31st International Conference of

Society for Environmental Geochemistry & Health

Heavy metal stabilization in EAFD using magnesia and Sorel cements

22-26 June 2015

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Introduction

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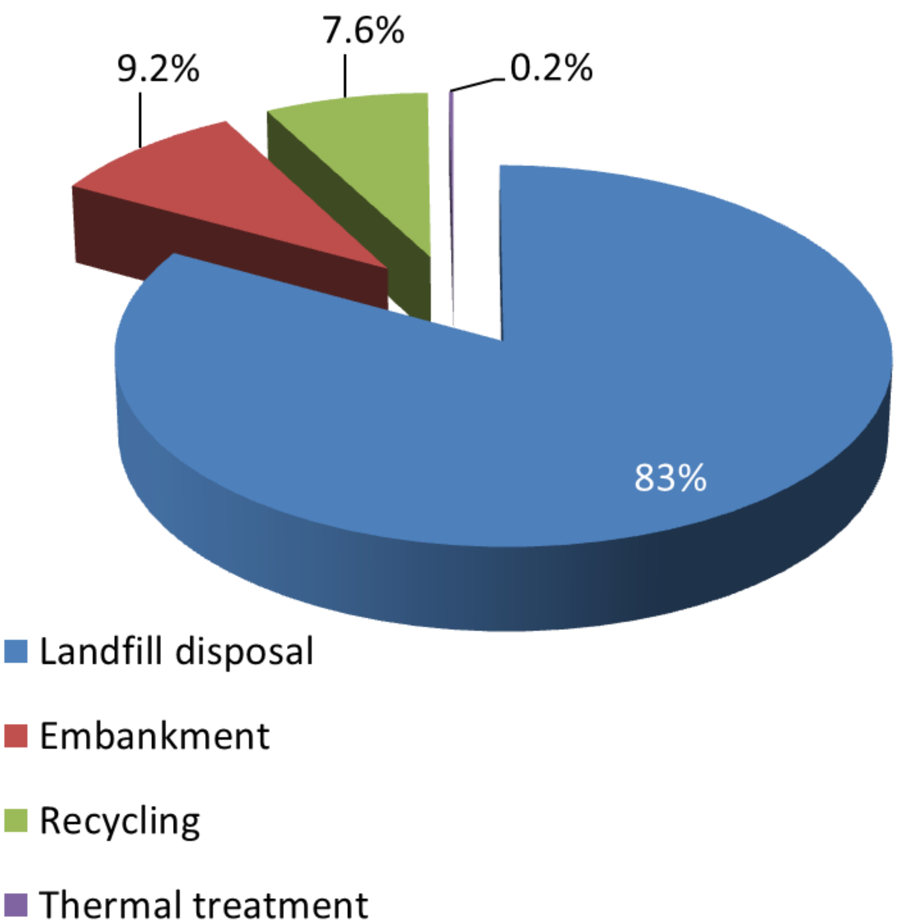
Industrial solid waste management in Greece



Major problem
Temporarily stored solid wastes next to industrial sites and illegal disposal

- Stabilization/solidification aims to convert hazardous substances to more stable chemical forms that are much less soluble, mobile and toxic, using various additives, such as portland and magnesia cements.
- Stabilized wastes can be safely disposed into the environment with minimal risk of leaching toxic substances and polluting surface water or groundwater resources.

Magnesia – MgO

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- MgO is a Grecian Magnesite S.A. product: microcrystalline caustic calcined MgO
- Nominal purity 83.41% (grade 83 CG)
- 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, i.e. agricultural, industrial & chemical, construction, steel & refractories & environmental
- Environmental applications: Flue gas treatment, soil decontamination and remediation, domestic and industrial solid waste treatment

Magnesia cements

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- Two types of magnesia cements:

