

Temperature-programmed desorption of oxalate from the goethite surface

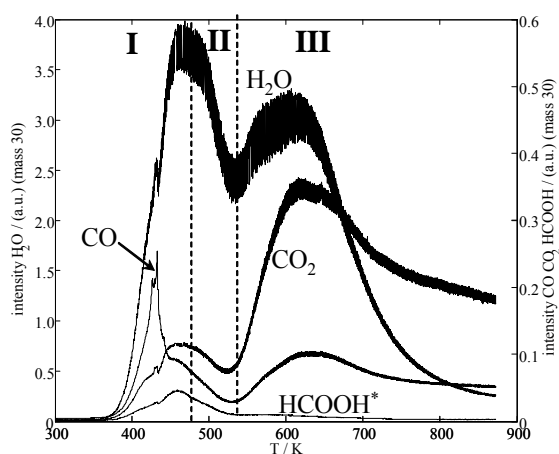
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The TPD-FTIR technique was used to investigate the relative thermal stabilities and decomposition reactions of different oxalate complexes adsorbed on the dry goethite surface. The measurements showed that important differences in coordination have a considerable impact on the thermal stability of the surface complexes.

Three important stages of desorption were identified from both TPD (Figure 1) and FTIR data in the 300-900 K range. Stage I (300-440 K) corresponds to the desorption of weakly-bound oxalate molecules with decomposition pathways characteristic of oxalic acid. Stage II (440-520 K) corresponds to the dehydration of key surface OH₂ groups responsible in stabilizing hydrogen-bonded surface complexes. These species can either decompose via typical oxalic acid decomposition pathways or convert to metal-bonded surface complexes. Finally, Stage III (520-660 K) corresponds to the thermal decomposition of all metal-bonded oxalate complexes, proceeding through a two-electron reduction pathway that converts oxalate to CO₂. Experiments in the absence of oxalate were used to assess the contributions from dehydration, dehydroxylation and decarbonation reactions from the goethite bulk.

Figure 1: TPD trace of goethite in the presence of 1.7 μmol/m² adsorbed oxalate. The dry powder was prepared from an aqueous suspension of goethite equilibrated in the presence of sodium oxalate at pH 6.5 and dried at room temperature.



Trace Elements and radio nuclides in Zegrze reservoir sediments (Poland)

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The Zegrze Reservoir (Poland) is located just north of Warsaw. It is formed by a dam constructed on the lower course of the Narew and the Bug rivers, near their flow in the Vistula river. Its surface area is about 33 km².

Material and methods

64 drilling cores sampled were collected from the reservoir. The cores were divided into 178 samples. Analyses of concentrations of Ag, As, Ba, Cd, Cr, Co, Cu, Hg, Pb, Se, Sr, Sb, Sn, Tl, V, and Zn and as well U (eU), Th (eTh), ⁴⁰K and ¹³⁷Cs were performed for the sediment grain fraction <1mm.

Results

It results that the concentration of the most trace elements in the sediments accumulated at the bottom of the reservoir are diversified. The silt sediments characterized higher contents of trace elements than the geochemical background while sand sediments show low concentrations. In sediments maximum concentration (mg/kg) of antimony was 4.3, arsenic – 17, barium – 355, cadmium – 11.9, chromium – 95, cobalt – 8, copper – 74, mercury – 0.72, nickel – 36, lead – 48, selenium – 1.2, silver – 3.4, strontium – 342, thallium – 0.4, tin 4.8, vanadium – 45 and zinc – 538. In Zegrze reservoir radio nuclides occur in concentrations similar to characteristic values for that type of sediments.

Silts with high contents of heavy metals were accumulated in reservoir near Nieporęt, nearby mouth of Żerań channel (chromium, zinc, cadmium, copper, nickel, lead, mercury), which is connected with Vistula river in industrial part of Warsaw. And silts with distinctly high contents trace metals occur near some touristic sites localized on reservoir rim.

Conclusion

The estimated volume of silts accumulated in reservoir was 7860000 m³ and their tonnage – 13.36 mln t. It was calculated that these silt sediments contain about 2.6 t antimony, 13.4 t arsenic, 227 t chromium, 9.4 t tin, 561 t zinc, 3.2 t cadmium, 94 t copper, 107 t nickel, 134 t lead and 0.7 t mercury.