Revised hazard classification of MSWI bottom ash

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Re-use of MSWI bottom ash (NL)

- Production MSWI bottom ash NL: 1.9 Mton/year
- Applications of re-use:
  - Mineral construction materials in road construction works and embankments
  - BA aggregates as replacement of gravel in concrete applications (e.g. pavement stones)
- Application of primary and secondary materials regulated in Soil Quality Decree
- Main granular application under isolated conditions
- Green deal bottom ash: 50% free use in 2017, 100% in 2020

Legislative background

- ✓ **WFD Directive 2008/98/EC, Regulation 1357/2014 (EC)**
- ✓ **CLP Regulation 1272/2008 (EC)**
- ✓ **LoW Commission Decision 2000/532/EC**
- ✓ *Regulation (EC) 1195/2006 amending Annex IV to Regulation (EC) 850/2004*

WFD, Annex III: defines the hazard properties and limit values

CLP: list of substances with known hazard information

LoW, Section 19: waste from waste management facilities

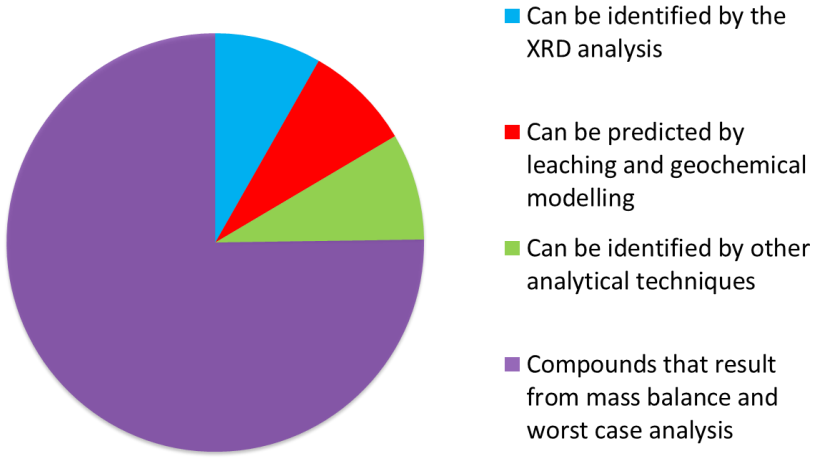
19 01 – waste from incineration or pyrolysis of waste

19 01 11* MH bottom ash and slag containing hazardous substances

19 01 12 MN bottom ash and slag other than those mentioned in 19 01 11

Hazard classification based on substances

- All possible substances need to be considered
- CLP contains (only…) ±4.500 substances (harmonised classification)
- Major challenge: most techniques measure elements, not substances



Tiered approach for classification

TIER 1. General screening

Relevance of each HP is assessed

TIER 2. Worst case assessment

Analysis of the material using its composition and assuming maximal concentrations of substances

TIER 3

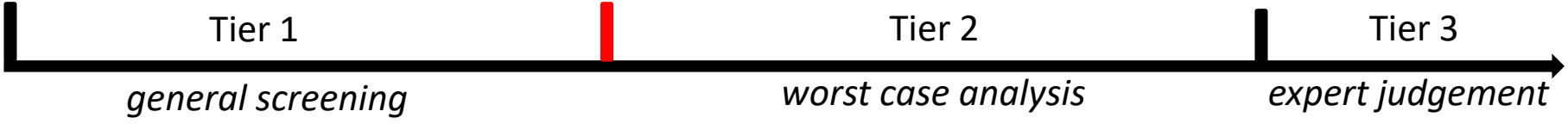
Assessment towards more realistic situations using more data from different sources

HPs not excluded at Tier 1 go to Tier 2;

HPs not excluded at Tier 2 go to Tier 3

Tier 1 – general screening

HP 1:	explosive
HP 2:	oxidising
HP 3:	flammable
HP 4 Σ :	irritant
HP 5:	STOT/Aspiration toxicity
HP 6 Σ :	acute toxicity
HP 7:	carcinogenic
HP 8 Σ :	corrosive
HP 9:	infectious
HP 10:	toxic for reproduction
HP 11:	mutagenic
HP12:	release of an acute toxic gas
HP 13:	sensitising
HP 14 Σ :	eco-toxic
HP 15:	yielding another substance



