Stabilization of heavy metals using low-grade magnesia EAFD, Portland and Sorel cement

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Stabilization/Solidification

- Stabilization/solidification (S/S) aims to convert hazardous substances to more stable chemical forms that are much less soluble, mobile and toxic, using various additives.

- Portland cement, hydrated lime, phosphoric compounds, pozzolanic materials, such as fly ash, have been commonly used as stabilizing additives in the S/S processes.

- Stabilization refers to those techniques that reduce the hazardous behavior of wastes by means of chemical reactions, whereas solidification refers to techniques that can generate a monolithic solid of high structural integrity.

- Stabilized/solidified wastes can be safely disposed into the environment with minimal risk of leaching toxic substances and polluting surface water or groundwater resources.

Magnesia (MgO)

- MgO is a Grecian Magnesite S.A. product (microcrystalline caustic calcined MgO)
- Nominal purity 83.4%
- Impurities: CaO, SiO_2, Al_2O_3, Fe_2O_3, SO_3
- Specific surface area 32 m^2/g, milled below 200 μm

- MgO: A widest spectrum of applications, such as agricultural, industrial & chemical, construction, steel & refractories & environmental
- Environmental applications: Flue gas treatment, soil decontamination and remediation, domestic and industrial solid waste treatment

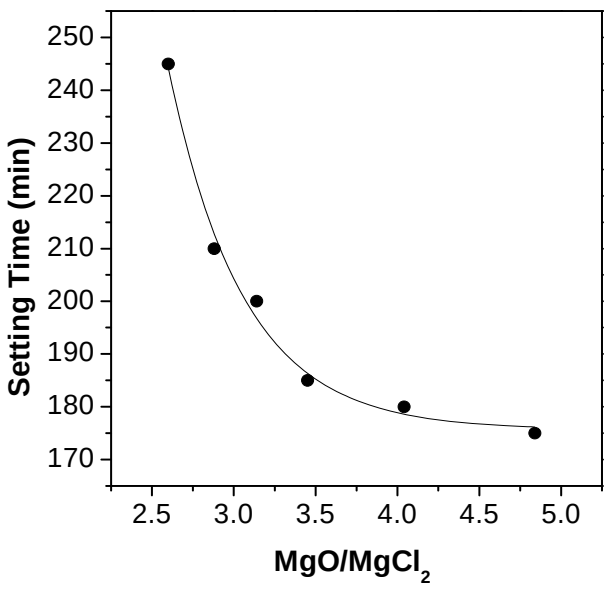
Magnesia cement

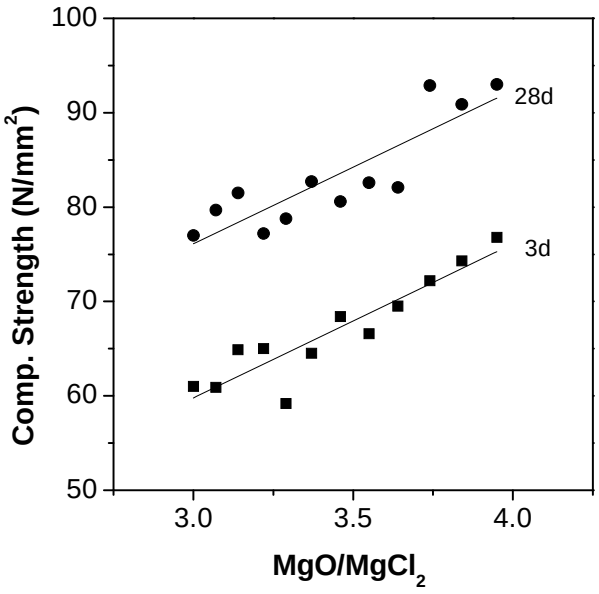
- Magnesium Oxychloride Cement (MOC) or Sorel Cement:

