

Transformation of slag from historical smelting slag dumps in the Tatra National Park (S Poland)

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Ore prospection, mining and smelting activity in the area of the Tatra National Park started in XV century and was continued until the end of XIX century. Production of Cu, Pb and Ag started relatively early. In XVIII and XIX century Fe metallurgy was dominating. Chemical and mineralogical composition of slag samples study was undertaken to recognize weathering processes and possible release of harmful elements to environment.

The slag from Cu, Pb, Ag smelting occurs as vesicular, blueish or greenish fragments. Wollastonite is dominant crystalline phase. In glassy fragments, often with perlitic cracks, rounded fragments of quartz occur. Wollastonite crystals dispersed randomly in glassy material are acicular in shape. Wollastonite in dense aggregates occurs as relatively big platy crystals. Voids in slag are lined or filled with calcite. Outer surface of damp is covered with calcite crust with dispersed wollastonite crystals. SiO₂ and CaO dominate in chemical composition of slag (54 to 66 wt.% and 16 to 24 wt.%). K₂O content is high (ca. 7 wt.%). LOI varies from 2 to 9 wt.%. Content of Cu, Pb, Zn contents are very low (3.3-9.3 ppm; 0.3-2.1 ppm; 3-14 respectively).

The slag from Fe smelting is black, dark or pale green, often vesicular. Slag can be completely amorphous or amorphous with small amount of crystalline matter. Crystalline slag is composed of pyroxene (mainly diopside) and leucite in various proportions. Iron or iron dominating alloys droplets are relatively common. Sulphides are scarce. SiO₂ and CaO dominate in these slags (47.9-49.3 wt.% and 14.8-19.6 wt.%) but content of MgO and Al₂O₃ is also significant (9.5-11.2 wt.% and 11.3-14 wt.%). LOI values are below 1.2 wt.% because of scarcity of secondary minerals. Fe₂O₃ content is between 0.8 and 2.2 wt.%.

Weathering of slag and formation of secondary minerals occur only on old damp covered by soil and vegetation. However, low content of harmful elements in slag suggests low probability of environmental hazard. The younger slags related to Fe production are devoid of weathering product.

Methylated naphthalenes in sediments and sedimentary systems: Revised thermodynamic properties based on a reconciliation of geochemical and calorimetric data

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Ten years ago, Richard and Helgeson [1] estimated the thermodynamic properties of crystalline and liquid methyl-, dimethyl-, and trimethylnaphthalenes from group additivity algorithms. It was later suggested to the second author of this communication that the melting temperatures at 1 bar of most of the methylated naphthalene isomers could not be accurately predicted from these properties (M. Zolotov, 2000, pers. comm.). In addition, the group additivity estimates could not account for the isomerization ratios which are observed in mature crude oils [2,3]. The latter ratios have been used together with ideal gas thermodynamic properties recommended by Alberty and Bloomstein [4], and the melting and boiling temperatures of the various isomers in the establishment of the present set of revised thermodynamic properties of the methylated naphthalenes.

The new stability order predicted for the crystals at 25°C from the revised Gibbs energies of formation is consistent with that obtained from molecular mechanics calculations [5], as is the order for the liquids at 200°C, but not at 25°C due to differences in melting and boiling temperatures as well as differences in enthalpies of melting and vaporization. If the revised apparent Gibbs energies for the liquids at ~200°C are consistent with the distribution of naphthalenes in mature crude oils, compositional data reported for low to intermediate maturity petroleum indicate that the establishment of mutual equilibrium among naphthalene isomers is sluggish. The latter conclusion further reinforces the suggestion made by Helgeson et al. [6] that alkylated naphthalenes and other polynuclear aromatic hydrocarbons are not in metastable equilibrium with the aliphatic, naphthenic, and monoaromatic fractions of crude oils.

[1] Richard and Helgeson (1998) *Geochim. Cosmochim. Acta* **62**, 3591-3636. [2] Alexander *et al.* (1985) *Geochim. Cosmochim. Acta* **49**, 385-395. [3] Radke *et al.* (1990) *Org. Geochem.* **15**, 17-34. [4] Alberty and Bloomstein (1985) *J. Phys. Chem. Ref. Data* **14**, 821-837. [5] Budzinski *et al.* (1993) *Energy Fuels* **7**, 505-511. [6] Helgeson *et al.* (2009) *Geochim. Cosmochim. Acta* **73**, 594-695.