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Classification of waste as hazardous or non-hazardous – the cases of ash and slag

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TEKEDO

The structure of this presentation

1. Introduction
2. Legal prerequisites
3. Objective and scope
4. One or more substances?
5. Forms of ocurrence of trace elements
6. Selection of reference substances
7. Conclusions

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Why do we need to classify waste as hazardous / non-hazardous under the EU framework directive on waste?

Protection of health and the environment	Conservative classification as hazardous directs the handling of the waste so that it is carried out in a safe manner (precautionary principle)
Conservation of natural resources, e. g. by utilisation of ash for forest fertilisation and geotechnical construction purposes	Cautious but realistic classification facilitates recycling and utilization

Labelling of chemicals versus classification of waste

Labelling of chemicals	Substances selected with regard to hazardous properties ⇔ part of the criteria for formulation
Classification of waste as hazardous or non-hazardous	Waste arrives to recycling plant ”as is” Composition varies

Classification - a significant issue

- 1,5 Mtonnes/year of ash generated in Sweden
  - by district heating facilities and forest industry
  - from combustion of biofuels and waste fuels
  - destination mainly landfilling and geotechnical constructions at landfills
- Slags are mostly by-products, but some waste is also generated
- => R&D for method for classification

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Glossary

Directive	European Union decision that member states are obligated to implement in national legislation
Ordinance	Swedish legislation issued by the Government
Regulation	1. EU legislation that is directly applicable to legal entities 2. Swedish legislation issued by a Competent Authority
Substance	A legal entity that may have little to do with what is referred to as substances and molecules in textbooks on chemistry

Waste and not waste

- Different legal acts apply to waste and not waste (products)
- Clarified in the new EU framework directive of waste
  - When a production residue is a by-product and when it is waste
  - When something that was waste has ceased to be waste

At present, the EU Commission is struggling with defining boundaries for different categories

Products – not waste

- Products that are not articles are
  - Either regarded as substances
  - Or mixtures of substances
- Substances and mixtures of substances have to be labelled
  - At present: substances in the EU ⇔ CLP = Classification, Labelling and Packaging
  - At present: mixtures in the EU ⇔ CLP or DPD = Dangerous Preparations Directive
  - After mid-2015: only CLP

Products, continued

- Purpose of labelling: to inform about potential hazard
- Most substances also have to be registered under REACH
- CLP and REACH are EU regulations
- Internationally, outside EU, labelling is made under GHS = Globally Harmonized System

Symbol of danger, e g	
Indication of danger	Explosive Oxidizing Flamable Toxic / Very toxic Corrosive / Harmful / Irritant Dangerous for the environment
Risk phrase	R¤¤
Safety phrase	S¤¤

Hazard pictogram for hazard class, e g	
Signal word	Danger Warning
Hazard statement	H¤¤¤ EUH¤¤¤
Precautionary statement	P¤¤¤

Waste

- At present classification of waste as hazardous ≈ labelling with symbol of danger under DSD/DPD
- New rules may be decided later this year, and to come in force at mid-2015
- Simplified algebraic expressions are to be expected
- Decisions are to be made between options in proposal document

The properties H4-H8, H10-H11

H4	Irritating	Summation
H5	Harmful	Summation
H6	Toxic	Summation
H7	Carcinogenic	Largest value
H8	Corrosive	Summation
H10	Toxic for reproduction	Largest value
H11	Mutagenic	Largest value

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Objective of the present work

- To determine strategy as to whether ash and slag should be regarded as one or more substances
- To identify and select reference substances for the analysis

- To summarize experiences made
- To present an outlook for the future in view of new legislation that is underway

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One or more substances?

