ENVIRONMENTAL QUALIFICATION OF ASH FROM WOOD-BASED RECYCLED FUELS FOR UTILIZATION IN COVERS FOR LANDFILLS

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About Sweden

- District heating ≈ 50 % ⇔ ≈ 50 TWh/y
- Wood based (including recycled fuels, paper sludge and bark, also peat)
- => ≈ 1 Mtonne of ash
- Domestic waste ≈ 50 % incinerated ⇔ ≈ 2 Mtonnes
- => ≈ 0,4 Mtonnes residue
- <⇔>
- Ash by far largest residue

Need & What is getting done?

- Need to simultaneously
  - Protect health and environment
  - Conserve & recycle
- Little ash is utilized outside landfill
- Considerable use at landfill but utilizing only a fraction of the potential in the materials
- A lot is deposited with resource consuming protection that is unreasonably high

Why this inefficiency?

- Directive of hazardous waste impossible to apply on ash in practice
- Acceptance criteria (at least as interpreted in Sweden) do not accommodate for the improvement in chemical and physical properties with time
- ⇔ ash is a very reactive material that cures and weathers which leads to self-stabilization

Approach, purpose & scope

- To combine
  - Science – based on ≈ best knowledge
  - Application – real examples
  - Regulation – fulfil intention
- Example of cover including seal at Telge Återvinning AB (4 hectares) on old domestic waste
- Need for research, communication & co-operation to qualify & improve qualification methodology

This presentation

- The regulations
- The application to use ash for seal and cover over domestic waste
- The environmental qualification, including
  - Characterization
  - Understanding mechanisms and processes
  - Application to regulation fulfillment
- Conclusions

Directive of hazardous waste & harmonized regulation

- Regulates the management of waste
- Based on European Waste Catalogue (EWC) code
- For some codes also content of hazardous substances
- A hazardous substance has at least one hazardous property
- Properties defined with the same risk phrases as for labelling of chemical products
- Summation over various substances having a certain property
- In some cases largest value

How to comply with the hazardous waste directive?

- Organic chemistry – relatively straightforward
- Inorganic chemistry of ash very complex – actual chemical forms cannot be found in data bases =>
- Necessary to identify reference substances as follows
  - **Known properties with regard to health and environment**
  - **Should represent relatively realistic forms for the element in question**
  - **Should represent actual substances in a conservative manner**
  - **Should represent the properties over time – however, initial contact with water is assumed**

How to comply with the hazardous waste directive? Continued.

- A special methodology has been developed on commission by
  - About 20 companies / plants
  - Branch organisations for heat generation and waste management (Värmeforsk Askprogrammet and Svenska Renhållningsverksföreningen – RVF)
  - The Swedish Environmental Protection Agency (and with support from the Swedish Chemicals Inspectorate)
- The methodology has been published by the branch organizations and is available to everyone (in Swedish only though)
- The methodology has been applied to about 20 plants
- The case of ash generated at Söderenergi and used at Telge Återvinning will be described in the following as an example

Acceptance criteria for landfilling

- Regards acceptability for landfilling of a certain material
- Must not be confused with classification in the categories hazardous – non-hazardous waste
- Largely based on leach tests according to certain European standards
- Non-hazardous waste may be deposited at a landfill for non-hazardous waste without leach tests
- Test methods & regulation state essentially nothing about materials development over time
- Grossly inadequate for highly reactive materials such as ashes