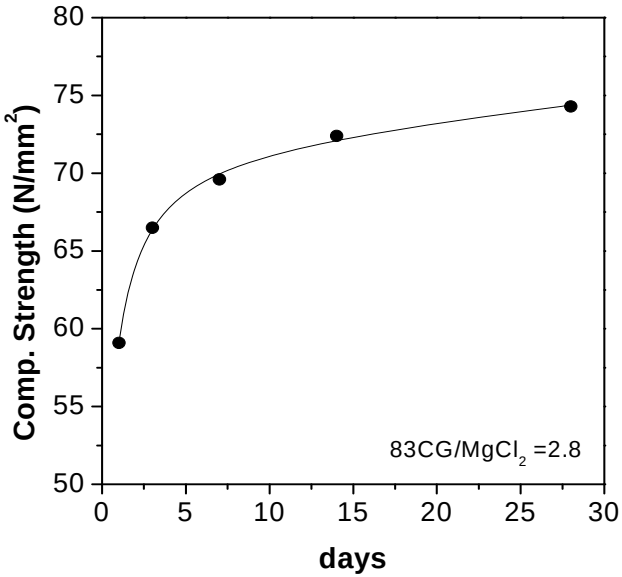
  $3MgO + MgCl_2 + 11H_2O \rightarrow 3Mg(OH)_2.MgCl_2.8H_2O$ (phase 3)

  $5MgO + MgCl_2 + 13H_2O \rightarrow 5Mg(OH)_2.MgCl_2.8H_2O$ (phase 5)
- High strength, abrasion resistance & bonding
- MOC lower water resistance than MPC
- Magnesium Phosphate Cement (MPC):

  $MgO + phosphate + H_2O \rightarrow phosphate\ phase$







Portland cement

- Ordinary Portland Cement (OPC): CEM II type
- High resistance (42.5 MPa)

Toxic elements could be fixed in the resulting hydrated compound through the respective hydration reaction:

$A + B + H_2O \rightarrow H(M)OH_2$

where

A: OPC

B: waste containing heavy metals

M: heavy metal

$H(M)OH_2$: hydrated compound containing M

Characterization of EAFD

➢ EAFD is a by-product of steel production in scrap recycling facilities

EAFD → L/S 10 L/kg, 10 rpm, 24 h

EN 12457-4 Standard leaching test

Decision 2003/33/EC
EAFD cannot be accepted in hazardous waste landfills (50 mg Pb/kg)

		mS/cm	mV
	pH	**EC**	**Redox**
EAFD	12.3	18.0	+41

	mg/kg of dry substance										
	As	**Ba**	**Cd**	**Cr total**	**Cu**	**Hg**	**Ni**	**Pb**	**Sb**	**Se**	**Zn**
EAFD	0.08	2.9	nd	4.4	nd	1.5	nd	650	0.03	1.2	nd

nd: not detected

*Values which exceed the regulation limits for disposal in non-hazardous waste landfills (Decision 2003/33/EC)

**Values which exceed the regulation limits for disposal in hazardous waste landfills (Decision 2003/33/EC)

Characterization of Pb-RFD

- Pb-RFD is produced during secondary lead production

Pb-RFD → L/S 10 L/kg, 10 rpm, 24 h

EN 12457-4 Standard leaching test

Decision 2003/33/EC
Pb-RFD cannot be accepted in hazardous waste landfills (5 mg Sb/kg)