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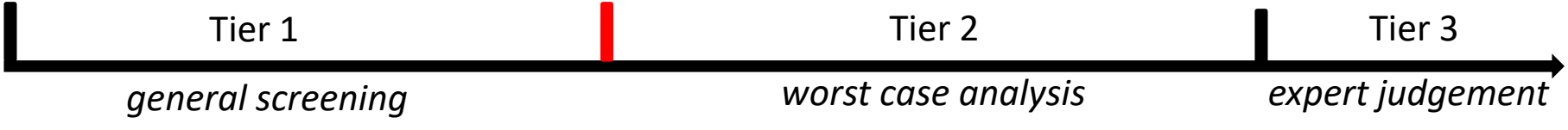
HP 8 Σ :	corrosive
HP 14 Σ :	eco-toxic



Tier 2 – worst case assessment

- Composition of MSWI bottom ash: 95 percentile values
- Consideration of substances (relevant HSC) for every hazard property
- Approach: start with “worst case” substances, exclude based on knowledge
- Assessment stops in Tier 2 when no hazard is displayed
- Otherwise: “go as far as we can go based on knowledge ” in Tier 3.

Max possible concentration

Cu total content **0.89%**
Assume all Cu bound in CuCl.
CuCl max - ?

Cu 64g/mol; Cl 35g/mol; CuCl 99g/mol

CuCl content: 0.89*99/64 = **1.4% max**

Most hazardous substance

$ZnSO_4$	161g/mol
$ZnCl_2$	135g/mol
Zn	65g/mol

Assume concentration limit 1%.
0.48% Zn → 1% $ZnCl_2$
0.40% Zn → 1% $ZnSO_4$

$ZnSO_4$ is more hazardous than $ZnCl_2$

Tier 2 – worst case analysis

HP 1: explosive
HP 2: oxidising
HP 3: flammable
HP 9: infectious
HP12: release of an acute toxic gas
HP 15: yielding another substance

HP 5: STOT/Aspiration toxicity
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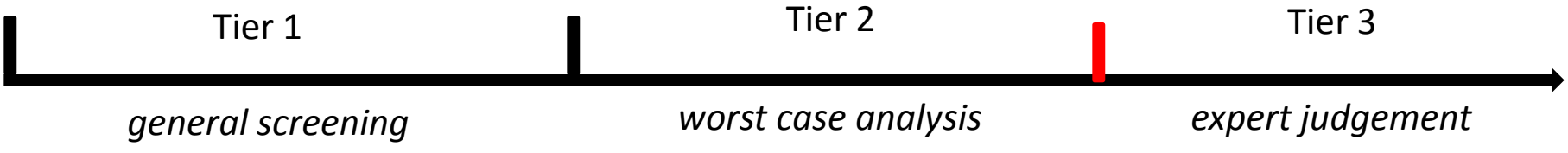
HP 13: sensitising

HP 4 Σ : irritant
HP 7: carcinogenic
HP 8 Σ : corrosive
HP 10:toxic for reproduction
HP 14 Σ : eco-toxic



Tier 3: HP7, carcinogenic

From Tier 2:

$NiSO_4$ (hazard index HI=1.33 >1) – soluble,

$NiSO_4$ → $Ni(OH)_2$, HI=0.82<1 → no HP 7 hazard from Ni compounds

Cat 1, H350	Cat 2, H351	Substance	REMARKS
0.1% limit	**1% limit**		
	0.47% < 1%	$PbCrO_4$	CrVI 0.8mg/kg ; Cr total 754mg/kg, if all Cr=Cr(VI), 1% limit is not exceeded
0.02% < 0.1%		$HPbAsO_4$	Arsenic is limiting element (47mg/kg), total Pb - 3969mg/kg
	0.08%	$PbCrO_4$+$PbMoO_4$+ $PbSO_4$	$PbSO_4$ too soluble to form this complex, also will not exceed 1% limit when Mo(81mg/kg) is the limiting element
	0.84%	$PbSO_4$+$PbCrO_4$	$PbSO_4$ too soluble to form this complex, also will not exceed 1% limit when all Cr is Cr(VI) and taken as the limiting element