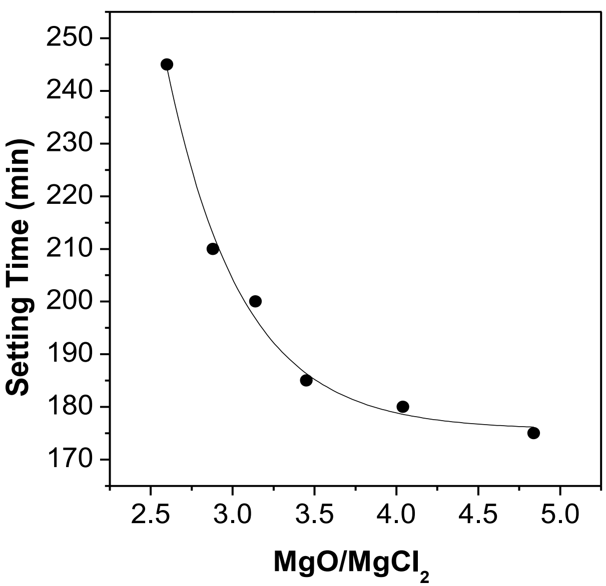
(a) Magnesium Oxychloride Cement (MOC) or Sorel Cement:

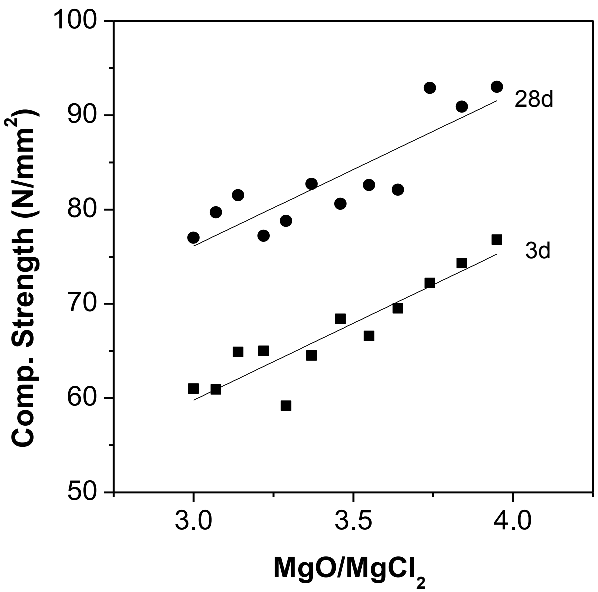
$5MgO + MgCl_2 + 13H_2O \rightarrow 5Mg(OH)_2.MgCl_2.8H_2O$ (phase 5)

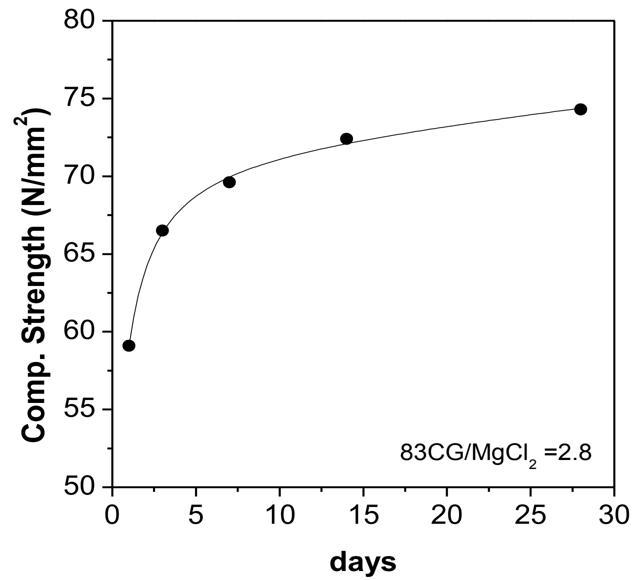
(b) Magnesium phosphate cement (MPC):

MgO + phosphate + $H_2O \rightarrow$ phosphate phase

- MOC, MPC: High strength, abrasion resistance & bonding
- MOC: lower water resistance than MPC







Electric arc furnace dust

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- EAFD is a by-product of steel production
- It contains Zn, Fe, Pb & Ca among others
- 15–20 kg EAFD/t of steel is generated

Table 1. Typical composition of EAFD

% wt. dry substance									
Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	PbO	SiO_2	ZnO	LOI
0.9	4.6	33.9	1.4	0.7	3.3	6.2	4.1	34.9	7.8

The current situation in Greece:

- Hydrometallurgical processes for heavy metal recovery from EAFD (Zn, Pb, Fe) have been developed, but the annual produced volume is considered fragmentary for a profitable operation.
- Approximately 30,000–40,000 t/year is produced.
- Almost the entire quantity of EAFD is transported abroad.

