment are associated mainly with sulfides and alloys of different metals.

**Keywords:** slag, mining, Ni-smelter, dump, environmental hazard

INTRODUCTION

The long term exploitation of metallic ores leads to formation of large amounts of wastes including barren rocks fragments, industrial constructions, incinerator ashes and slags. They commonly contain significant amounts of potentially toxic metals such as Ni, Cr, Pb, Cu, Zn. Metals present in slags are generally associated with phases which have low solubilities in water (silicates, oxides and glass; Piatak *et al.* 2004) but many recent studies (Manz, Castro 1997; Lottermoser 2002; Parsons *et al.* 2001; Piatak *et al.* 2004) show that trace elements leached from slags may have negative effects on the environment (soil and water pollution).

The nickel ores in Szklary (Lower Silesia, SW Poland) are spatially and genetically related with Tertiary weathering crust derived from ultrabasic rocks (serpentinites). The origin of weathering crust in Szklary has been a subject of numerous studies since eighteenth century (Dubinska *et al.* 2000 and references therein).

The nickel mining and smelter activity in Szklary was stopped in 1982 but dumps consisting of metallurgical waste are still present in this area and represent sources of Ni and Cr contamination of the surroundings.

The aim of this paper is to present mineralogical and chemical properties of slags occurring on the highest dump situated in Szklary. The dump is approximately 200 meters long, 150 meters wide and 12 meters high. It consists of mining and metallurgical waste deposited for over 100 years during reworking of nickel ores in Szklary.

SAMPLES AND METHODS

Several representative slag samples were collected from the top of the dump for bulk chemical analyses, thin sections and X – ray diffraction (XRD) analyses. Bulk chemical analyses were performed on crushed slag samples at the Institute of Geological Sciences,

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University of Wrocław. Total concentrations of major and trace elements were determined by combination of titration and atomic absorption spectroscopy. Thin sections of slags were studied by optical microscopy and SEM – EDS (PHILIPS XL 30, accelerating voltage 20 kV) at the University of Limoges. Microprobe analyses were made using CAMECA SX 50 microprobe at the University of Paris Jussieu. The microprobe was operated at an accelerating voltage of 15 kV, a beam current of 4 nA and counting time 10 s for all the elements. Two sets of standards were used: (1) for metals and sulfides and (2) for silicate and oxide phases. XRD analyses were performed at the University of Limoges using a SIEMENS 5000 diffractometer with CuK $\alpha$  radiation from 2° to 65°, by steps of 0,02° and with step time of 15 s.

## RESULTS

Collected slag samples are usually isometric, of size ranging from few to dozens of centimetres. The margins of slags are vesicular (vesicles from microscopic up to tens of millimetres) whereas the cores are massive. Dominant type of slags appears glassy, macroscopically similar to obsidian. It has colour ranging from black to dark green. Second major type of slag displays spinifex texture and is dark grey to black in colour. Several intermediate varieties of slag also occur. Rounded, small (up to few millimetres) metallic drops are macroscopically visible in all slag types.

The 5 of the sampled slags are composed of glass, silicate, oxide and sulfide and metallic phases. The bulk chemical compositions of slags are plotted together with microprobe analyses of glassy slag background on the two ternary diagrams (FeO-CaO-SiO<sub>2</sub> and SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub>; Fig. 1). These diagrams have been chosen as they include the four most abundant oxide components present in the slags. The slags are mostly composed of SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub> and FeO; minor amounts of MgO, Na<sub>2</sub>O and K<sub>2</sub>O sometimes also occur. The chemical composition of the glassy matrix is very similar to bulk chemical composition of slags. Some of metal trace elements (Ni, Cr, Cu, Zn) occur in significant amounts in the slag (up to: 0.56 wt.% of Ni; 1.34 wt.% of Cr; 0.22 wt.% of Cu; 0.25 wt.% of Zn).

The matrix in all slags consists of glass which is composed of SiO<sub>2</sub>, FeO, CaO, Al<sub>2</sub>O<sub>3</sub> as major components (Fig. 1). Silicate phases include fayalite, larnite which occur as long crystals and form spinifex texture, single crystals of plagioclase (present in one, predominantly glassy sample). Oxide minerals are represented by chromium-rich spinels (Fig. 2). Sulfide and metallic phases are volumetrically minor components of the slag, but they are environmentally significant because of their potentially more reactive state (Piatak *et al.* 2004, Parsons *et al.* 2001) and metal content. The most abundant and widely dispersed sulfides in the investigated samples are: pentlandite (Fe,Ni)<sub>9</sub>S<sub>8</sub>, godlevskite (Ni<sub>8</sub>FeS<sub>8</sub>) and digenite (Cu<sub>9</sub>S<sub>5</sub>). Metallic phases occur as small inclusions (< 10  $\mu$ m) in sulfides and they are predominantly composed of mixture of Ni (up to 60 wt.%) and Fe (up to 35 wt.%). Mixtures of Cu (up to 83 wt.%), Sn (up to 11 wt.%) and Cu, Fe, Ni are also present in the studied slags.