HP 4 / HP 8: irritant / corrosive

- Additive hazard – contributions from all relevant substances added together
- No pH criteria in WFD

- **HP8 (corrosive) – no hazard** (Na, K, Zn – most contributing)
- **HP 4 (irritant) – no hazard** (Ca, Fe – most contributing)

pH consideration: CLP (pH<2, pH>11.5) versus WFD (no pH criterion)

HP 10: toxic for reproduction

Pb substances	**Estimated amount, % from total amount of Pb**
$PbCO_3$, PbO, $Pb(OH)_2$, metallic Pb, and $Pb_3(PO_4)_2$	**Together** consume maximum 14.5% of total Pb – geochemical modelling results
Unknown forms of Pb	Remaining 85.5% of total Pb

		g/mol	Pb total 95%, %	Fraction of total Pb, **worst case**, %	Max concentration at assumed equal distribution, %
0.3% limit	$PbCO_3$	267	0.40	14.5	0.07
0.3% limit	PbO	223	0.40	14.5	0.06
0.3% limit	$Pb(OH)_2$	241	0.40	14.5	0.06
CLP, 0.3% limit	Pb metalic	207	0.40	14.5	0.07
CLP, 0.3% limit	$Pb_3(PO_4)_2$	812	0.40	14.5	0.08
0.3% limit	Unknown forms		0.40	85.5	0.34

Unknown forms can render hazardous classification

3969mg/kg as 95 percentile

No HP 10 hazard from unknown forms of Pb if Pb < 3500mg/kg

(3500*0.855 = 0.3% - at HP 10 limit)

Tier 3 - expert judgement

- **HP 7 (carcinogenic) – no hazard**
- **HP 4 (irritant) / HP8 (corrosive) – no hazard**
  pH consideration: no pH criteria in WFD. CLP does contain criteria(pH<2, pH>11.5)
- **HP 10 (toxic for reproduction)**
  3969mg/kg as 95percentile for Pb
  No hazard for bottom ash samples with Pb < 3500mg/kg
  No distinction between massive (non hazardous) and powder forms
- **HP 14 (eco-toxic) – next slides**

HP 14: eco-toxic

- Total content as a basis (95 percentile)
- All relevant substances (H400, H410, H411, H412, H413)
- Stability analysis (e.g. $PbSO_4$)
- Tracing the most contributing worst case substances
  CuCl, ZnO, $Pb_3(PO_4)_3$, $Ni_3(PO_4)_2$
- All M factors assumed to be 1
- Application of 5 summation methods

	Concentration limit, %	TOTAL CONTENT ASSESSMENT, %	Criteria
Method 1	25	8.2	H400
No M factors	25	318.7 √	**100*H410** + 10*H411 + H412
No cut-off values	25	7.0	H410 + H411 + H412 + H413
Method 2	25	8.2	M*H400 (M=1)
H400, H410: 0.1%			
H411, H412: 1%	25	28.0	**10*H410** + H411
Method 3	0.1	3.1	H410
	2.5	0.4	H411
No M factors	25	3.3	H412
No cut-off values	25	0.2	H413
Method 4	2.5	3.1	M***H410** (M=1)
No cut-off values	25	0.4	H411
Method 5	25	8.2	H400
Method 1	25	283.5 √	**100*H410** + 10*H411 + H412
Cut-offs from Method 2	25	6.0	H410 + H411 + H412 + H413