Characterization of EAFD

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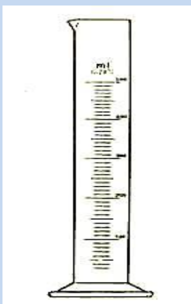
EAFD



Deionized water

EN 12457-2 Standard leaching test

L/S 10 L/kg
10 rpm
24 h

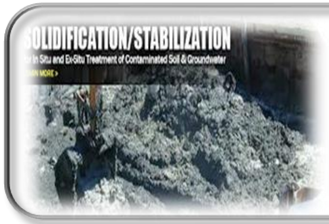
EAFD cannot be accepted in hazardous waste landfills

pH	EC (mS/cm)	Redox (mV)
12.3	18.0	+41

EU Decision 2003/33/EC

mg/kg of dry substance															
As	**Ba**	**Cd**	**Cr total**	**Cu**	**Hg**	**Ni**	**Pb**	**Sb**	**Se**	**Zn**	**F^-**	**Cl^-**	**SO_4^{2-}**	**DOC**	**TDS**
0.08	2.9	nd	4.4	nd	1.5	nd	650	0.03	1.2	nd	31	34000	21200	114	126500

nd: not detected



Stabilization process

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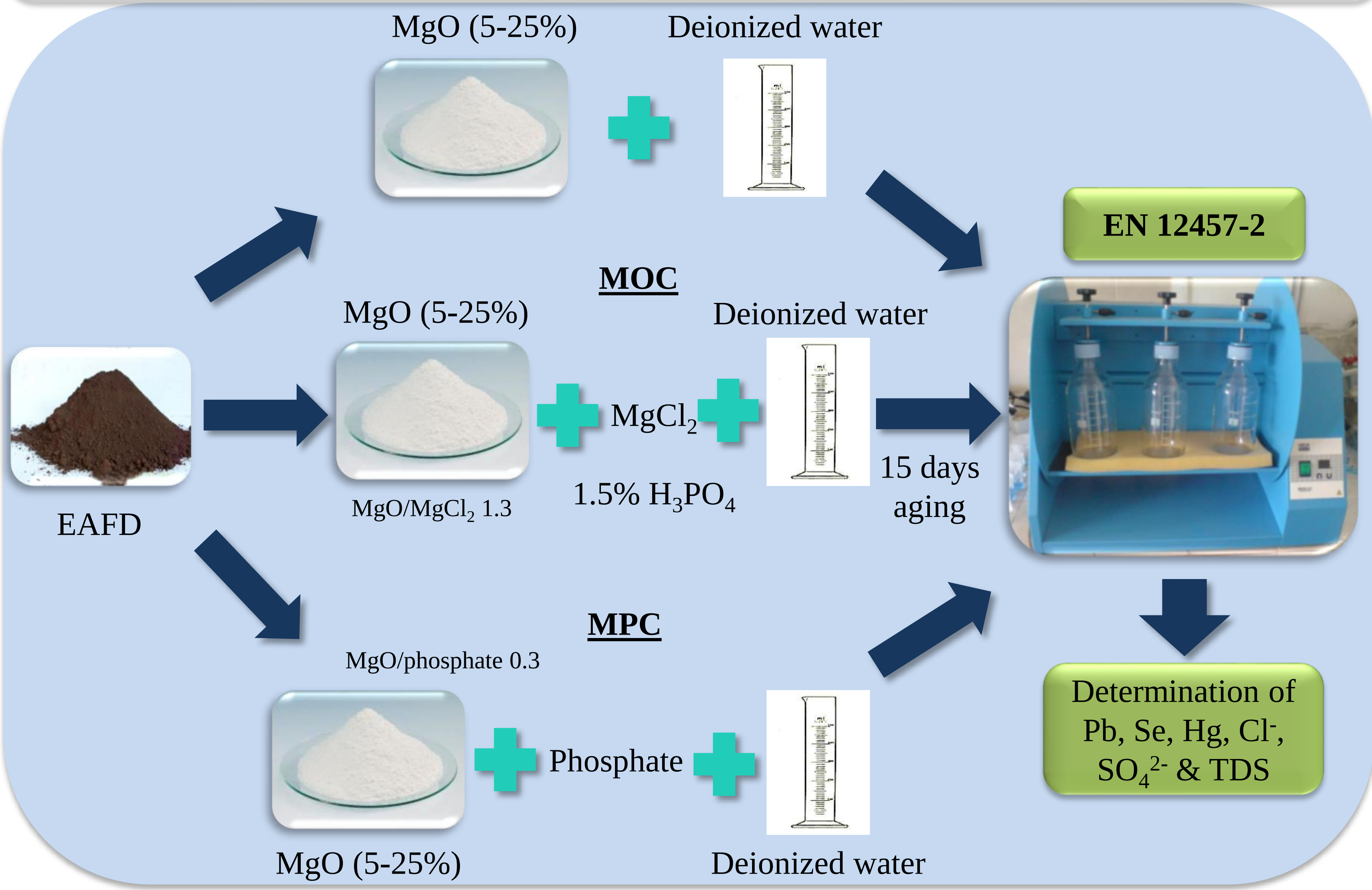

