Why trace elements are often immobilized in ashes and slags. On the role of solid solution in iron (hydr)oxides.

Rolf Sjöblom, rolf.sjoblom@tekedo.se, Luleå University of Technology.
Bengt Noläng, bengt.nolang@bensystems.se, BenSystems.

Objective, scope and main conclusions

The objective of the work was to determine the role of solid solution in iron (hydr)oxides for the immobilization of trace elements in ashes and slags.

The scope of the work included the following:
- To study the availability of elements to the water phase for different ageing times
- To search and analyse literature
- To make thermodynamic calculations which include the features of solid solubility and aqueous solution

Iron (hydr)oxides are of paramount importance for efficient long-term immobilization of many transition elements and other elements in ashes and slags.

Results and conclusions

The major elements in ashes and slags form phases in which they are major elements. The minor elements do not usually form such phases. Instead, they become incorporated - atom by atom - in the crystal lattices of the phases formed by the major elements. This makes the minor elements as inaccessible as the major elements into which they have been incorporated.

Iron-rich phases are well known scavengers for many transition elements and other elements. Iron- and manganese (hydr)oxides are largely responsible for continually cleaning up the sea. The reason for this is that the trace elements go into solid solution. (This has been known for decades among inorganic chemists, geochemists and geologists).

The low content of transition and heavy elements in the sea cannot be explained by thermodynamic calculations in which it is assumed that the trace elements form phases in which they are major elements. Nonetheless, such assumptions are often used in the areas of waste and environmental impact assessment. In fact, commercial programmes are not available that simultaneously include the features of solid solution and aqueous solution.

Such calculations have been performed in the present work and they clearly show a strong effect for Zn. Scavenging effects have also been observed experimentally. The above conclusions are supported also by the literature search and analysis.

Solid solution in iron-rich phases presupposes a surplus of iron relative to the trace element in question. This condition is usually met in ashes and slags. Cr-III is stabilized even at high pH conditions.

Leach tests

Leach tests were carried out on four ashes moistened at two different levels, and aged at three different times without access to air. The leach rates of most elements decreased very substantially, and e. g. for zinc, the leaching decreased with up to three orders of magnitude compared to fresh fly ash. Leaching of zinc is frequently below what may be expected from its oxide. The observations thus support a conclusion that the trace elements are immobilized through solid solution.

Literature survey

In general, the conditions for substitution in phases rich in iron and manganese are as follows:

1 The charge of the replacing atom should not differ by more than one unit.
2 The effective radius of the replacing atom should not differ by more than ± 15 %.

Effective ionic radii for various elements are tabulated in the literature. Such values in combination with the requirements 1 and 2 above clearly indicate that many elements have a strong tendency to form solid solutions with iron.

These effects take place at high as well as at low temperature. They are observed in soil, and it was found that ash and slag behave in the same way as soil. It has been reported in the literature that iron-rich phases in ash are enriched with other elements of similar ionic radii.

Thermodynamic calculations

Thermodynamic calculations were conducted for the system $(Zn_xFe_{1-x})Fe_2O_4$, and for various values for x. The end points x=0 and x=1 correspond to magnetite (Fe_3O_4) and franklinite ($ZnFe_2O_4$), respectively. Magnetite and franklinite both occur in nature. Magnetite is a common mineral while franklinite is rare.

The results show that the availability for zinc in the pore water is drastically influenced by the formation of a solid solution. Moreover, the effect is larger, the lower the total concentration of zinc. This concentration behaviour is quite different from that of when a trace element is assumed to be a major element in a phase of low abundance.

References

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