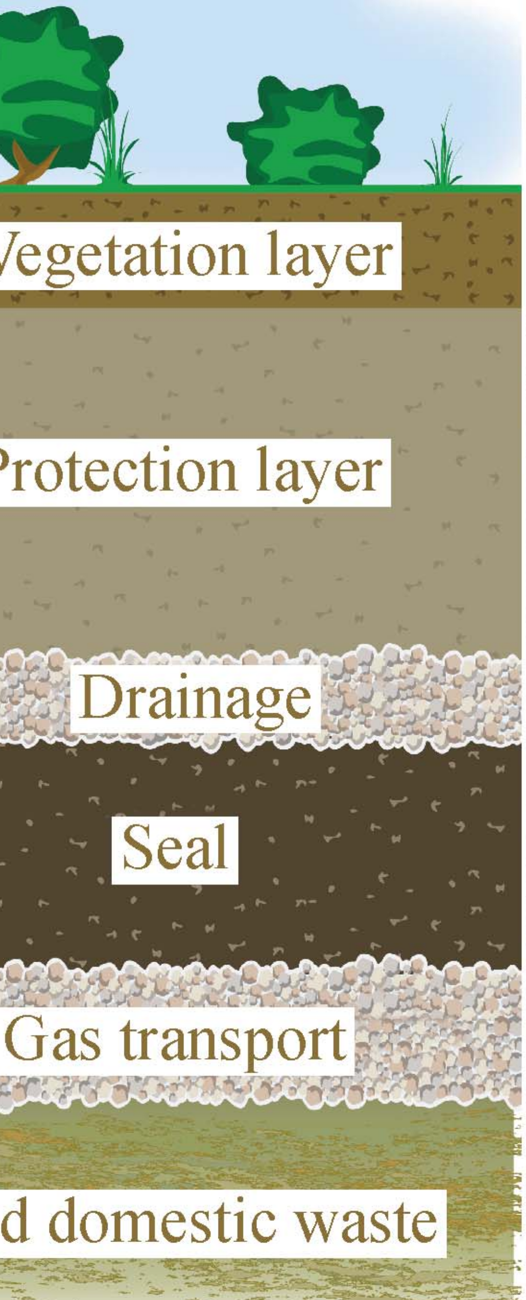
Comparison hazardous waste directive – acceptance criteria

Hazardous waste directive	**Acceptance criteria**
Regulates handling (& in one case acceptance)	Regulates acceptance to type of landfill
Content of substances having hazardous properties	Leach rates (mostly)
Potential	Availability


The ash store
Tests with covers
on old domestic waste
Test area 4 hectars
Tveta Recycling Plant
outside Södertälje near Stockholm, Sweden

