

# WHY ARE TRACE ELEMENTS OFTEN EFFICIENTLY IMMOBILISED IN ASHES AND SLAGS?

## On the role of solid solution in iron (hydr)oxides.

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### RESEARCH QUESTION:

- Why are trace elements often observed to be efficiently immobilized in ashes and slags?
- Especially after ageing, and
- especially in relation to the corresponding simple oxides.
- And why is the actual availability often lower than that calculated using commercially available computer codes?

### SCOPE

- To test availability (leach testing)
- To carry out a literature survey
- To simulate solid solution in thermodynamic calculations

### MAIN CONCLUSION

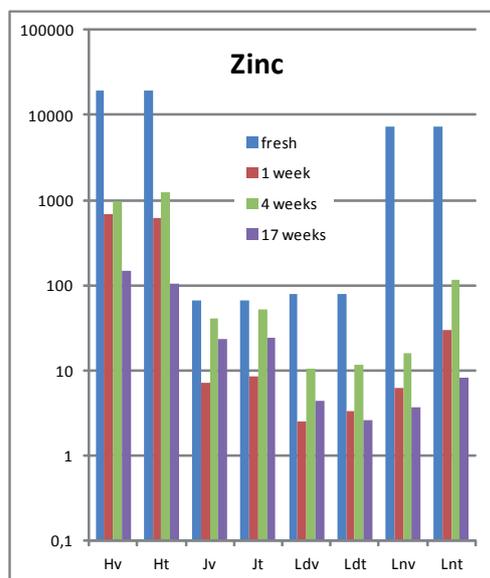
Iron (hydr)oxides are of paramount importance for efficient long-term immobilization of many transition elements and other elements in ashes and slags.

### RESULTS AND CONCLUSIONS

- The major elements form phases in which they are major elements.
- The minor elements do not usually form phases in which they are the major elements.
- 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 (see below) and they clearly show a strong effect for Zn.
- Scavenging effects have also been observed experimentally (see below).
- The above conclusions are supported by the literature search and analysis (see below).
- 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



Leaching of zinc (in mg/kg dry weight) from four different fly ashes (H, J, Ld and Ln) after ageing during different times and at two different moisture contents ( $v > t$ ). No access to air. A slightly modified SS-EN 12457-3 test was used (L/S 10). The levels of zinc in these ashes range from 1.2 to 7.3 %.

Ashes and slags, and especially fly ashes, react strongly with water and also with carbon dioxide and oxygen in the air. As is obvious from the above figure, such ageing may be associated with very substantial reductions in the leach rates. They frequently fall below the solubilities of the respective simple oxides, thus supporting the conclusion that trace elements are immobilized by solid solution in iron-rich phases.

The leach tests were also carried out in order to determine how samples might be prepared before testing according to the acceptance criteria for landfilling. Here, the test method specified (SS-EN 12457-3) is not applicable to materials that react with the leachant. It was recommended as a result of these tests that samples be aged before testing with a pertinent amount of water for at least one week, and preferably for more than one month.

### LITERATURE SURVEY

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

- The charge of the replacing atom should not differ by more than one unit.
- The effective radius of the replacing atom should not differ by more than  $\pm 15\%$ .

Examples of radii can be found in the table below. It is obvious from the table that many elements substitute excellently with iron.

Examples of solid solutions and solid solubility at high temperature are shown in the figure to the right. The examples in the figure refers to high temperatures, but it was concluded that the situations are similar also at low temperature.

It was also found that stabilisation of heavy elements by solid solubility takes place in the same way in ashes and slags as it does in soil.

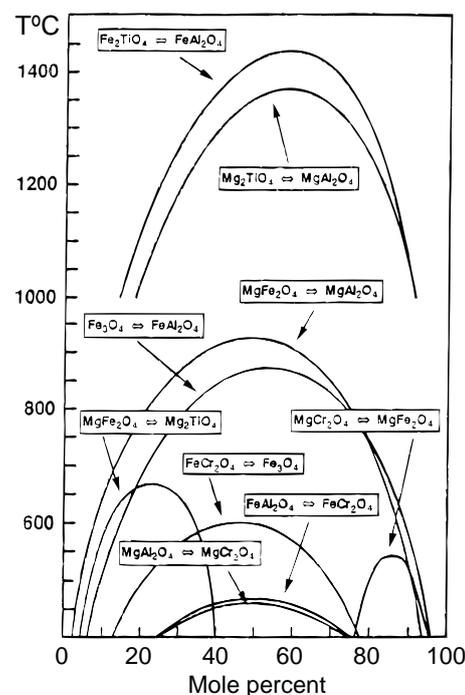
It has been reported that phases in the microstructure of an ash that were high in iron also had considerably elevated concentrations of a number of trace elements.

Ionic radii for trace elements and some others, Angstrom.

Ox no	I		II		III		IV
	low	high	low	high	low	high	
Na	1,02						
K	1,38						
Mg		0,72					
Ca		1,00					
Al					0,53		
Ti		0,86*			0,67*		0,61
V		0,79			0,64		0,63
Cr		0,73	0,82		0,62		
Mn		0,67	0,82	0,58	0,65		
Fe		0,61	0,77	0,55	0,65		
Co		0,65	0,74	0,53	0,61		
Ni		0,70		0,56	0,60		
Cu		0,73					
Zn		0,75					
Mo							0,70
Cd		0,95					
As					0,58		
Sb					0,76		
Pb		1,18					
Cs	1,70						
Ba		1,36					

\* unusual oxidation number

### THERMODYNAMIC CALCULATIONS



Comparison of calculated miscibility gaps for some spinels. Figure modified after Ghiroso M S and Sack R O. Thermochemistry of the oxide minerals. Ch. 6 in Reviews in mineralogy, Vol. 25. Oxide minerals: petrologic and magnetic significance. Min. Society of America, 1991.

Thermodynamic calculations were conducted for the system  $(Zn_{1-x}Fe_x)_2Fe_2O_7$  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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- Sjöblom, R., *Pertinent methodology for basic characterization of ash for acceptance for landfilling*. (Swedish title: *Lämplig metodik för grundläggande karakterisering av aska för acceptans på deponi*). Avfall Sverige, Report U2011:22, October, 2011.

- Papers available at [www.classification.se](http://www.classification.se).
- Journal article in preparation.