		mS/cm	mV
	pH	**EC**	**Redox**
Pb-RFD	11.2	17.6	+456

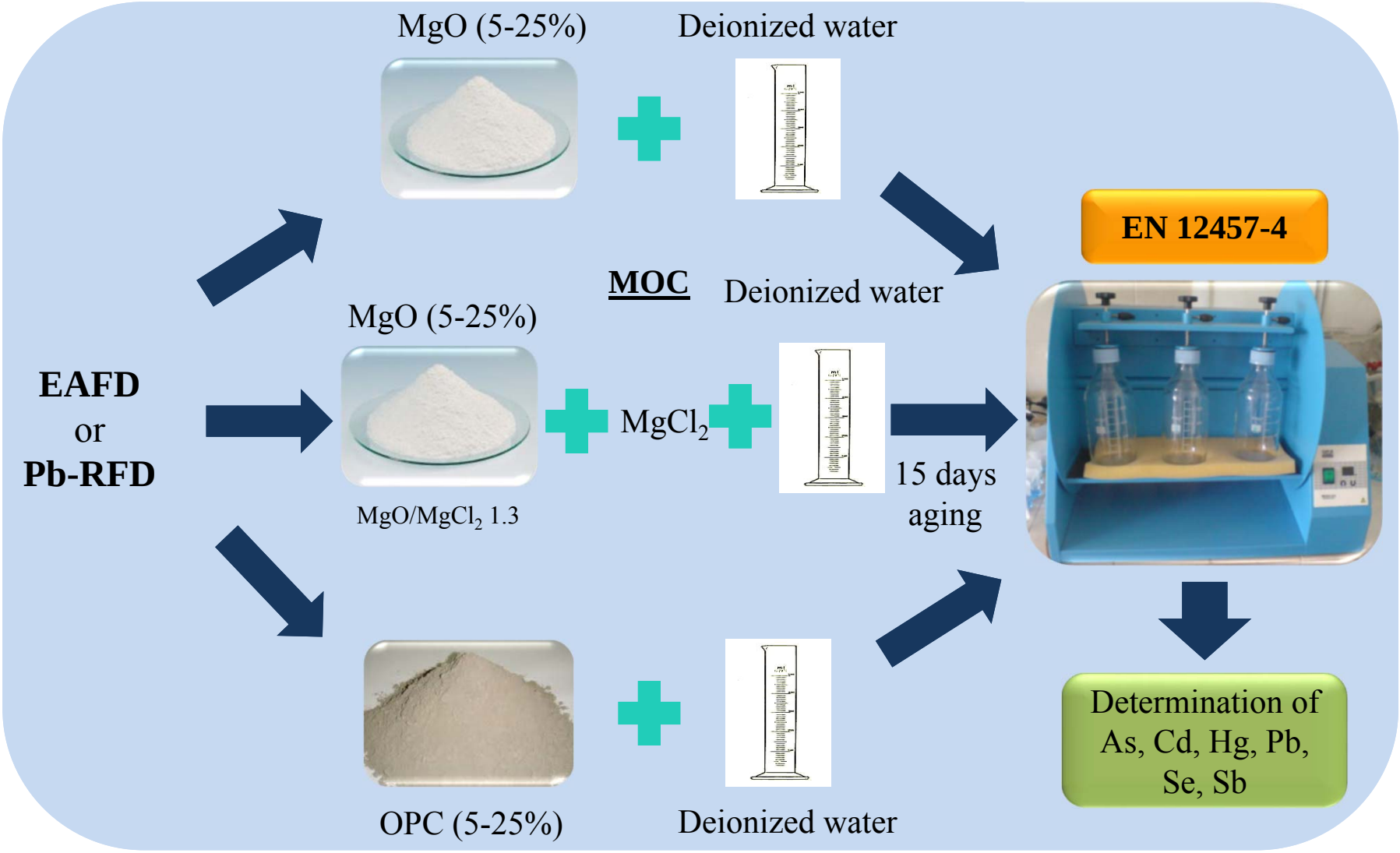
	mg/kg of dry substance										
	As	**Ba**	**Cd**	**Cr total**	**Cu**	**Hg**	**Ni**	**Pb**	**Sb**	**Se**	**Zn**
Pb-RFD	4.5	1.0	2.2	0.6	0.4	1.5	nd	11	12	4.3	nd

nd: not detected

*Values which exceed the regulation limits for disposal in non-hazardous waste landfills (Decision 2003/33/EC)