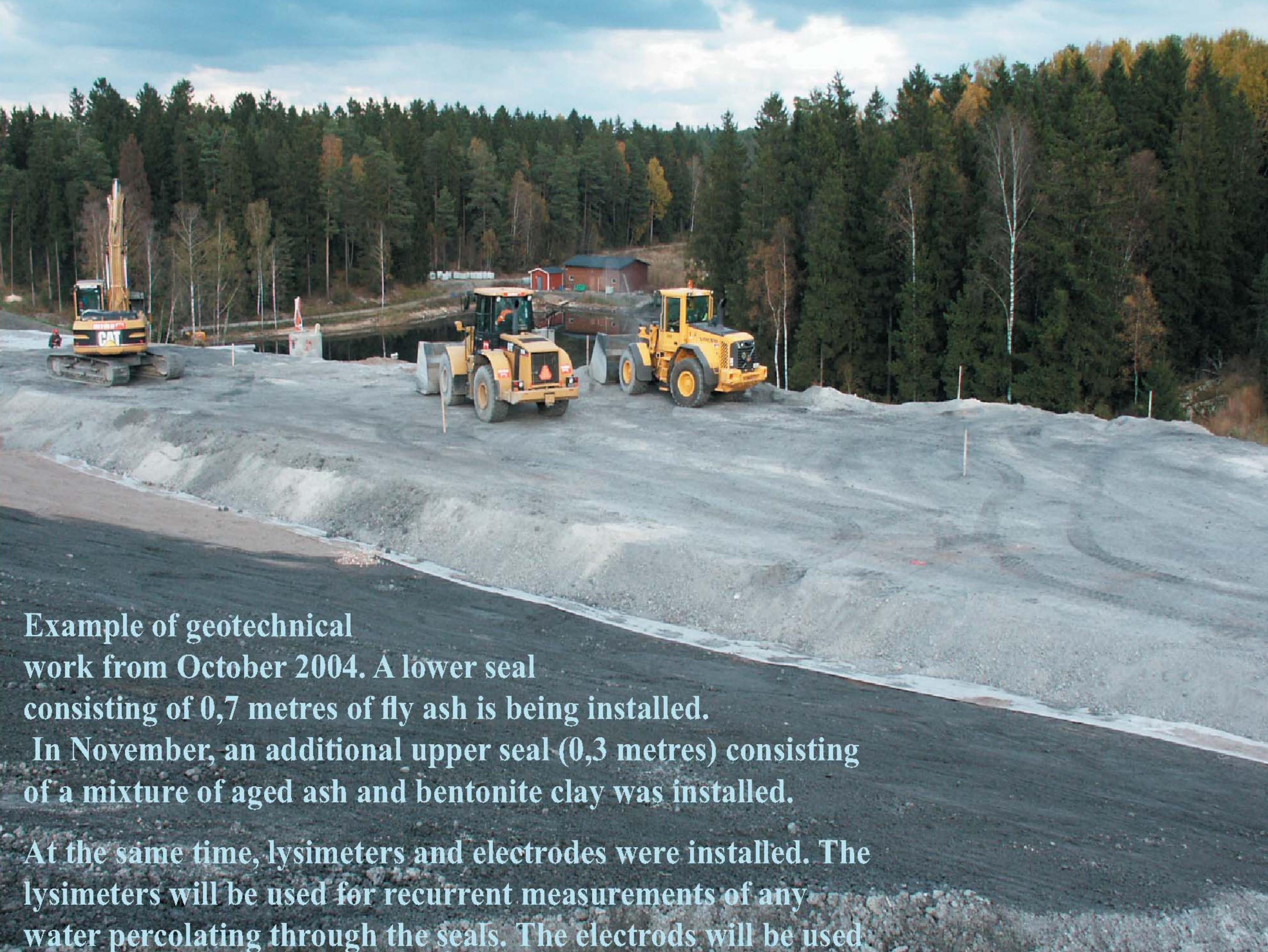
...in the different test covers

Tveta Landfill Cover Project



Basic ideas behind the *Tveta Landfill Cover Project*:

- **Utilization of recycled materials, especially ash from wood-based fuels**
- **The cover should have suitable mechanical properties with regard to differential settlements in the waste as well as slope stability**
- **The cover should have suitable chemical properties to resist undesired influences from other materials as well as to undergo continuous improvement in properties**
- **The results and conclusions should have a sound and**



Example of geotechnical
work from October 2004. A lower seal
consisting of 0,7 metres of fly ash is being installed.
In November, an additional upper seal (0,3 metres) consisting
of a mixture of aged ash and bentonite clay was installed.

At the same time, lysimeters and electrodes were installed. The
lysimeters will be used for recurrent measurements of any
water percolating through the seals. The electrods will be used