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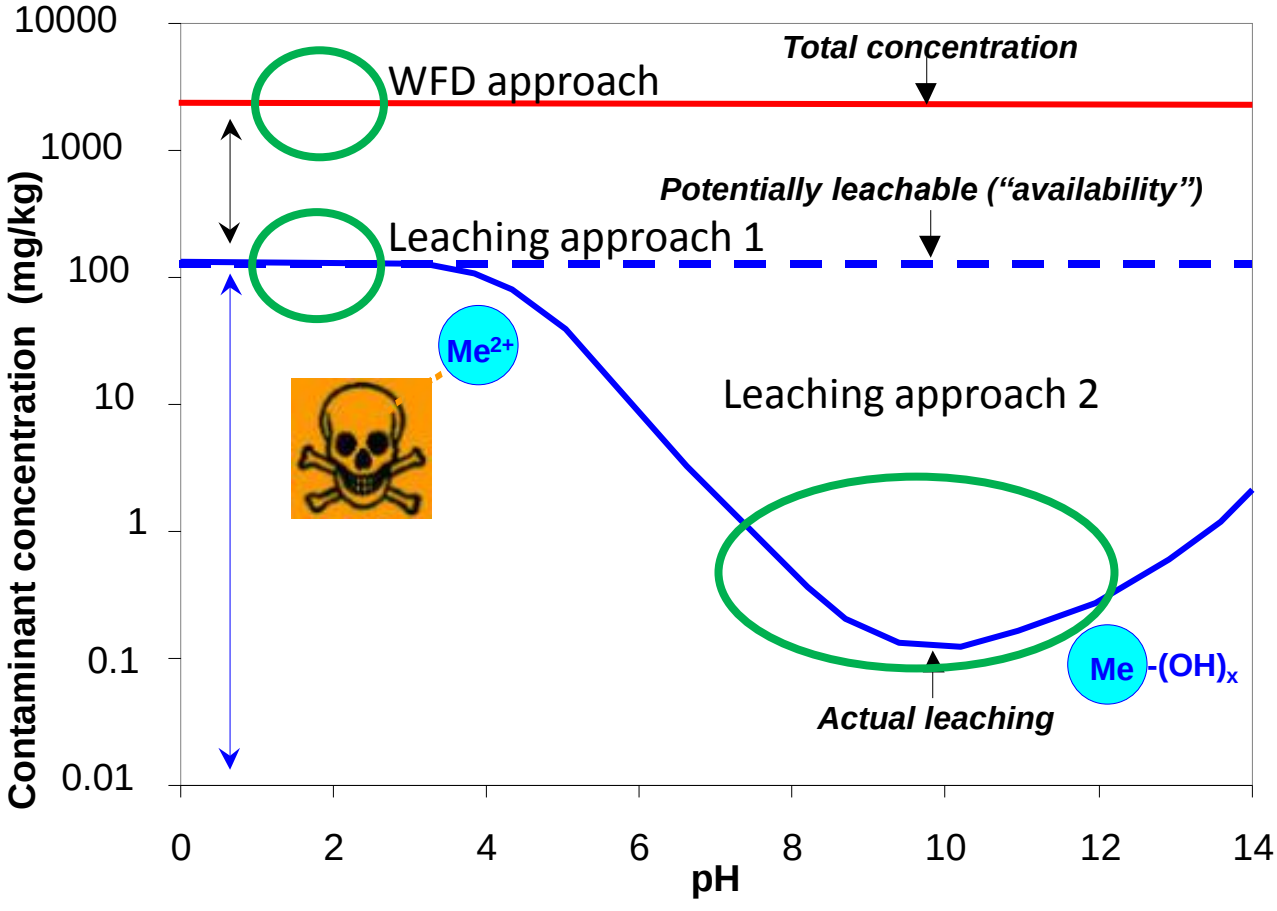
effect of cut-off values

Why is leaching a relevant mechanism?

- Ecotoxic effects are posed only when substances are in solution (ECHA guidance)

- Exposure from eco toxic substances is limited by their solubility and availability in the water phase

Total composition versus leaching



- Not the total content is relevant but potential and actual leaching!
- Leaching depends strongly on pH for most elements

	Concentration limit, %	AVAILABILITY DATA at pH=2, %	Criteria
Method 1	25	1.2	H400
No M factors	25	100.0 √	**100*H410** + 10*H411 + H412
No cut-off values	25	2.3	H410 + H411 + H412 + H413
Method 2	25	1.2	M*H400 (M=1)
H400, H410: 0.1%	25	9.6	**10*H410** + H411
H411, H412: 1%			
Method 3	0.1	1.0	H410
	2.5	0.0	H411
No M factors	25	1.3	H412
No cut-off values	25	0.0	H413
Method 4	2.5	1.0	M***H410** (M=1)
No cut-off values	25	0.0	H411
Method 5	25	1.2	H400
Method 1	25	97.5 √	**100*H410** + 10*H411 + H412
Cut-offs from Method 2	25	2.3	H410 + H411 + H412 + H413