## CONCLUSIONS

Two main types of slag occur on the dump in Szklary (1) entirely glassy and (2) glassy with a spinifex texture. The chemical composition of all slag types is similar. Various metallic trace elements are present within slags occurring on the dump in Szklary in relatively high concentrations (up to: 0.56 wt.% of Ni; 1.34 wt.% of Cr; 0.22 wt.% of Cu; 0.25 wt.% of Zn). The chemical composition of glass, being the major component of

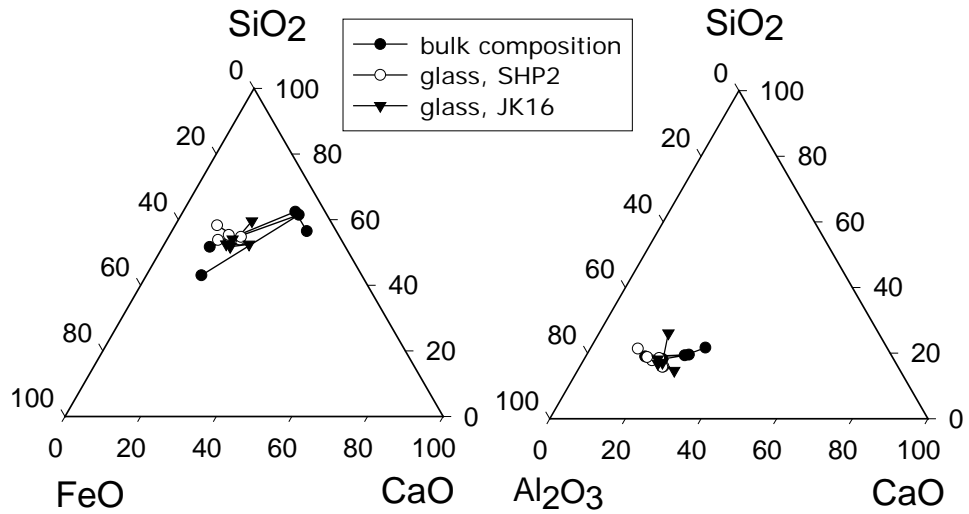


Fig. 1. Bulk chemical composition of slags and composition of glassy background (EMPA) plotted on FeO-CaO-SiO<sub>2</sub> and SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> ternary diagrams (Eusden *et al.* 1999).

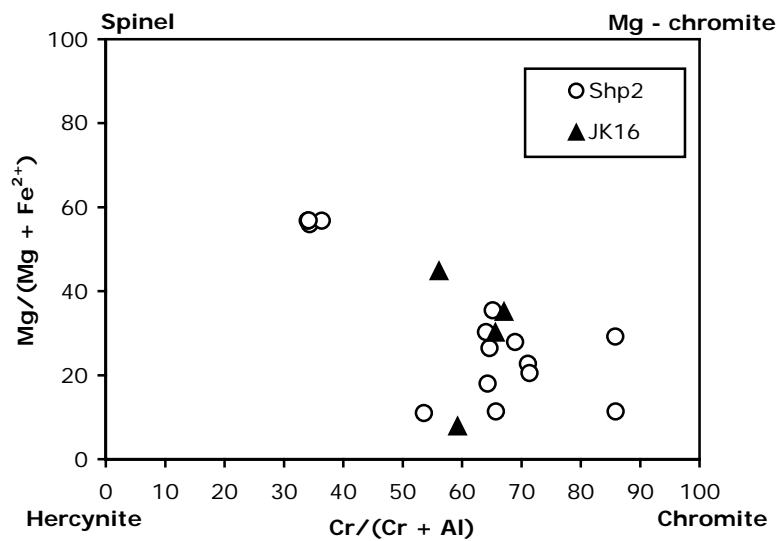


Fig. 2. Composition of spinels from two slag samples within the hercynite-chromite-spinel-magnesiocromite quadrilateral (EMP analyses).

studied material, is monotonous. Silicates and oxides are minor components, except spinels they do not contain significant amount of potentially toxic elements (up to 0.13 wt.% Ni and 0.15 wt.% Cr). The most toxic metals, such as Ni, Cu, Sn are associated with sulfide minerals or occur as metallic phases.

The glass, silicates and oxides are known to be rather resistant to weathering (Ettler *et al.* 2001, Parsons *et al.* 2001), whereas sulfides and metallic phases are highly reactive (Piatak *et al.* 2004, Parsons *et al.* 2001). The further environmental study will concern the fate of the sulfides and metallic phases during the slags weathering.

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