Stabilization - Results

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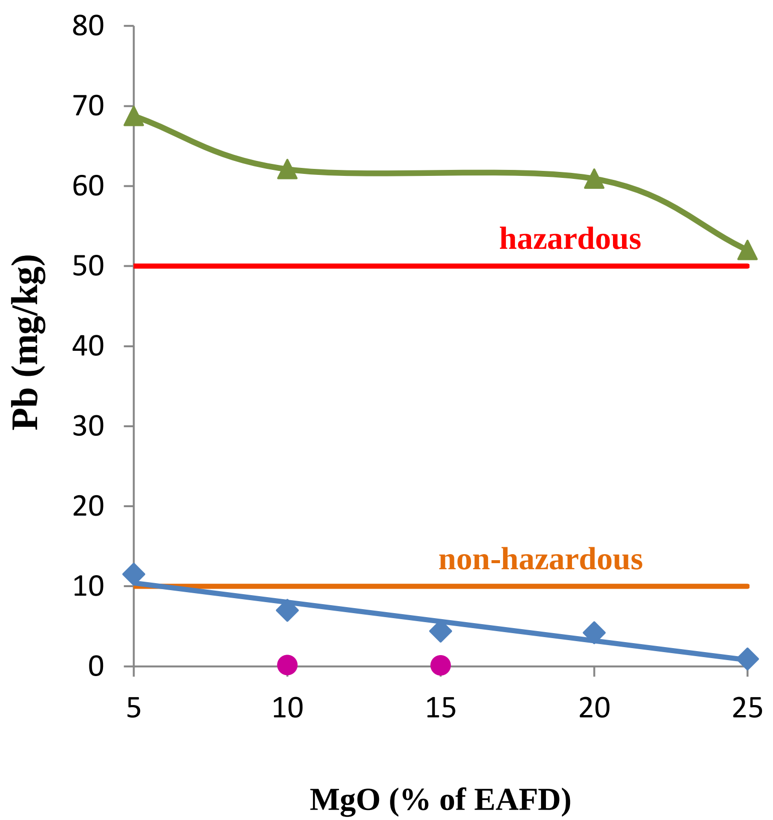
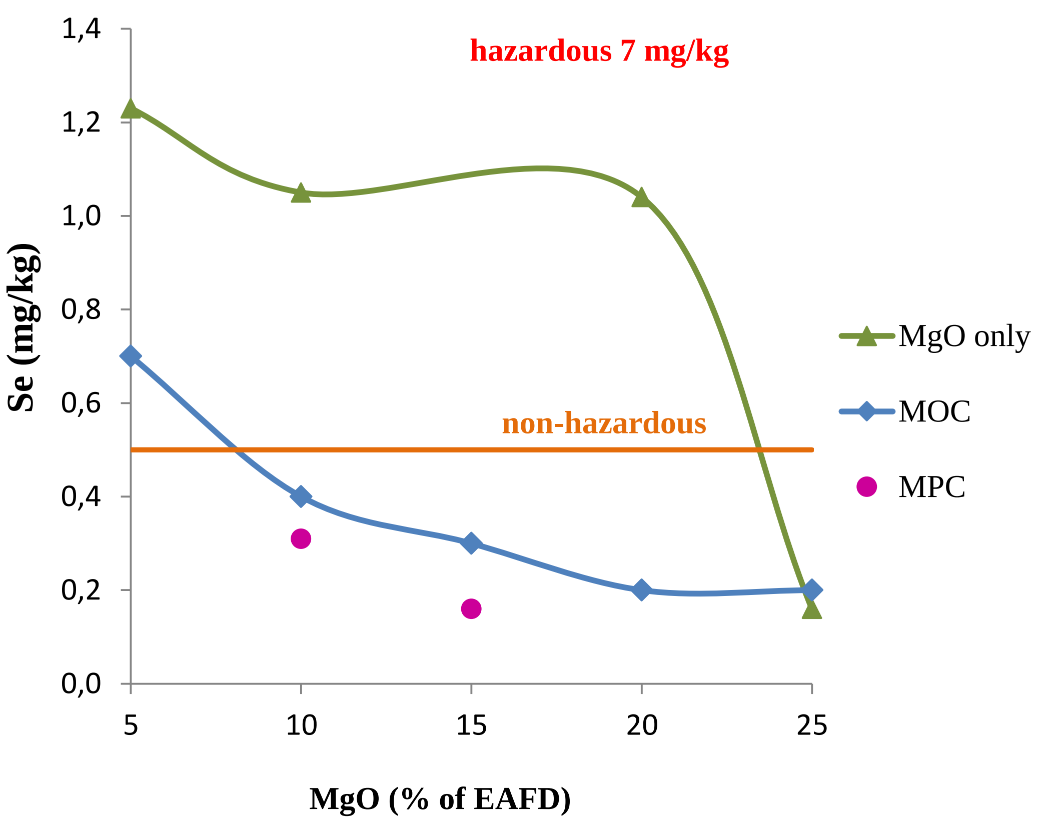
- MgO only: pH ~12.0, MOC: pH 9.8-12.3, MPC: pH 11.4
- MOC, MPC: Hg nd, MgO only: Hg 0.01-0.06 < limit of inert waste
- MgO acts as a buffering agent
- MOC, MPC: very good bonding behavior, significantly decreased leaching of Pb, Se, Hg