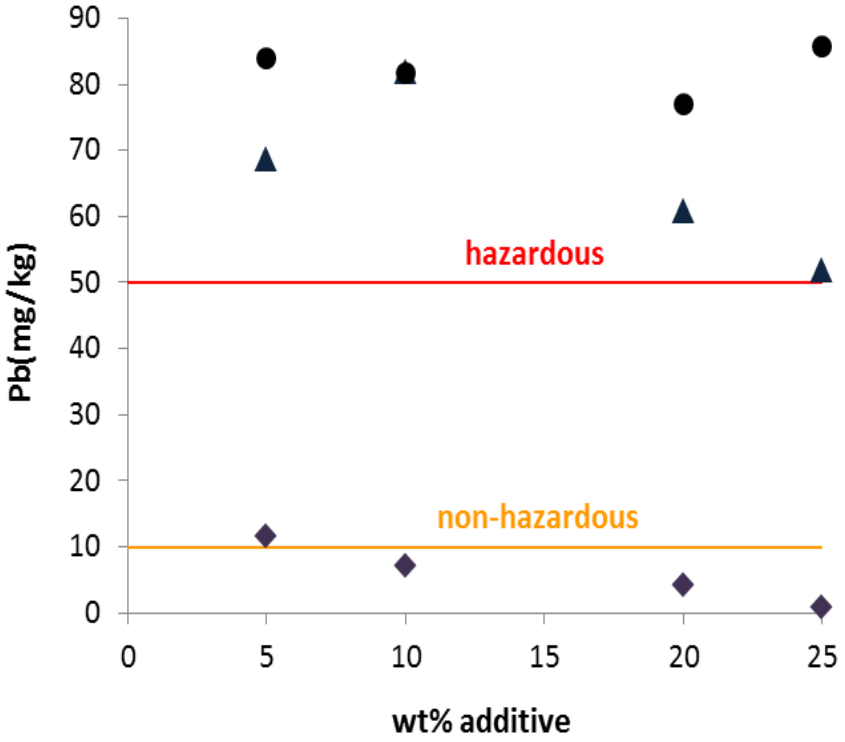
**Values which exceed the regulation limits for disposal in hazardous waste landfills (Decision 2003/33/EC)