The ash store at the Tveta recycling plant

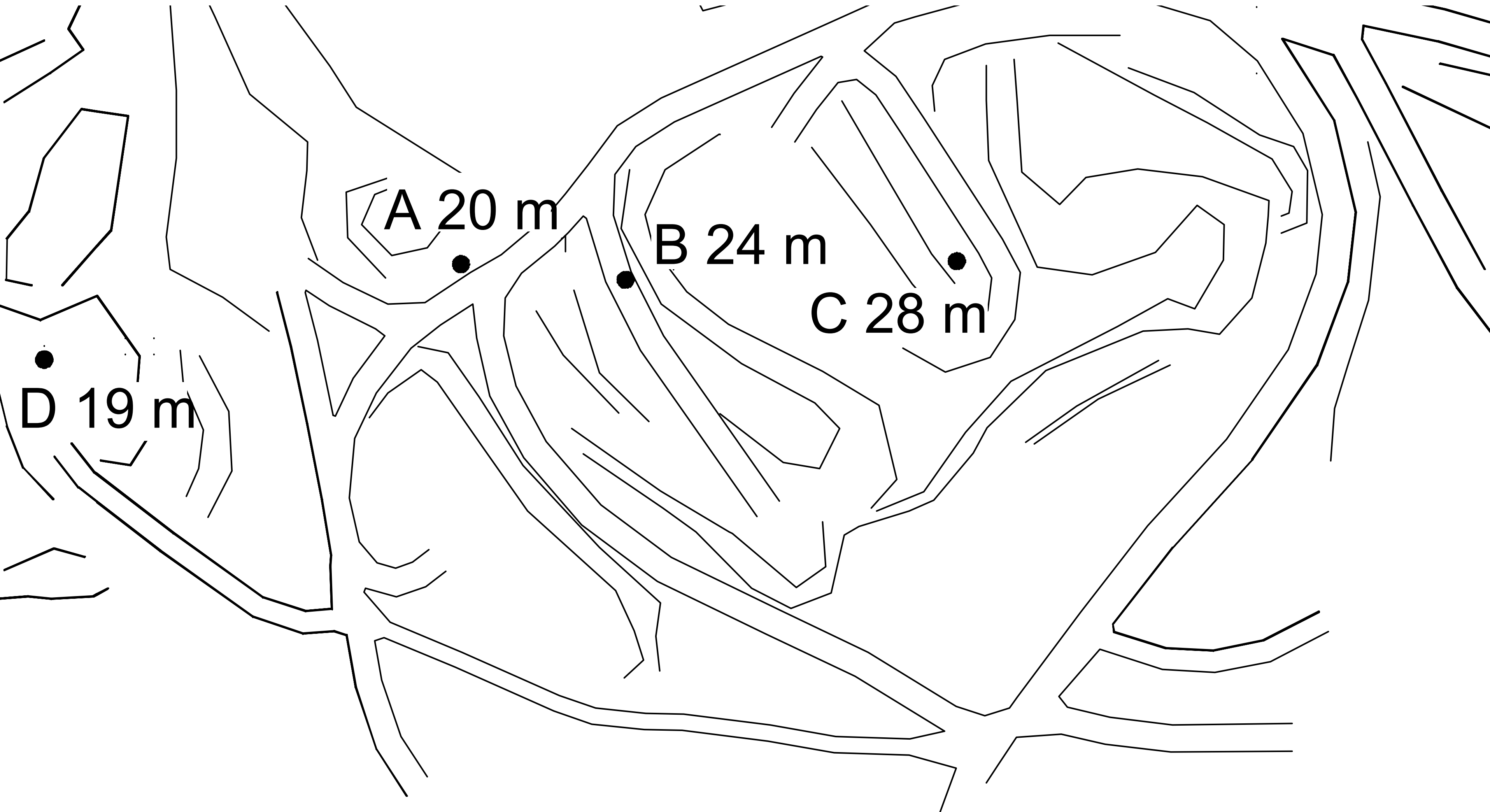
This photograph was taken i
September 2002 at which tin
the store comprised about 60
thousand metric tonnes of as

The ash is strongly consolidated due to various chemical reactions which start as soon as the ash is contacted with water. The initial pH is usually well above 10


Please note carefully the apearance of the material as it will
be concluded below that it is very impervious and monolitic

The material was collected in a drum using a cyclone. Two composite samples were taken for every meter, one of which was subsequently crushed to < 6 mm and homogenized.

Positions of the drill holes together with their total depths. Largest horizontal distance between holes 168 m.



Aged ash placed in small heaps for weathering and further ageing (*e g* bsorption of carbon dioxide) before mixing with bentonite clay (cf text). amples were taken at the positions indicated.

xamples of measurements carried out are as follows:

- moisture content
- pH of contact water
- electric conductivity of contact water
- soluble salts
- hardness
- electron microscopy
- packing properties (proctor)
- permeability
- thermogravimetry
- chemical analyses
- leach tests

Minor elements, mg/kg

Table 1. Minor elements in ash at the store at the Tveta Recycling Plant in mg/kg (ppm by weight) figured as elements. Samples taken from drill hole A (cf Figure 2).