Stabilization - Results

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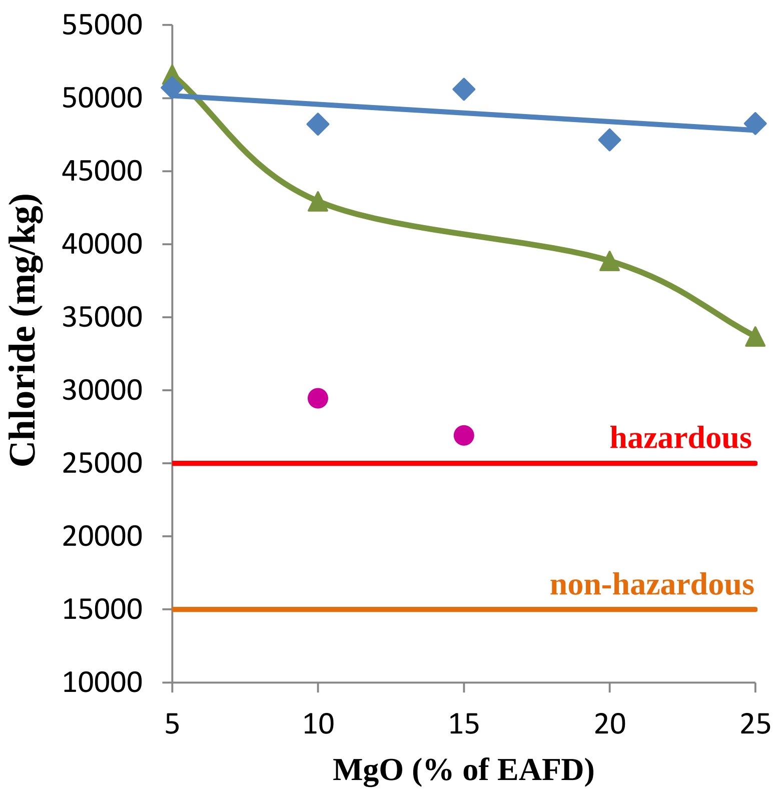
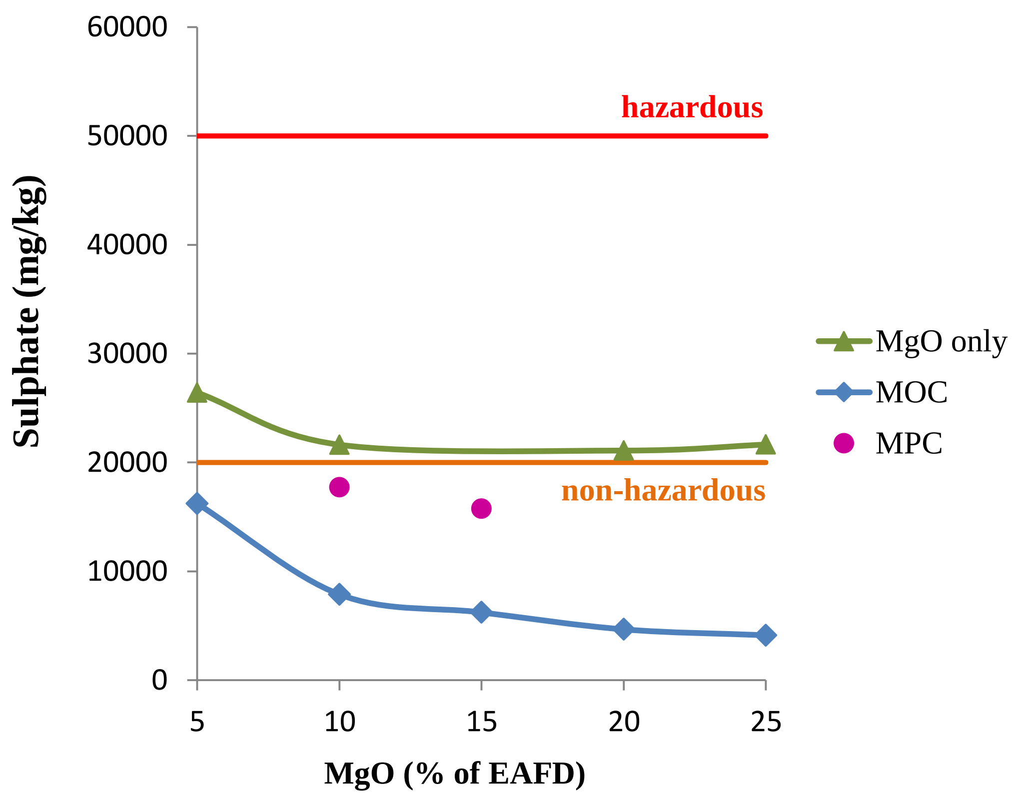
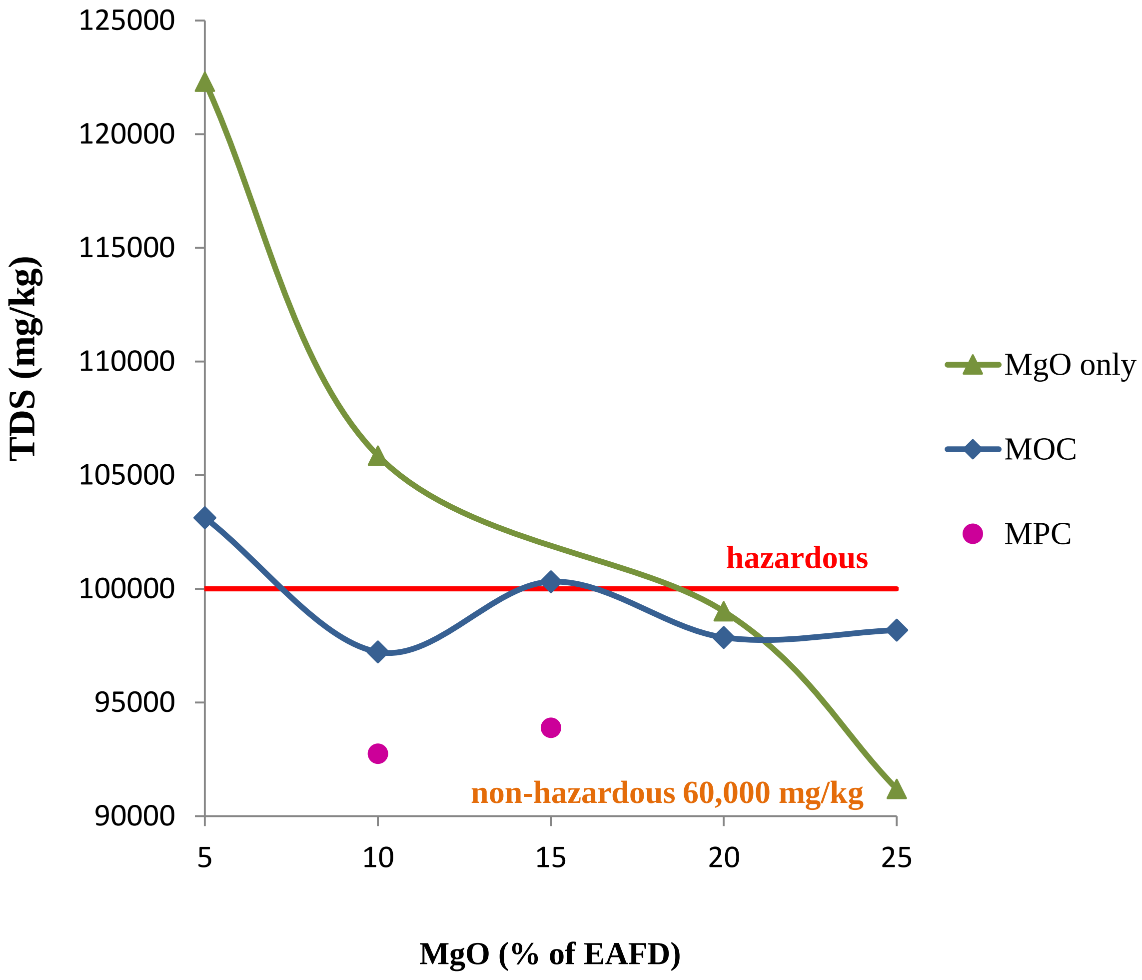
- MOC increases Cl^- leaching
- MOC, MPC: poor water stability
- MPC: Dilution of EAFD with sand (1:1) resulted in a stabilized waste accepted in non-hazardous waste landfills (Cl^- 21,000 mg/kg)
- MOC, MPC: SO_4^{2-} < limit of non-hazardous waste





Stabilization - Results



- TDS can be used alternatively to the values for SO_4^{2-} and Cl^-.
- MOC: TDS below the limit value for waste acceptable in hazardous waste landfills above 10% MgO addition.
- MPC: TDS < limit hazardous waste
- MPC: TDS 66,600 mg/kg when EAFD is diluted with sand 1:1 ratio
- MgO only: TDS below the limit value for waste acceptable in hazardous waste landfills above 20% MgO addition.

Conclusions

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- EAFD may pose a risk to human health and the environment, if not managed and disposed of safely.
- The proposed stabilization process, using magnesia cements (MOC, MPC), is an effective method for heavy metal immobilization.
- Pb, Hg & Se are below the maximum limits for non-hazardous waste landfills, when using MgO above 10% at magnesia cements.
- MOC increases Cl^- leaching, while using MPC does not increase the leached Cl^-. Lower heavy metals leaching in the case of MPC than MOC.
- Using only MgO manages to reduce Pb leaching, but not below the limit value for non-hazardous waste landfills.

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Acknowledgements

This research has been co-financed by the European Union (European Social Fund - ESF) and Greek national funds through the Program "PAVET" – Project: Environmental applications of magnesia and utilization of produced by-products.

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