Classification of ash as hazardous or non-hazardous waste - Swedish approach & experience

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The structure of this presentation

1. Introduction
    1. Ash management in Sweden
    2. Legal prerequisites
    3. What is ash?
2. Approach to classification
    1. Hypothetical forms of occurrence
    2. Fresh and aged ash
    3. Solid solution
    4. One or more substances - testing
3. Conclusions and outlook

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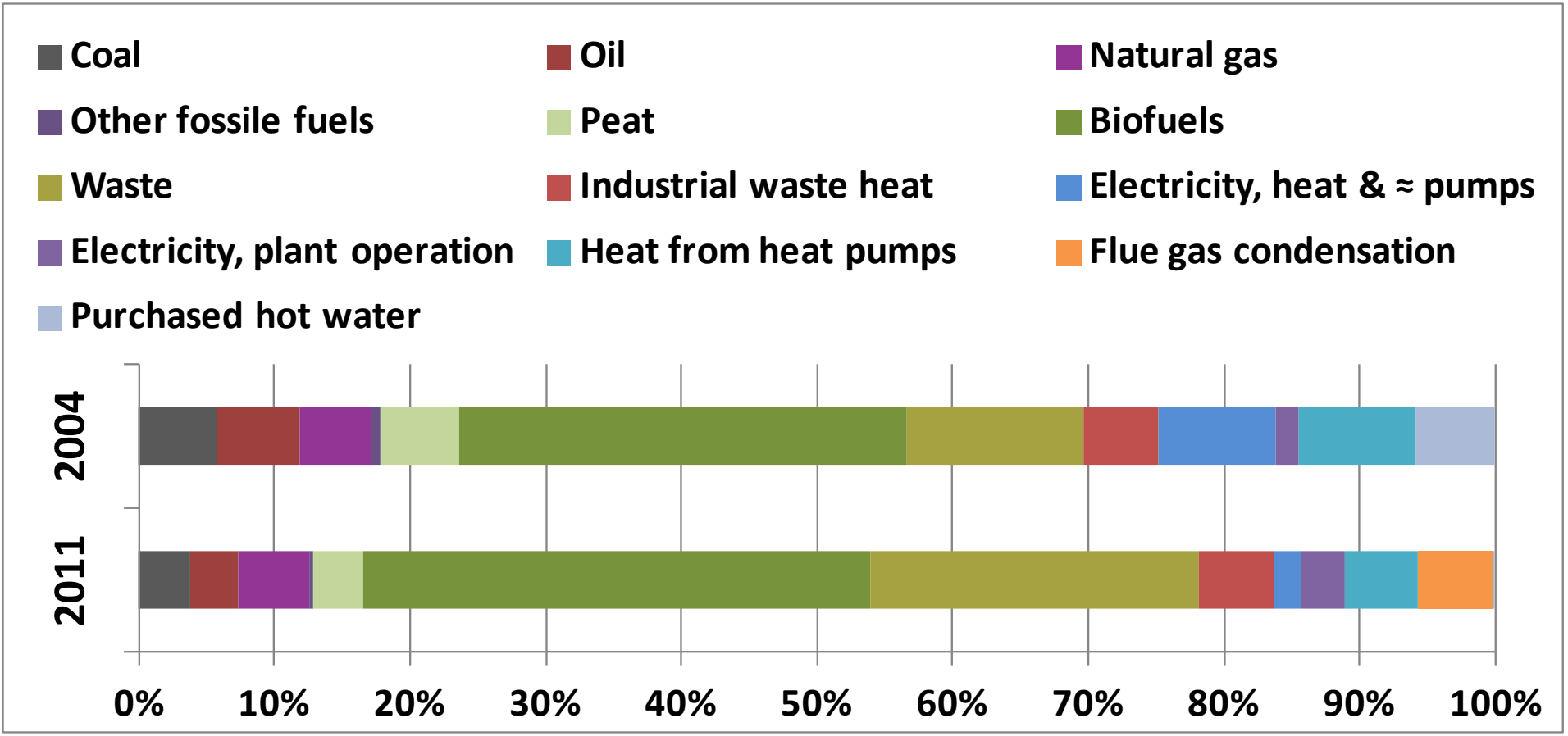
The Swedish district heating plants – sources for heat and electricity generation



Incineration (total population ≈ 9 M)