Ele-ment	0-1 m	2-3 m	4-5 m	6-7 m	8-9 m	11-12 m	13-14 m	15-16 m	16-17 m
Sb	7	7	8	5	3	5	6	6	6
As	28	30	28	22	10	13	13	19	19
Pb	99	119	97	72	47	81	95	105	105
Co	38	41	42	32	25	32	31	33	33
Cu	114	110	130	95	80	100	91	71	71
Cr	132	150	134	126	112	115	116	80	80
La	36	56	37	42	44	38	34	40	40
Mo	11	20	6	9	6	8	6	9	9
Ni	98	109	121	93	74	104	99	102	102
V	231	240	277	198	135	146	147	123	123
Zn	203	194	179	144	123	204	271	519	519
Cd	1	1	1	1	0	1	1	2	2
Hg	1	1	1	1	1	1	1	1	1

Leached fraction together with legal limit for disposal at landfill for non-hazardous waste, mg/kg

Table 2. Leached fraction in mg/kg (ppm by weight) figured as elements in mg divided by dry weight of total in kilograms. Liquid to solid rate is 10 ml/g. Method used is SS-EN 12457-3. All values are below statutory limits, cf text. Statutory limits according to the acceptance criteria for disposal at a landfill for non-hazardous waste is also shown for comparison.

Ele-ment	0-1 m	2-3 m	4-5 m	6-7 m	8-9 m	11-12 m	13-14 m	15-16 m	16-17 m	Legal limit
As	0,01	0,02	0,03	0,03	0,05	0,03	0,07	0,05	0,06	*2*
Ba	0,51	0,65	0,67	0,89	0,59	0,55	0,60	0,38	1,08	*100*
Cd	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	*1*
Cr	0,02	0,07	0,05	0,02	0,01	0,03	0,01	0,01	0,01	*10*
Cu	0,03	0,02	0,01	0,01	0,01	0,01	0,01	0,02	0,34	*50*
Hg	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	*0,2*
Ni	0,02	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,07	*10*
Pb	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	*10*
Zn	0,01	0,02	0,01	0,01	0,01	0,01	0,01	0,02	0,01	*50*

Interpretation

- Leach rates below statutory limits in all cases ⇔ acceptance to landfill for non-hazardous waste
- Generally very low leach rates – in contrast to that of fresh ash
- pH typically between 8 and 10 – initially typically around 12 (with $Ca(OH)_2$)
- Generally believed to be due to carbonation
- But carbonate content low