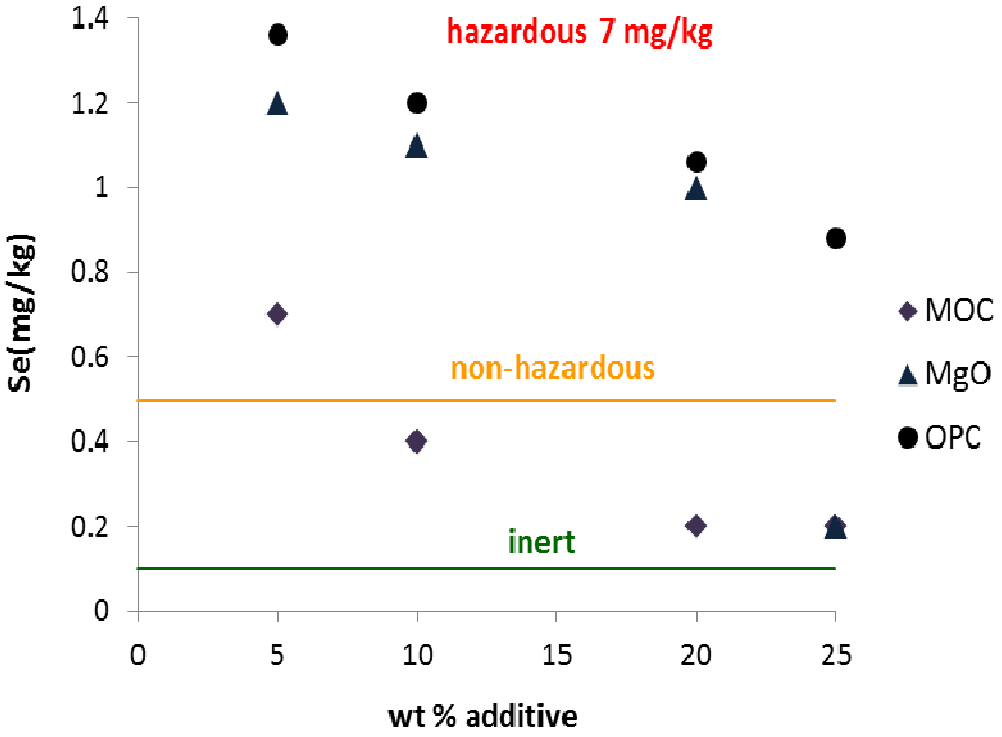
Stabilization: Method



Stabilization of EAFD: Results

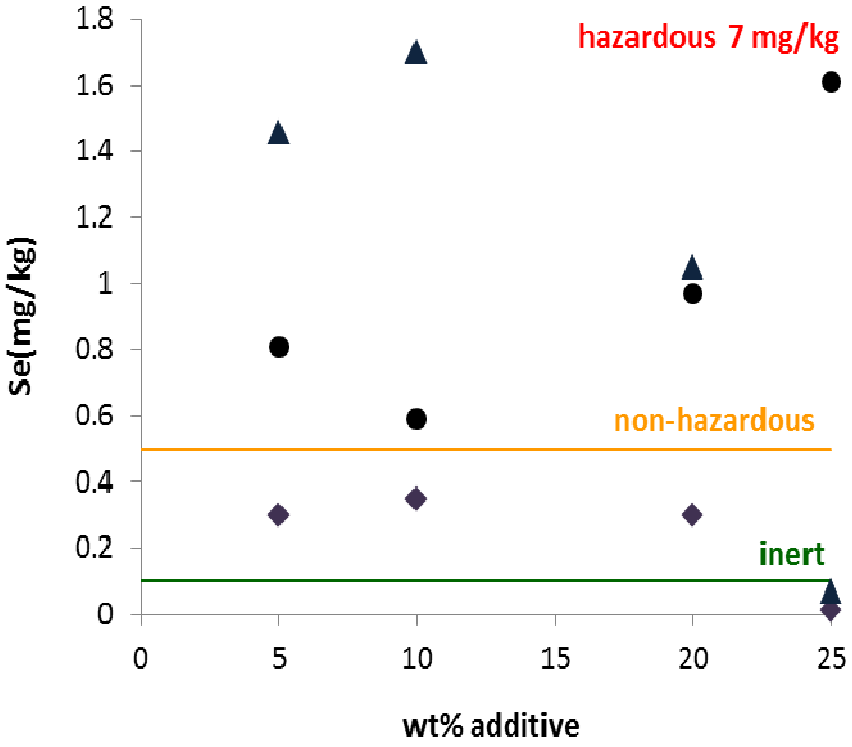
- MOC: Hg nd
- OPC: Hg nd, MgO: Hg nd/0.01 mg/kg (< limit values of non-hazardous wastes)
- MgO: pH 11.0-12.0, OPC: pH 11.5-12.0, MOC: pH 9.8-10.2
- MOC: very good bonding behavior, significantly decreased leaching of Hg, Pb and Se