- Volumes of waste incinerated annually
  - 2.2 million tonnes of domestic waste
  - 3 million tons of other waste
- As a result of mainly incineration in combination with recycling (including ash), the volumes landfilled have decreased from
  - 6.1 Million tonnes in 1994
  - to only 1.4 million tonnes in 2013

Ash generation

- Ash content highly variable between the fuels
  - 0.5 % by weight in stem wood
  - ≤ 30 % by weight in waste
- A total of ≈ 1.7 million tonnes of ash are generated annually, mostly from incineration
- Most of it is utilized as construction and stabilization material in landfills
- Some is actually landfilled
- Only ≈ 2 % of all the ash is returned to the forest as a nutrient

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Situation < June 1st 2015:

EU Directives & associated implementations in national legislations

- Classification of waste
  - waste framework directive
  - hazardous waste directive
- Labelling of chemicals
  - DSD = Dangerous Substances Directive
  - DPD = Dangerous Preparations Directive

Situation ≥ June 1st 2015:

EU regulations

(which apply directly in all EU countries without implementation into national legislation)

- Classification of waste
  - New EU regulation
    (≈ content can be found in a protocol from a EU Commission working group)
- Labelling of chemicals
  - CLP

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¤¤¤

Purpose of classification

- Differentiate the handling of waste according to the inherent hazard potential
- [At least in the case of Sweden] in one case constitute basis for acceptance to landfilling in that:
  - Non-hazardous waste can be deposited on a landfill for non-hazardous waste without leach testing
- [Otherwise, acceptance to a landfill is largely based on leach criteria]

Acceptance for landfilling

Directive on the landfill of waste	**Waste Directive & classification as hazardous or non-hazardous**
Governs acceptance to a landfill in general	Governs acceptance to a landfill for the case of non-hazardous waste and a landfill for non-hazardous waste
Leach criteria	Properties of the constituent substances
Refers to a fraction of the total mass that comprises water leachable species with hazardous properties	Refers to the content of hazardous substances independently of their availability to the water phase

⇔ Acceptance might be highly different depending on the details of the chemical structures

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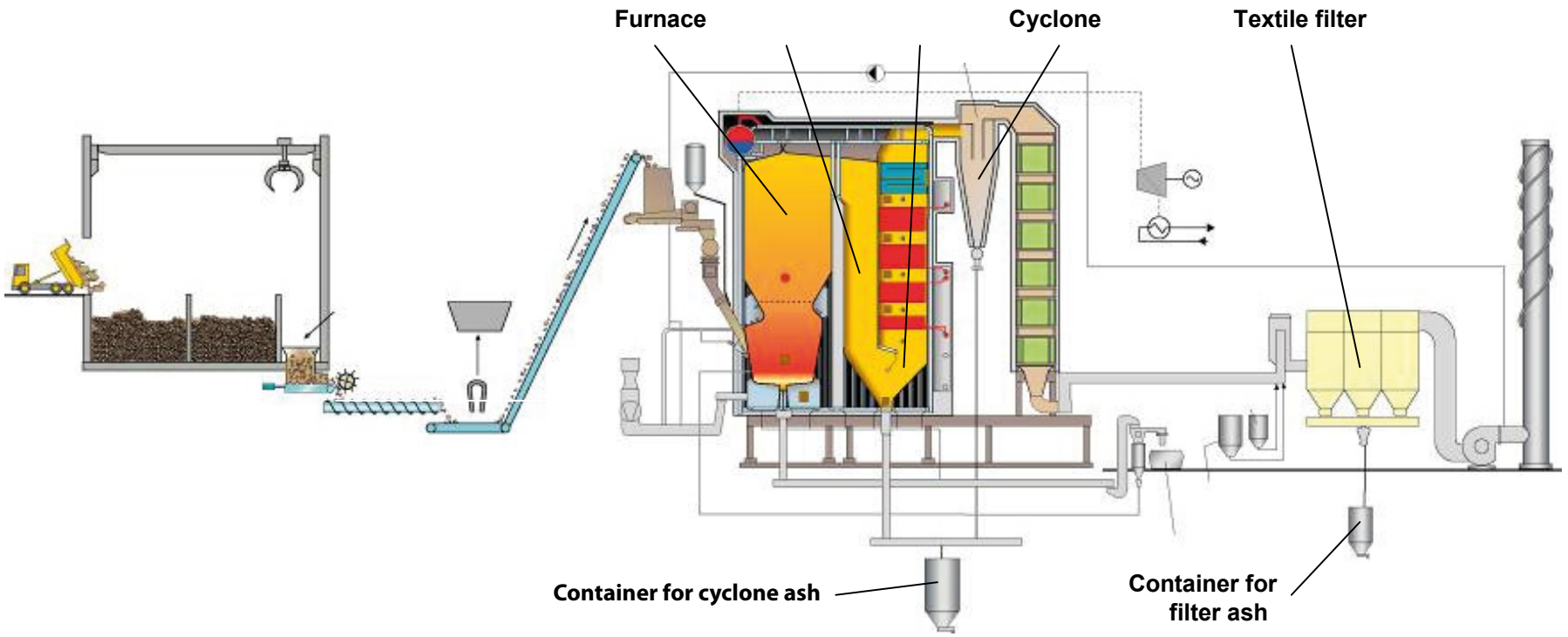
What is ash?

