

## SUMMARY

Multielement analysis of flue gas residues from secondary lead smelting was tested using seven decomposition methods on four different flue gas residues and certified reference materials (CRM) CPB-2 (Pb concentrate, CCRMP). The studied samples contained both silicates and also high contents of phases with Pb, primarily Pb chlorides and sulphates. Solutions prepared by various decomposition methods were analysed using ICP OES (Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, Sn, Sr, Ti, Tl, V, Zn). Greater yields were found for most of the elements by combined decomposition (with fusion) and decomposition by sintering. Nonetheless, both methods exhibited major losses of volatile elements (As, Bi, Sb, Tl). Thus, one of these methods must always be combined with a method of decomposition in a closed system. The work also demonstrates that, for investigation of untraditional waste geological materials (e.g. flue residues from high-temperature industrial processes), it will be necessary in the future to produce new certified reference materials with anomalous chemical and mineralogical compositions, which are not currently available on the market.

Laboratory extraction tests were performed on two different types of flue residues – kinetic (30 days) with ratio L/S = 10 and an extraction test with various L/S ratios (0.5; 1; 5; 10; 50; 100; 500 and 1000) (48 h). The solutions from all the L/S tests exhibited rapid dissolution of the primary phases. The extract with high L/S ratio, corresponding to long-term extractability, indicated that the primary phases (caracolite ( $\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}$ ) and  $\text{KPb}_2\text{Cl}_5$ ) were dissolved and formed stable anglesite ( $\text{PbSO}_4$ ). During the extraction, primary amorphous  $\text{PbSO}_3$  partly crystallized and formed secondary anglesite. This is in accordance with the finding that only anglesite was found in historically exposed soils around metallurgical plants. In order to dispose of flue residues by recycling in reducing shaft furnaces, soluble salts can be removed from the flue residues by washing with L/S > 50 and the remaining insoluble residue (mainly anglesite) could be returned to the production process batch together with the primary recycled Pb materials. Various mineralogical compositions determined by the type of cooling liquid used (pure water vs. alkaline waste water) affect the reactivity of the flue residues. The flue residue that was separated following cooling of the combustion products with pure water is more reactive than flue residue separated following cooling with alkaline waste water. Extraction experiments on flue residue from Pb metallurgy *in situ* in various soil systems demonstrated that bags made of polyamide mesh can be used for study of the exposure of flue residues in the soil profile. During one year, 62 – 66% of the flue residue was dissolved, especially caracolite ( $\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}$ ) and  $\text{KPb}_2\text{Cl}_5$ , with formation of a secondary phase – anglesite ( $\text{PbSO}_4$ ),  $\text{PbSO}_3$  and traces of carbonates. There are only small differences in the results between sites located in forest areas and sites in open areas. The main factor affecting extraction of Pb and its subsequent distribution into the soil profile is the pH, in contrast to Cd and Zn, which are practically independent of the pH. A substantial fraction of the extracted metals (mainly Cd and Zn) was found in the labile soil fractions. The data were in agreement with experiments performed in the laboratory. To determine the release kinetics of Pd and Pt from the automobile catalysts were performed batch leaching experiments. It can be stated that a suitable laboratory test can predict the behaviour of flue residues and automobile catalysts in the natural environment.

The experiments performed in the submitted work included the determination of low concentrations of sulphur in geological materials and validation of two methods – inductively coupled plasma optical emission spectrometry (ICP OES) and combustion methods with infrared detection using fifteen CRM. It was demonstrated in experiments that the ICP OES method is suitable for determination of total sulphur in geological materials with various sulphur contents (including low concentration about 10 mg/kg). An analytical protocol was proposed for elimination of the effect of the matrix (especially for high Ca and Al contents of the order tens of wt. %). It was confirmed that a combustion method with infrared detection is a suitable alternative for determination of contents above 50 mg/kg S in geological materials.