Vitamins

- Are divided into
  - Fat soluble and
  - Water soluble
- It was found that
  - the fat soluble vitamins comprise A, D, E and K, and
  - The water soluble ones comprise B and C
- It was also found that there is further subdivison, e g there are B_1, B_2 … B_{12} vitamins

Ash

- According to Wallerius 1759, ash is a substance with the following symbol

  🝗

- Alternatively, we can regard ash as a blend of some basic ash

  🝗$_0$

  with further constituents or impurities

  🝗$_1$ 🝗$_2$ 🝗$_3$ etc

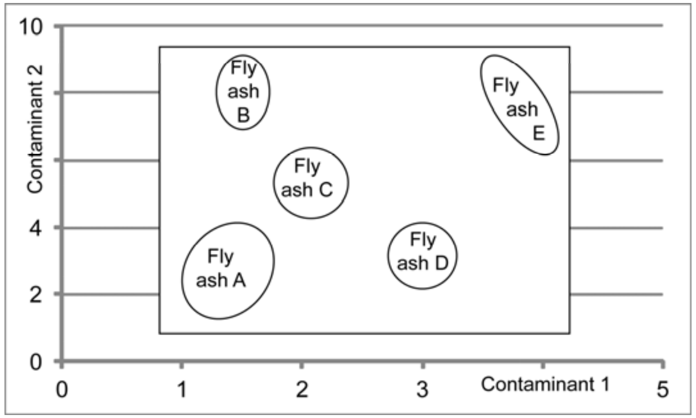
One or more substances, cont

One substance	Large volumes of material having closely the same composition	Representative sample can be tested for several properties
Several substances	Small or moderate volumes having different compositions	Easier to test constituents if such can be identified

Actually, constituents may have been tested already, and the results may be available in open data bases

Does it matter?

Rectangular area illustrates the intervals that have to be considered if the ashes A – E are regarded as one substance



Is this view supported by the Agencies and Authorities?

- Yes, and reference can be made to
  - OECD
  - ECHA, the European Chemicals Agency which oversees the DSD/DPD and the CLP labelling systems in Europe
  - The United Nations, who are responsible for the GHS international labelling system

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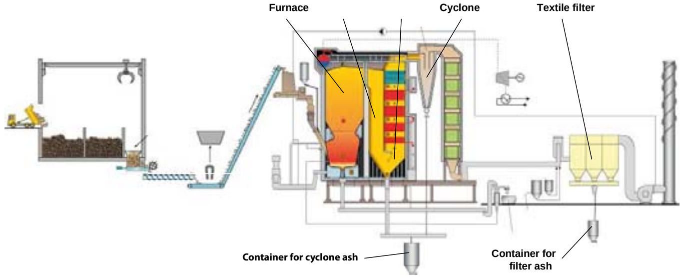
Fly ash and other ashes



Fractional condensation of volatile elements and compounds.
Partial melting of the ash and consequent formation of reactive glass phase

Some ash chemistry

- Assumed that the ash is contacted with water and air => ageing processes from instant to weeks and years
- Some of the Zn and Pb may have formed chlorides initially. They are instantly hydrolysed on contact with water.
- pH initially at around 12,5 indicating portlandite ($Ca(OH)_2$) but after a few years may be < 10 even without carbonation

Solubility (log scale) of alumina and silica versus pH

Main elements Ca, Si, Al, Fe ⇔ high reactivity

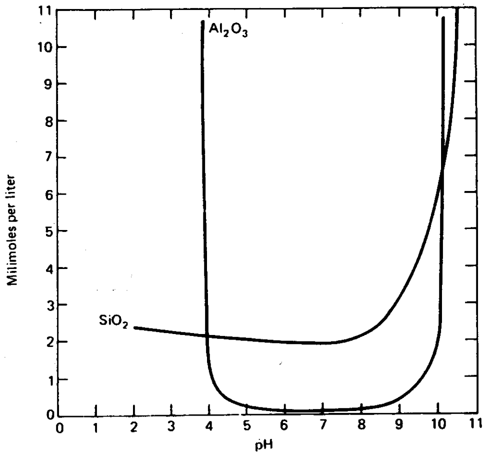
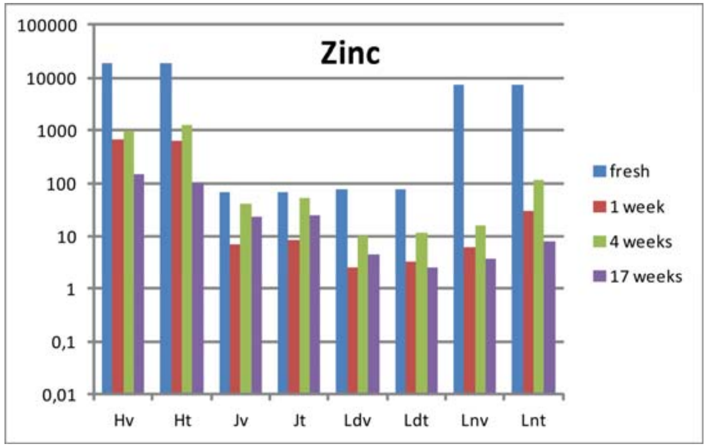