Ash	**Comparison / example**
One or more substances?	Chemical product / blend of ingredients
Inert grains with contaminants on the surfaces?	Contaminated soil
Lime added during the flue gas cleaning?	Mortar
Highly reactive glass phase?	Some coal ash & volcanic ash
High temperature minerals?	Melting / igneous rock or partial melting / metamorphic rock
Low temperature minerals?	Diagenesis / weathering / sedimentary rock
Solid solution of trace & minor elements into the phases formed by the major elements?	Takes place universally in minerals. Most common fate for trace elements.

Fly ash and other ashes



Fractional condensation of volatile elements and compounds.
Partial melting of the ash and consequent formation of reactive glass phase (e. g. 40 % ot total weight)

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

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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

“Mission impossible”

- Actual forms of occurrence
  - Very complex
  - Do not exist in data bases from Authorities
- Approach to use reference substances for various contaminant elements such that
  - Hazardous properties are known & exist in data bases from Authorities
  - Represent actual substances in a cautious manner

In most cases simple oxides & pessimistic choice of valence – "harmonised classifications" in DSD and CLP

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

To be discussed later:

Mixed oxides with solid solution in iron-rich phases or equivalent

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

Reference substances, properties and risk phrases

Property	H6 Toxic	H6 Toxic	H5 Harmful	H8 Corro-sive	H8 Corro-sive	H4 Irritant	H4 Irritant	H7 Carcino-genic	H7 Carcino-genic	H10 Terato-genic	H10 Terato-genic	H11 Muta-genic	H11 Muta-genic
Code	TT+	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										
lead(II) oxide			YES							YES	YES		
cadmium(II) chloride	YES	YES						YES		YES		YES	
kobalt(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								
lantanium(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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Solubility (log scale) of alumina and silica versus pH

