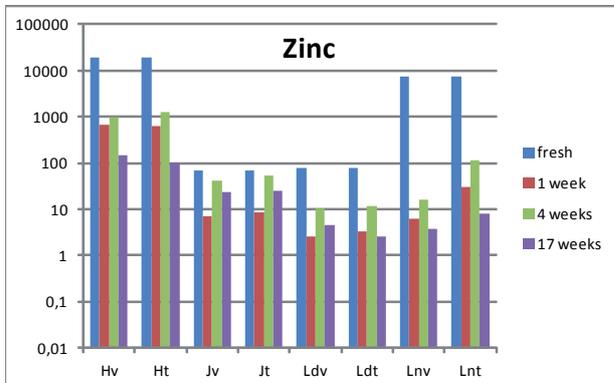


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## Why is zinc so efficiently immobilised in ash?



**Above.** 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 ( $v > t$ ). 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 %.

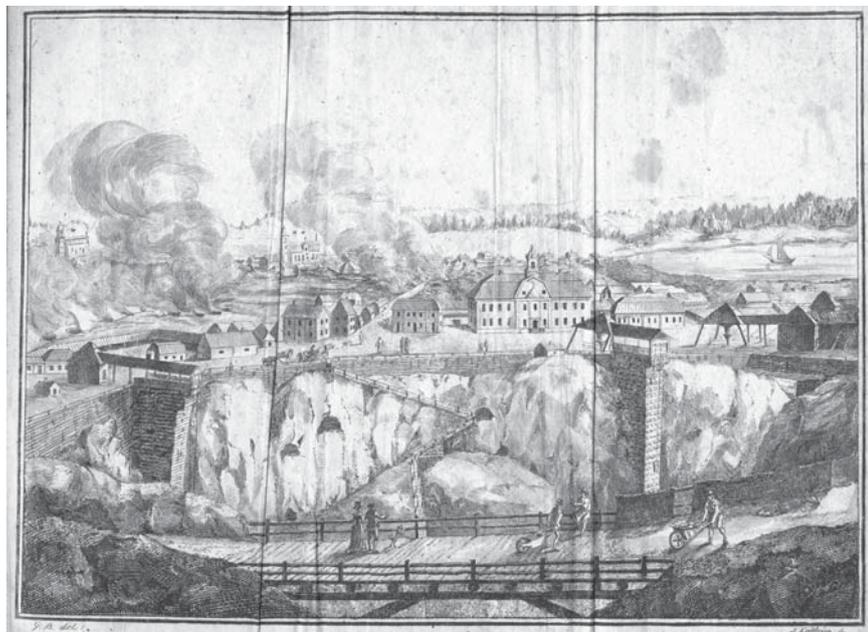
Data and illustration from Avfall Sverige - Swedish Waste Management, Report U2011:22, 2011.

**Right.** The Falun copper mine in Sweden at around the year 1780. The sulphide ore was roasted in a number of furnaces a few hundred yards away from the mine in which process sulphur dioxide was released.

Tailings containing pyrite weathered and formed additional sulphuric acid.

The low pH mobilised transition metals and heavy metals to give enormous releases.

## How can the environment around the Falun copper mine be relatively healthy in spite of > 1000 years of mining and after a total fallout of $\approx 30$ kg of sulphuric acid per square metre?



## Background and hypothesis

Ashes can be used for forest fertilisation and geotechnical construction purposes only if health and the environment are adequately protected. Availability of pollutants (trace elements) to the pore water is a major issue in any such assessments. It can be determined by leach testing and estimated by thermodynamic calculations.

Leach testing for the purpose of assessments of the long-term behaviour should be carried out using properly aged material (cf the figure above) as well as water with a composition representative for the installation in question.

Thermodynamic calculations reflect the status after a long time when chemical equilibrium may have been established. It is frequently assumed in such calculations that the trace elements form phases in which they are major elements.

However, it has been known for decades among inorganic chemists, geochemists and geologists that trace elements in nature typically do not form phases in which they are major elements. Instead, they go into solid solution into phases formed by the major elements. This means that they become dispersed - atom by atom - in the lattices of such phases, usually by replacing major elements in the process. Typically, phases rich in iron as well as manganese form sinks for a large number of elements.

Nonetheless, few commercially available computer codes - if any - offer the feature of solid solubility in combination with aqueous solutions.

## Objectives

The objectives of the present work are as follows:

1. To make a literature search in order to determine if the situation is the same in ashes
2. To make thermodynamic calculations which include the features of solid solubility and aqueous solution
3. To attempt to determine what role, if any, that solid solubility has played for the surprisingly good health of the environment around the Falun copper mine.

## Results from the 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  $\pm 15$  %.

Ionic radii for trace elements and some others, Angstrom.

| Ox no | I    | II   |       | III  |       | IV   |
|-------|------|------|-------|------|-------|------|
| Spin  |      | 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  |      | 0,60  |      |
| Cu    |      |      | 0,73  |      |       |      |
| Zn    |      |      | 0,75  |      |       |      |
| Mo    |      |      |       |      |       | 0,70 |
| Cd    |      |      | 0,95  |      |       |      |
| As    |      |      |       |      | 0,58  |      |
| Sb    |      |      |       |      | 0,76  |      |
| Pb    |      |      | 1,18  |      |       |      |
| Cs    |      |      |       |      |       |      |
| Ba    | 1,70 |      | 1,36  |      |       |      |

\* unusual oxidation number

Examples of radii can be found in the table above. 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 as it does in soil.

One recent reference 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.

## Results from the thermodynamic calculations

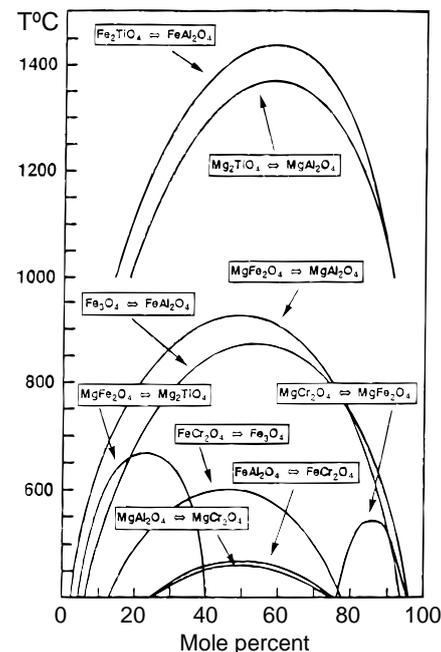
Thermodynamic calculations were conducted for the system  $(Zn_xFe_{1-x})Fe_2O_4$ , and for various values for x. The end points  $x=0$  and  $x=1$  correspond to magnetite ( $Fe_3O_4$ ) and franklinite ( $ZnFe_2O_4$ ), respectively. Magnetite and franklinite both occur in nature. Magnetite is a common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

## Results on mill tailings and acid drainage

Ash can buffer sulphidic mine tailings such that acidic conditions may be avoided. At the ordinary pH values thus achieved, iron in the ash will act as a scavenger for many of the heavy elements. Soil may have a similar but usually a much slower and weaker effect.



Comparison of calculated miscibility gaps for some spinels. Figure modified after Ghiorsio 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.