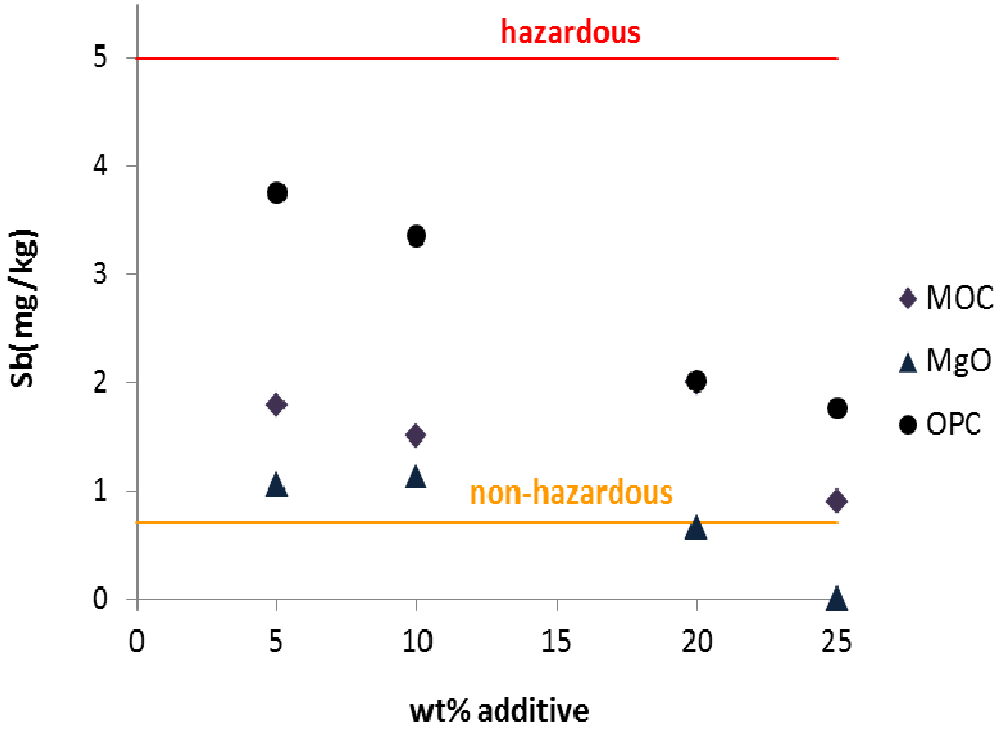




Stabilization of Pb-RFD: Results

- MOC: As, Cd, Hg, Pb nd
- MgO, OPC: As, Cd, Hg, Pb < limit values of non-hazardous wastes
- MgO: pH 10.0-11.0, OPC: pH 10.5-11.0, MOC: pH 9.5-10.0
- MOC: very good bonding behavior, significantly decreased leaching of heavy metals





Stabilization of wastes using MPC: Method

MPC

EAFD or **Pb-RFD**

MgO (5-25%)

MgO/phosphate 0.3

phosphate

Deionized water

15 days aging

EN 12457-4

Determination of As, Cd, Hg, Pb, Se, Sb

Stabilization of wastes using MPC: Results

EAFD

EAFD				mg/kg of dry substance
wt % MgO	**pH**	**Hg**	**Pb**	**Se**
5	10.1	0.12	4.4	0.12
10	10.5	0.01	3.0	0.14

- MPC: very good bonding behavior, significantly decreased leaching of Hg, Pb and Se (below the limit values of non-hazardous wastes)

Pb-RFD

- MPC: very good bonding behavior, significantly decreased leaching of heavy metals

Pb-RFD							mg/kg of dry substance
wt % MgO	**pH**	**As**	**Cd**	**Hg**	**Pb**	**Sb**	**Se**
10	10.3	0.2	nd	0.04	1.7	2.8	0.8
20	10.6	0.2	nd	0.02	0.2	0.7	0.3

nd: not detected

*Values which exceed the regulation limits for disposal in non-hazardous waste landfills (Decision 2003/33/EC)

Conclusions

- EAFD and Pb-RFD cannot be accepted in hazardous waste landfills.
- Using only MgO or OPC manages to reduce heavy metal's leaching, above the expected dilution, but not below the limit values for non-hazardous waste landfills.
- The proposed stabilization process, using magnesia cement (MOC, MPC), is an effective method for heavy metal immobilization.
- Stabilized EAFD with MOC: Pb, Hg & Se are below the maximum limits for non-hazardous waste landfills, when using MgO above 10 wt%.
- Stabilized EAFD with MPC: Pb, Hg & Se are below the maximum limits for non-hazardous waste landfills, when using MgO above 5 wt%
- Stabilized Pb-RFD with MOC or MPC: As, Cd, Hg, Pb, Sb & Se are below the maximum limits for non-hazardous waste landfills, when using MgO above 20 wt%.

Acknowledgements

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Thank you for your attention

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