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

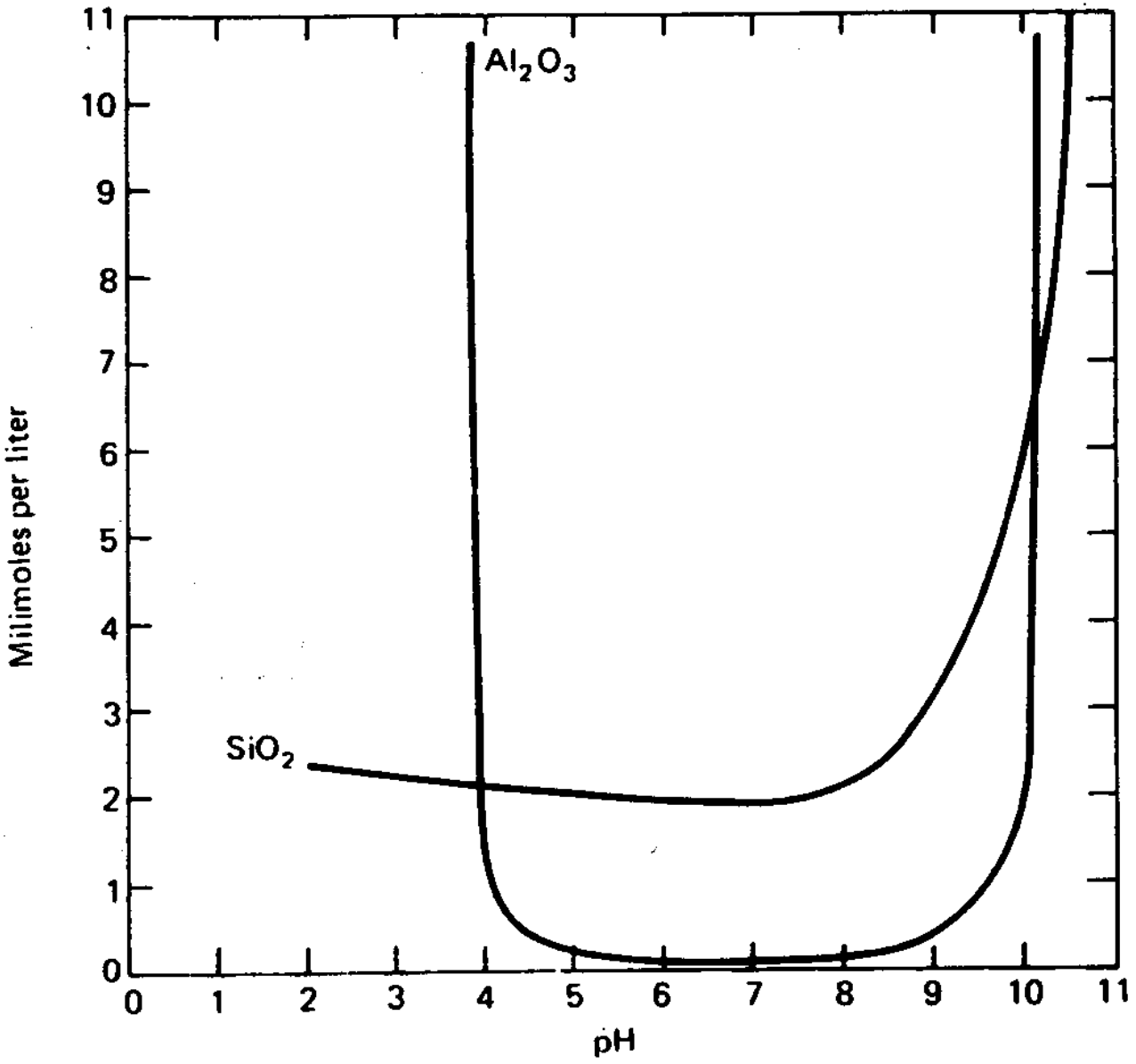


Figure 4.5 Solubility of alumina and amorphous silica in water (Keller, 1964).

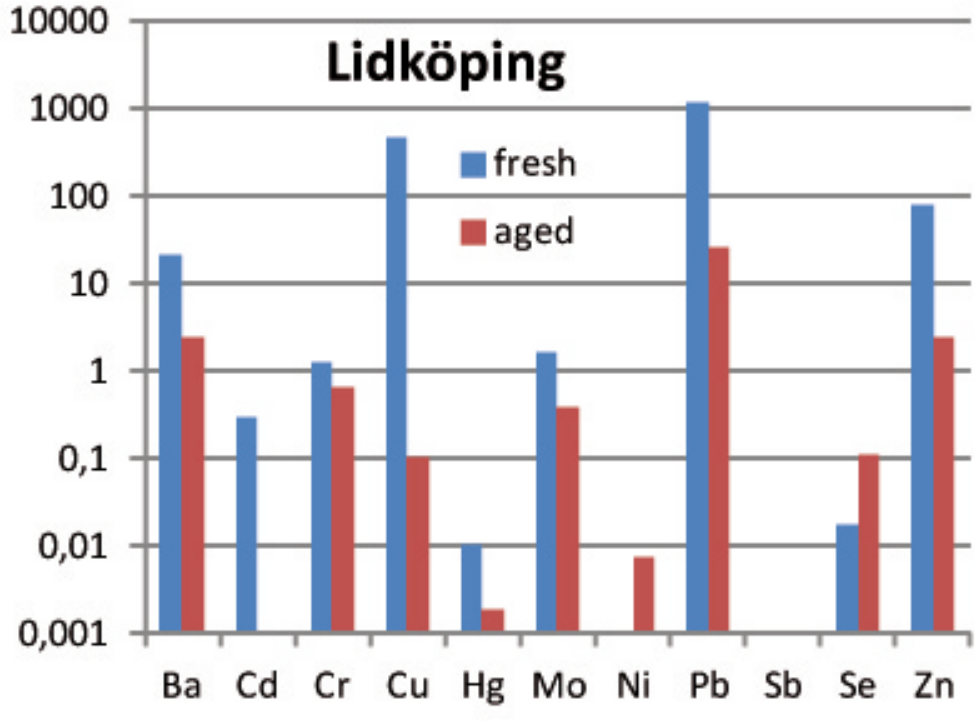
Availability of trace elements to the water phase