Figure 4.5 Solubility of alumina and amorphous silica in water (Keller, 1964).

Availability of trace elements to the water phase

In four fly ashes, the leaching of zinc decreases with increased contact time with pore water



Commonly percieved versus scientific facts well known to inorganic chemists, geochemists & mineralogists since decades

Solid solution

- Trace elements do not for the most part form phases in which they are major elements
- Trace elements are usually dispersed – atom by atom – in phases formed by the major elements
- Therefore inaccessible

Commonly percieved but not correct

- Trace elements mostly form phases in which they are major elements
- Availability to pore water depends on the solubilities of such phases
- Therefore accessible

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		0,56	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				

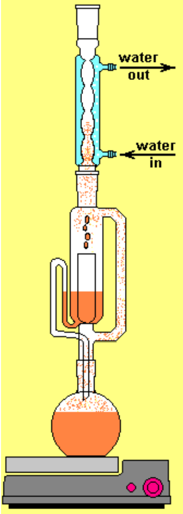
* unusual oxidation number

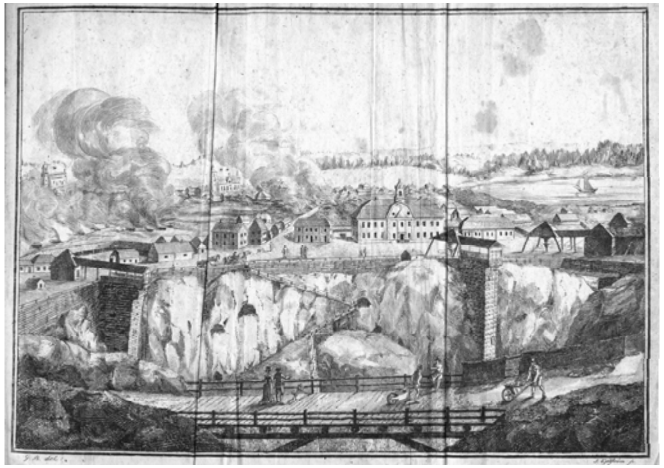
Ionic radii for trace elements and some other elements, Angstrom

Natural analogue - leaching
in distilled water for ≈ a billion years

SOXHLET-LEACHING
Invented in 1879 by Franz von Soxhlet.

Batchwise leaching with distilled leachant





The Falun copper mine at around the year 1780.
How can the environment around the mine be relatively healthy in spite of a total fallout of ≈ 30 kg of sulphuric acid per m^2 during > 1000 years of mining?

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In most cases simple oxides & pessimistic choice of valence

- Arsenic-III
- Barium-II
- Cobalt-II/III
- Copper-II
- Chromium-VI
- MolybdenumVI
- Antimony-III
- Vanadium-V
- Zinc-II