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effect of cut-off values

	Concentration limit, %	LEACHED DATA at pH 7-12, %	Criteria
Method 1	25	**1.2**	H400
No M factors	25	**4.5**	**100*H410** + 10*H411 + H412
No cut-off values	25	**1.3**	H410 + H411 + H412 + H413
Method 2	25	**1.2/12/120**	M*H400 **(M=1/10/100)**
H400, H410: 0.1%	25	**0.0**	**10*H410** + H411
H411, H412: 1%			
Method 3	0.1	**0.0**	H410
	2.5	**0.0**	H411
No M factors	25	**1.3**	H412
No cut-off values	25	**0.0**	H413
Method 4	2.5	**0.0/0.3/3**	M***H410** **(M=1/10/100)**
No cut-off values	25	**0.0**	H411
Method 5	25	**1.2**	H400
Method 1	25	**1.3**	**100*H410** + 10*H411 + H412
Cut-offs from Method 2	25	**1.3**	H410 + H411 + H412 + H413

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effect of M-factors

HP 14 summary

	Total content M = 1	Max leached at pH = 2 M = 1	Leached at pH 7 - 12 M = 1	Leached at pH 7 - 12 M = 10	Leached at pH 7 - 12 M = 100
Non-hazardous		M2, M4	M1, M2, M3, M4, M5	M1, M2, M3, M4, M5	M1, M3, M5
Hazardous	M1, M2, M3, M4, M5	M1, M3, M5			M2, M4

Conclusions

- **HP1 – HP9, HP11-HP13, HP15 are not displayed by MSWI bottom ash**

- **HP 10 (toxic for reproduction)**

  No hazard for bottom ash samples with Pb < 3500mg/kg

  No distinction between massive (non hazardous) and powder forms

  3969mg/kg as 95percentile for Pb

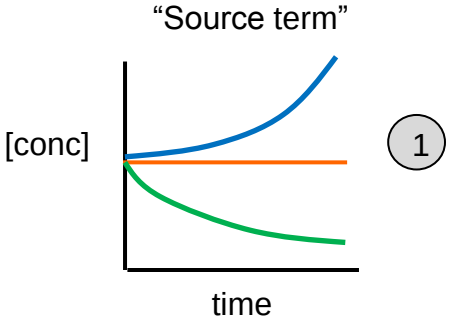
  Dataset revision suggested

- HP 14 (Ecotoxic)

  Hazardous for bottom ash using any of the 5 methods

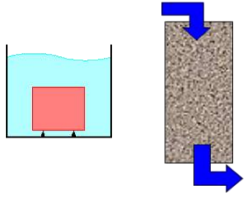
  Towards a more risk-based approach using leaching would give a more realistic and workable solution

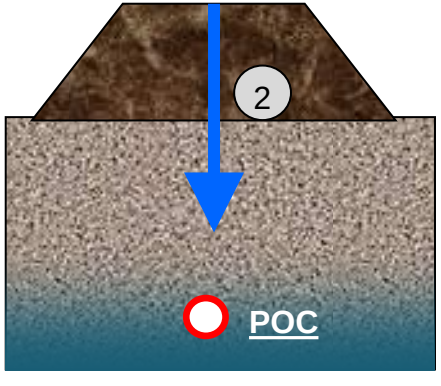
Outlook: HP14 based on risk assessment



Iterations

emission criterion (e.g., leaching test)





Iterations until concentration at POC meets groundwater criterion

4

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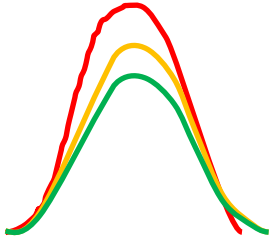

Impact assessment system consistent with CENT/TS 16637-1

Thank you for your attention!

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