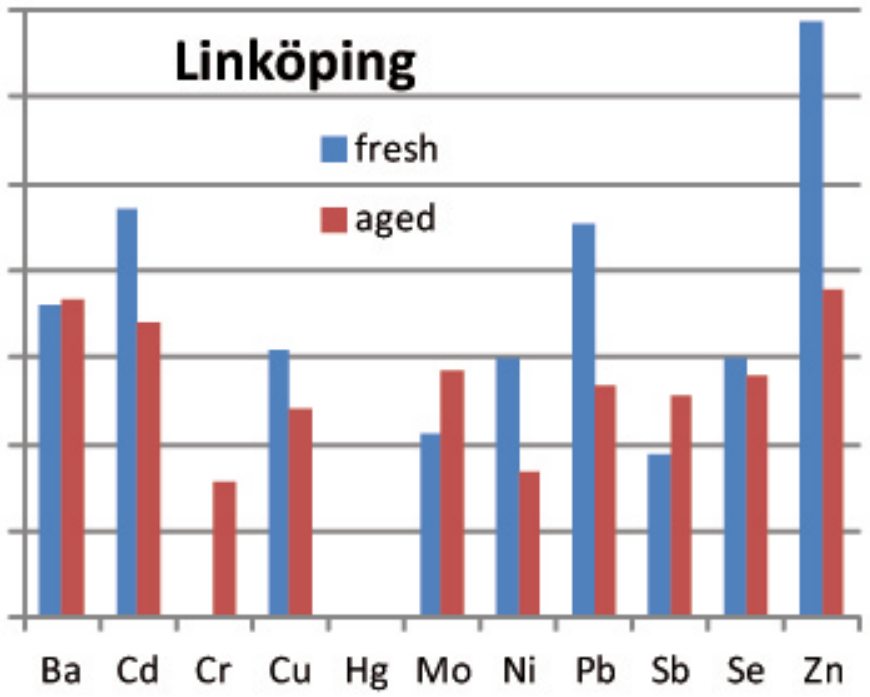
Leach testing for acceptance criteria for landfilling (Swedish legislation)

- EN 12457-3 batch leaching test must not be used for samples that react with water
- One should aim at “equilibrium conditions”

=> before testing

  - mixing with some water
  - ageing for ≥ one week





Examples of results from batch leaching tests.
Fresh (blue) and aged (red) fly ash.

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Solid solution ⇔

1. Ionic radii differ by < or ≈ 15 %
2. Ionic charges differ by ≤ 1 unit
3. Smaller radius & higher charge => stronger bonding
4. Difference in electronegativity not too great

- Small degree of substitution more favoured than large ⇔ enthropy effect
- Substitution highly structure dependent (e. g. Pb-II in calcite versus aragonite)

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 / Ångström

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Mixed oxides with solid solution in iron-rich phases (or equivalent)