Solubility (log scale) of alumina and silica versus pH

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

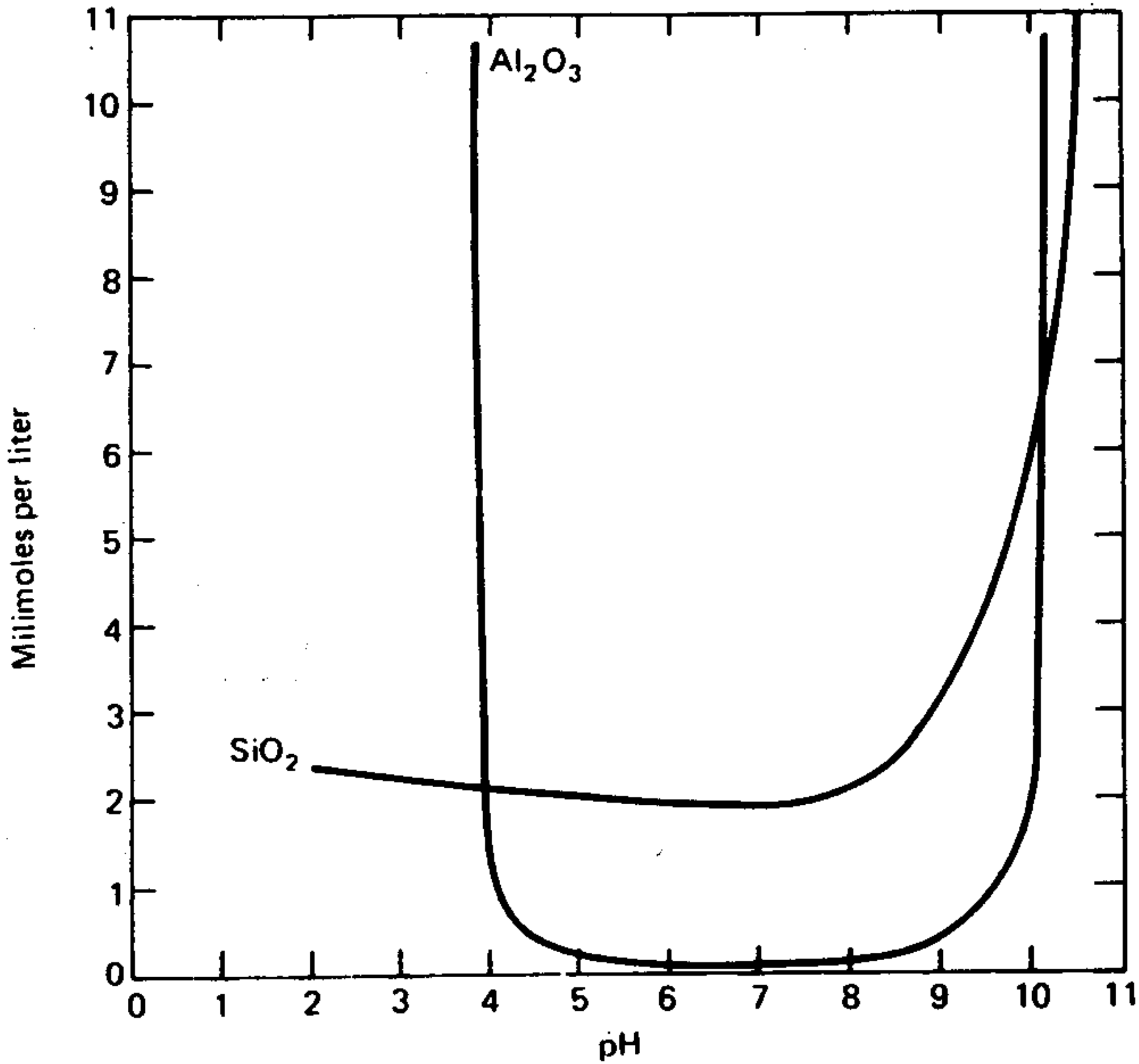


Figure 4.5 Solubility of alumina and amorphous silica in water (Keller, 1964).

Phases in ash after maturation ≠ from those formed in the furnace

Table 3. Minerals phases identified in incinerator ash after ageing [24]. Less abundant phases are labelled with italic fonts.

Silicate		**Oxide**	
Melilite	$(Ca,Na)_{2(}Al,Mg)(Si,AL)_2O_7$	Hematite	Fe_2O_3
Wollastonite	$CaSiO_3$	Magnetite	Fe_3O_4
Clinopyroxene	$(Ca,Na)(Fe,Mg,Al)(Si,Al)_2O_6$	**Carbonate**	
Plagioclas	$(Ca,Na)Al(Al,Si)Si_2O_8$	Calcite	$CaCO_3$
K-Feldspar	$(K,Na)(AlSi_3O_8)$		
Biotite	$K(Mg,Fe)_3(Al,Fe)Si_3O_{10}(OH,F)_2$	**Hydroxide**	
Muscovite	$KAl_2Si_3Al)O_{10}(OH,F)_2$	Portlandite	$Ca(OH)_2$
Montmorillonite	$(Na,Ca)_{0,3}(Al,Mg)_2SiO_{10}(OH)_2 \cdot nH_2O$	*Goethite*	$FeO(OH)$
Hydrate		*Boemite*	$AlO(OH)$
Hydrocalumite	$Ca_2Al(OH)_6[Cl_{1-x}(OH)_x] \cdot 3H_2O$	*Gibbsite*	$Al(OH)_3$
Hydrated Gehlenite	$Ca_2Al_2SiO_7 \cdot 2H_2O$	**Phosphate**	
Sulphate		Apatite	$Ca(PO4)_3$
Anhydrite	$CaSO_4$		(Cl,F,OH)
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$		
Gypsum	$CaSO_4 \cdot 2H_2O$		

