BIO-MINERALIZED MAGNETITE IN BOTTOM SLUDGE OF A CLOGGED GEOTHERMAL WELL

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The investigated sample was taken from the bottom sludge of a clogged geothermal reinjection well as part of DESTRESS project. Characterization of the solid part of the sample was done by XRF, XRPD and optical + SEM-EDS methods. Black colour of the sludge and sampling conditions point to a reducing environment.

Mineral phases were identified by XRPD pattern was interpreted using Rietveld refinement method. The sample are primarily composed of main rock forming phases of clastic sediments, i.e. quartz, clay minerals (illite, illite-smectite, subordinately kaolinite and chlorite), feldspars, carbonates. The i/sm 11A is the disordered mix-layer of illite-smectite clay mineral phase with low swelling capacity. Sulphur content is very low (0.27%) and sulphide phases were not detected by XRPD. Remarkable feature is the high amount (10.7%) of magnetite which is in line with the significant Fe2O3 content measured by XRF (27.9%) and very low sulphur content.

Crystallite size of the magnetite is very fine, 21 ± 5 nm. The nano-particle size (d: 21 nm) of the magnetite indicates the activity of $Fe^{(III)}$-reducing bacteria in the sludge. The share of mineral phases with volatile components is low, which shows that the predominant part of the LOI (7.5%) is from the decomposition of organic matter. The main chemical components based on WDX-XRF are SiO_2 (43.8%), Al_2O_3 (11.16%) and Fe_2O_3 (27.9%).

Two grams of the sample was washed in acetone to release the fines and obtain the coarser-grained (> 125 μm) fraction. The dried coarser-grained fraction was separated to magnetic and non-magnetic subfractions. Non-magnetic subfraction was composed of sub-angular to rounded quartz grains and well-rounded, light-brown grains of clay-rich concretions with maximum grain size of 1 mm. The magnetic grains comprise the other ca. 40% of the sample and reach maximum 1 mm size. Contrary to the clay concretions, the magnetic grains are always angular and usually platy. Surface is dull and usually black, some grains have reddish or reddish-brown discolouration on the surface.

SEM-EDS observation of selected magnetic grains showed that the surface is covered by globular, botryoidal aggregates. Using high magnification, desiccation cracks are seen on the surface along the globule boundaries. Based on these observations, the magnetic grains have an iron oxide rim on the surface of the grains. The iron oxide rim has a few micrometres thickness only and forms globular, botryoidal aggregates, which have been desiccated under vacuum. The cores of the magnetic grains are composed of ankerite or SiO_2-rich silicates/concretions. The globular, botryoidal form of the iron oxide rim and its desiccation indicates the intensive bacterial activity which produces the nanocrystalline magnetite. One grain composed of globular aggregates of ankerite crystals was also selected to the SEM-EDS analysis. This aggregate is composed of 3-5 micrometres siderite rhombohedrons. This siderite has a 10-11% Ca replacing $Fe^{(II)}$. Rhombohedral crystals are perfect, or slightly resorbed. This aggregate is probably the result of in situ bacterial activity.

Activity of $Fe^{(III)}$-reducing bacteria, such as Geobacter sulfurreducens or Shewanella oneidensis combines the oxidation of organic compounds or hydrogen with reduction of minerals with short-range order (e.g. ferrihydrite), leading to release of Fe^{2+}_{aq} and precipitation of siderite and magnetite (Byrne et al. 2011). Precipitation of magnetite and siderite is expected at reducing, alkaline environments which might take place in the bottom of the reinjection well under presence of bacterial activity.

References

BYRNE, J. M., TELLING, N. D., COKER V. S., PATTRICK, R. A. D., VAN DER LAAN, G., ARENHOLZ, E., TUNA F., LLOYD J. R. (2011): Nanotechnology 22, 455709

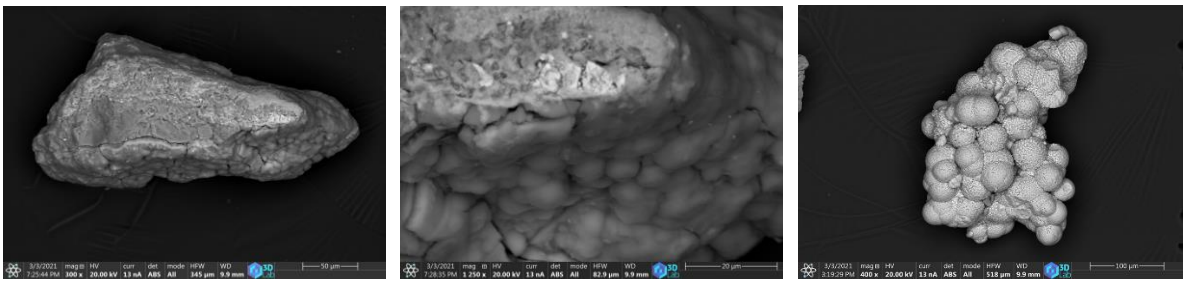

Fig 1.: SEM-BSE images of the bio-mineralized magnetite