- Cr-III
  (in iron-rich phase)
- Ferronickel
- Franklinite
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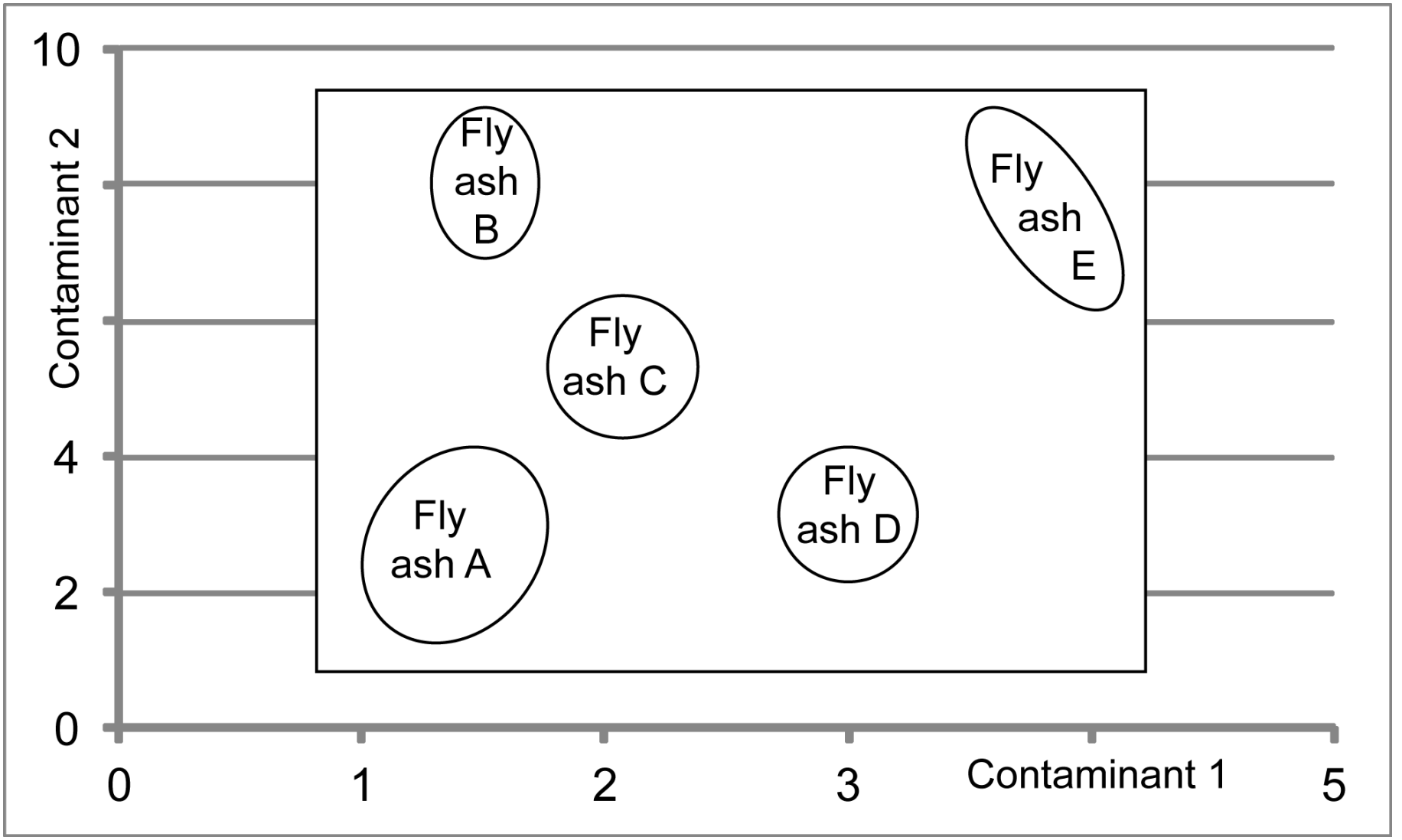
Does it matter?

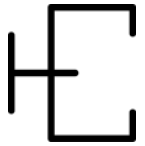
Rectangular area illustrates the intervals that have to be considered if the ashes A – E are regarded as one substance

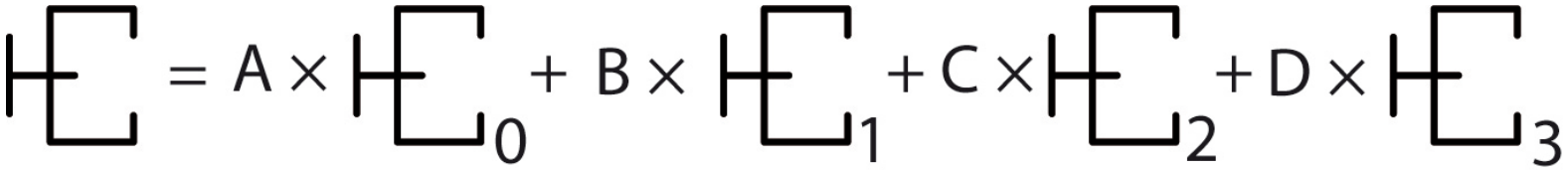


One or more substances

- Classification can be based on
  - Ash = one substance (DSD)
  - Ash = mixture (preparation) of several substances (DPD) [above approach]
- Rationale for present choice: impractical to test every quality of ash
- But:
  - Testing on ecotoxicity has shown that above method may substantially overestimate hazard
  - Provisions in CLP (bridging) and REACH (read across) for not testing every quality of ash

One or more substances, continued

- According to Wallerius 1759, ash is a substance with the following symbol: 
- Some properties of an ash might be expressed e. g. as a linear combination of the properties of a number of ashes that have been tested:



- Requirements regarding ecotoxicity will not be quantified in the new regulation on classification
- Special tests are under consideration