Maturation processes

- Phases formed in furnace at high temperature not stable under ambient conditons
- High pH from portlandite ($Ca(OH)2$) => increased solubility of silicate & aluminate => reactivity
- Chemical sintering & formation of impervious structures - metamorphosis
- Sinks for heavy metals
- Formation of clay minerals

Speciation of minor elements

- Dependent on the phases of the major elements
- Incorporation into these phases
- Mixed oxides with iron (heavy metal sink)

Selection of reference substances

- Appear in data bases for hazardous substances
- Reasonably realistic
- Conservative

Table 4. Reference substances for selected metallic elements in ash

Reference substance	Comment
antimony(III)oxide	Valence usually III but V plausible at high pH values. III is selected because it is the most pessimistic choice.
arsenic(III)oxide	Valence usually III put V plausible at high pH values. III is selected because it is most pessimistic.
barium(II)oxide	Usually barium appears as sulphate. When level of sulphate is insufficient for this, hydroxide may form. It is selected because it is the most pessimistic choice.
lead(II)oxide	Lead oxide as well as chloride may form initially but lead oxide is formed after contact with water. Sulphate and carbonate are other reasonable forms but they have the same classification as lead oxide. Other lead compounds may form but are expected to be less soluble.
cadmium oxide	Initially formed cadmium chloride hydrolyses after contact with water.
cobalt(II,III)oxide	According to [14]
copper(II)oxide	According to [14]
50/50 Cr(VI) / Cr(III) oxides	Special analysis, *cf* text.
chromium(III)oxide	Special analysis, *cf* text.
mercury(II)chloride	All ashes are low in mercury. Chemistry complex. Chloride form most pessimistic.
lantanum(III)oxide	According to [14]
nickel(II)oxide	According to [14]
vanadium(V)oxide	According to [14] and the most pessimistic form
zinc(II)oxide	Zinc oxide as well as chloride may form initially but oxide form is formed after contact with water.

Testing against the quantified properties in the hazardous waste directive ⬄ all values below statutory limits ⬄ OK for landfill for non-hazardous waste without leach testing

Type of hazard	0-1 m	2-3 m	4-5 m	6-7 m	8-9 m	11-12 m	13-14 m	15-16 m	16-17 m	Upper limit
Highly toxic	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	*0,1*
Toxic	0,05	0,06	0,06	0,04	0,03	0,04	0,04	0,03	0,03	*3*
Harmful	0,19	0,23	0,21	0,21	0,15	0,18	0,19	0,17	0,15	*25*
Corrosive	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	*1*
Corrosive	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	*5*
Irritant	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	*10*
Irritant	0,05	0,05	0,05	0,04	0,03	0,03	0,03	0,03	0,03	*20*
Carcinogenic	0,01	0,01	0,02	0,01	0,01	0,01	0,01	0,01	0,01	*0,1*
Carcinogenic	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	*1*
Toxic f repr	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	*0,5*
Toxic f repr	0,04	0,04	0,05	0,04	0,02	0,03	0,03	0,02	0,02	*5*
Mutagenic	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	*0,1*
Mutagenic	0,04	0,04	0,05	0,04	0,02	0,03	0,03	0,02	0,02	*1*
Highly toxic	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	*0,1*

General conclusions

- Acceptance criteria
  - Leach rates very low after some time <= maturation
  - Misleading to use data from fresh material
- Classification hazardous waste directive
  - There exists a methodology for classification
    - Feasible
    - Conservative
    - Takes into account all heavy element atoms

Comments

- There is a need for robust assessments which can find broad acceptance
- They should not be sensitive to individual judgement
- This is especially important for ecotoxicity since there are no numerical limits in this case

=> Need for international communication, co-operation & network formation

- Anyone interested please contact any of the authors
- Their addresses & this presentation available at www.tekedo.se/Kalmar