Geophysical Research Abstracts
Vol. 14, EGU2012-7898, 2012
EGU General Assembly 2012

Formation of secondary minerals in a lysimeter approach - A mineral-microbe interaction

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Heavy metal contamination of large areas due to uranium mining operations poses a serious long-term environmental problem. In the Ronneburg district (eastern Thuringia, Germany), leaching of low grade uranium bearing ores (uranium content < 300 g/t) occurred from 1972 to 1990 using acid mine drainage (AMD; pH 2.7-2.8) and diluted sulphuric acid (10 g/l). Secondary mineral phases like birnessite, todorokite and goethite occur within a natural attenuation process associated with enrichment of heavy metals, especially Cd, Ni, Co, Cu and Zn due to a residual contamination even after remediation efforts.

To reveal the processes of secondary mineral precipitation in the field a laboratory lysimeter approach was set up under in situ-like conditions. Homogenized soil from the field site and pure quartz sand were used as substrates. In general, in situ measurements of redox potentials in the substrates showed highly oxidizing conditions (200-750 mV). Water was supplied to the lysimeter from below via a mariotte′s bottle containing contaminated groundwater from the field. Evaporation processes were allowed, providing a continuous flow of water. This led to precipitation of epsomite and probably aplowite on the top layer of substrate, similar to what is observed in field investigations. After 4 weeks, the first iron and manganese bearing secondary minerals became visible.

Soil water samples were used to monitor the behaviour of metals within the lysimeter. Saturation indices (SI) for different secondary minerals were calculated with PHREEQC. The SI of goethite showed oversaturation with respect to the soil solution. SEM-EDX analyses and IR spectroscopy confirmed the formation of goethite. Geochemical data revealed that goethite formation was mainly dominated by Eh/pH processes and that heavy metals, e.g. Zn and U, could be enriched in this phase.

Although Eh/pH data does not support formation of manganese minerals, Mn(II)-oxidizing bacteria (MOB) could be isolated from field soil samples, supporting the fact that microorganisms may influence this natural attenuation process. Laser ablation ICP-MS data reveal accumulation of manganese in MOB biomass on Mn(II)-containing agar plates. Furthermore, it was possible to show the importance of iron on this process, as some MOB isolates were able to oxidize manganese independently from the iron content, whereas some are not. The latter isolates are only able to oxidize manganese if iron is present in the media.

In the lysimeter, SEM-EDX data showed microorganisms in organic rich phases together with the occurrence of manganese, oxygen, and nickel, indicating manganese oxides enriched in nickel. Although this new mineral phases could not yet be identified microprobe EDX results from polished thin sections showed needle-like mineral structures that are similar to the birnessite and todorokite samples observed from field samples.

Hence, the lysimeter experiment revealed that the formation of iron and manganese minerals that are involved in heavy metal natural attenuation is result of both abiotic and biotic processes.