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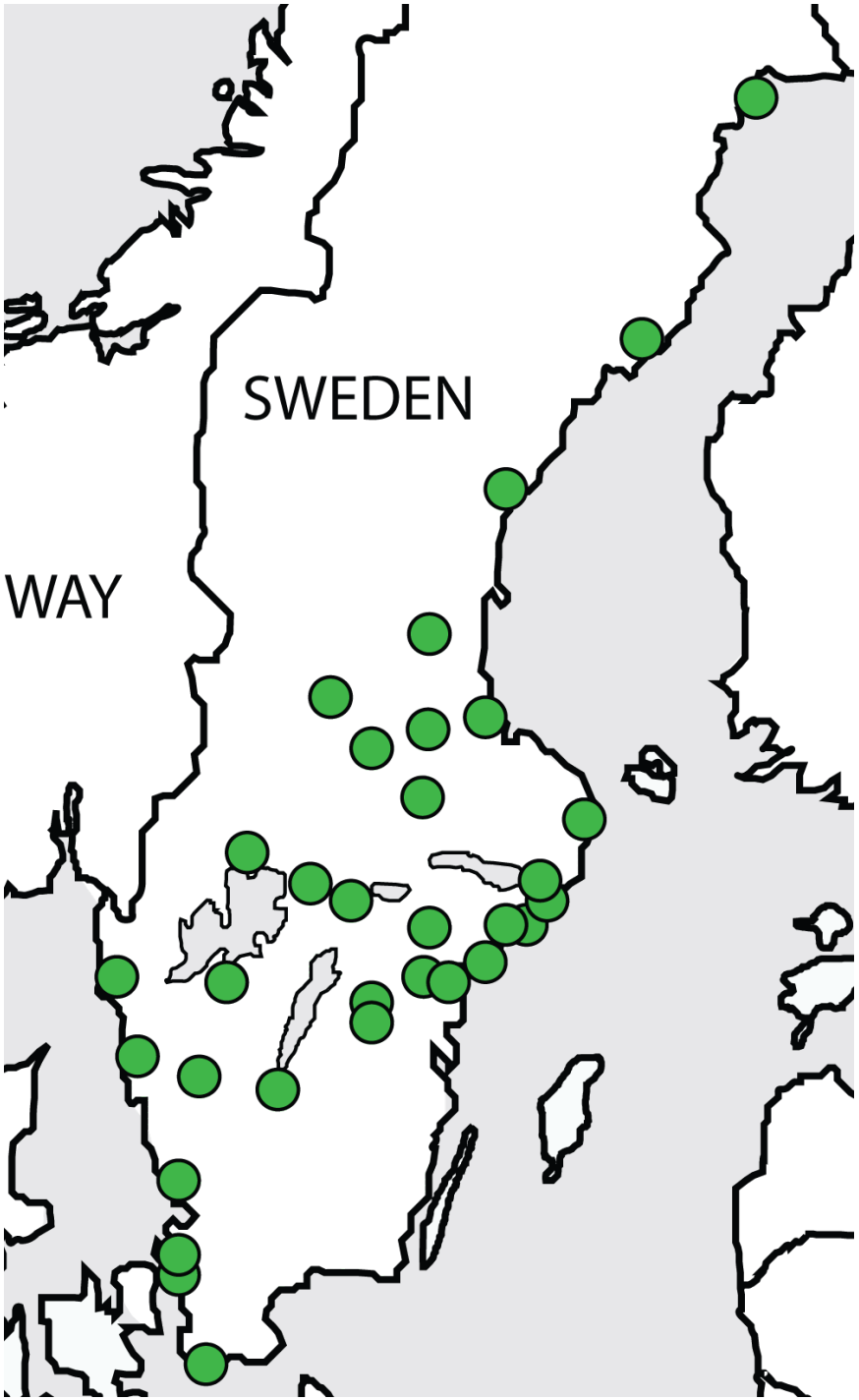

Examples of industrial plants that have used the present method for classification of ash (and slag) as hazardous and non-hazardous

Cases in which Tekedo AB has been involved only

(more information at www.classification.se)

Conclusions and outlook

- There exists a method by means of which ash can be classified as hazardous or non-hazardous
  - In a cautious manner
  - In a somewhat realistic manner
  - In an efficient manner
- The method is applicable also when the base for classification is shifted to the new EU regulation and to CLP

Τηανκ ψου φορ ψουρ αττεντιον!