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Improving heavy metal separation from contaminated shooting range soils in Switzerland

In order to optimize the heavy metal separation from shooting range soils, the binding forms of the metals and the assemblages and associations with minerals were investigated and described using optical methods (transmitted and reflected light microscopy), scanning electron microscopy (SEM), powder X-ray diffraction (XRD) and chemical analysis (ICP-OES and XRF).

The chemical and mineralogical investigations performed on different grainsize fractions of the non-washed material showed that both the highest concentrations as well as the highest loads of Pb and Sb are at the finest fraction (<63 μ m). The same investigations on fractions of the washed material showed that the soil becomes depleted in the finer grainsize fraction, which is successfully removed during the washing process. The highest contributor for the Pb and Sb contamination in the washed soil (problematic material) is the medium sand fraction (125 - 250 μ m).

With the use of heavy liquids, a good separation of the denser contaminated particles could be achieved in the laboratory. The investigations using optical microscopy and SEM on these heavier concentrates from different samples showed that in addition to metallic Pb particles, the presence of lead carbonate (cerussite) was identified. This was also demonstrated by an optimized XRD method, with which metallic and lead carbonate could be distinguished and detected semiquantitatively. It was also verified with SEM analysis that larger amounts of Pb are bound to carbonates and iron oxides through sorption or co-precipitation. No crystalline phase with Sb as a major constituent was identified using XRD analysis, but the metal was present in Fe oxide precipitates and carbonate surfaces identified with SEM.

Although the density separation worked well in the laboratory, the use of this method on an industrial scale may not be feasible.



BSE image of older projectiles (GP 11)

During a sampling campaign at the washing plant, the contribution to the overall metal loads of the individual washing steps was examined and special attention was paid to the washed sand fraction of $63 \ \mu\text{m} - 4 \ \text{mm}$. This fraction and the untreated starting sample (0 - 4 mm) were assayed by the methods described above. In addition, sequential chemical extraction on the samples of interest was carried out. With this method, it was confirmed that most of the lead is associated to carbonates, followed by associations with Fe oxides, but the contribution of adsorbed and exchangeable Pb is minor. About 20-25% of the total lead could not be mobilized with any extraction step. Antimony shows the same binding preferences but more than 50% was not mobilized during the procedure.

An extraction test under acidic conditions with HCl showed that by reducing the pH value to 2, it was possible to mobilize most of the lead bound to carbonates. However, most of antimony is not mobile under acidic conditions where it is supposed to be sorbed onto iron oxides.

The desired reduction of Pb concentration below 250 ppm in these samples is unrealistic, but 500 ppm could be achieved by the removal of lead bound to carbonates. Due to the high carbonate content in the range of 10%, the use of a large amount of acid on an industrial scale is unlikely to be financially sustainable unless the newly formed Pb carbonates dissolve (comparatively) faster than calcite. In addition, the depletion of antimony under acidic conditions is inadequate.

It is concluded that the optimization is possible, but a chemical treatment is hardly financially sustainable. A remaining option to work on could be a more efficient density separation of the soil particles in order to achieve a higher separation rate of these contaminants.



EDS analysis along a line in older projectile: composition of 94 % Pb, 4 % Sb and 1 % C

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