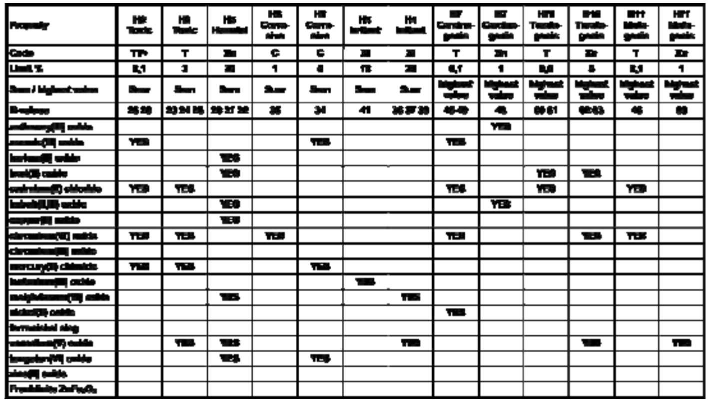
Mixed oxides with solid solution in iron-rich phases

- Cr-III
  (in iron-rich phase)
- Ferronickel
- Franklinite
  $ZnFe_2O_4$

Limitations

- Actual parameters should be within the ranges studied generically
- Content of iron sufficient in order for iron-rich phases to form
- The ratio of trace element to iron should be low
- Leach rates should be found to be low
  (and leached amount + a large margin for uncertainty should be counted as “worst case”)

Reference substances, properties and risk phrases



Property	[illegible] Toxic	[illegible] Toxic	[illegible] Harmful	[illegible] Corrosive	[illegible] Corrosive	[illegible] Irritant	[illegible] Irritant	[illegible] Carcinogenic	[illegible] Carcinogenic	[illegible] Teratogenic	[illegible] Teratogenic	[illegible] Mutagenic	[illegible] Mutagenic
Code	T+	T	Xn	C	C	Xi	Xi	T	Xn	T	Xn	T	Xn
Limit %	0,1	3	25	1	5	10	20	0,1	1	0,5	5	0,1	1
Sum / highest value	Sum	Sum	Sum	Sum	Sum	Sum	Sum	highest value	highest value	highest value	highest value	highest value	highest value
R-values	26 28	23 24 25	20 21 22	35	34	41	36 37 38	45-49	40	60 61	62-63	46	68
antimony(III) oxide									YES				
arsenic(III) oxide	YES				YES			YES					
barium(II) oxide			YES										
iron(III) oxide			YES							YES	YES		
cadmium(II) chloride	YES	YES						YES		YES		YES	
cobalt(II,III) oxide			YES						YES				
copper(II) oxide			YES										
chromium(VI) oxide	YES	YES		YES				YES			YES	YES	
chromium(III) oxide													
mercury(II) chloride	YES	YES			YES								
lanthanum(III) oxide						YES							
molybdenum(VI) oxide			YES				YES						
nickel(II) oxide								YES					
ferronickel slag													
vanadium(V) oxide		YES	YES				YES				YES		YES
tungsten(VI) oxide			YES		YES								
zinc(II) oxide													
Franklinite $ZnFe_2O_4$													

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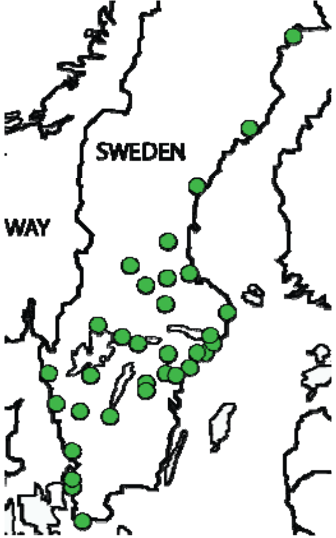
Conclusions

- There exists a method by menas of which classification of ash and slag can be made
  - In a cautious manner
  - In a somewhat realistic manner
  - In an efficient manner
- The method has been recurrently questioned (by ourselves) and the knowledge base has been continuously improved
- In no case have we found that we have not been sufficiently cautious
- Instead, in some cases, precautions have been partially lifted
- The method is applicable also when the base for classification is shifted from DSD/DPD to CLP
- The approach is actually also applicable to non-waste under REACH



Examples of industrial plants that have used the present method for classification of ash (and slag) as hazardous and non-hazardous

Cases in which Tekedo AB has been involved only

(more information at www.classification.se)