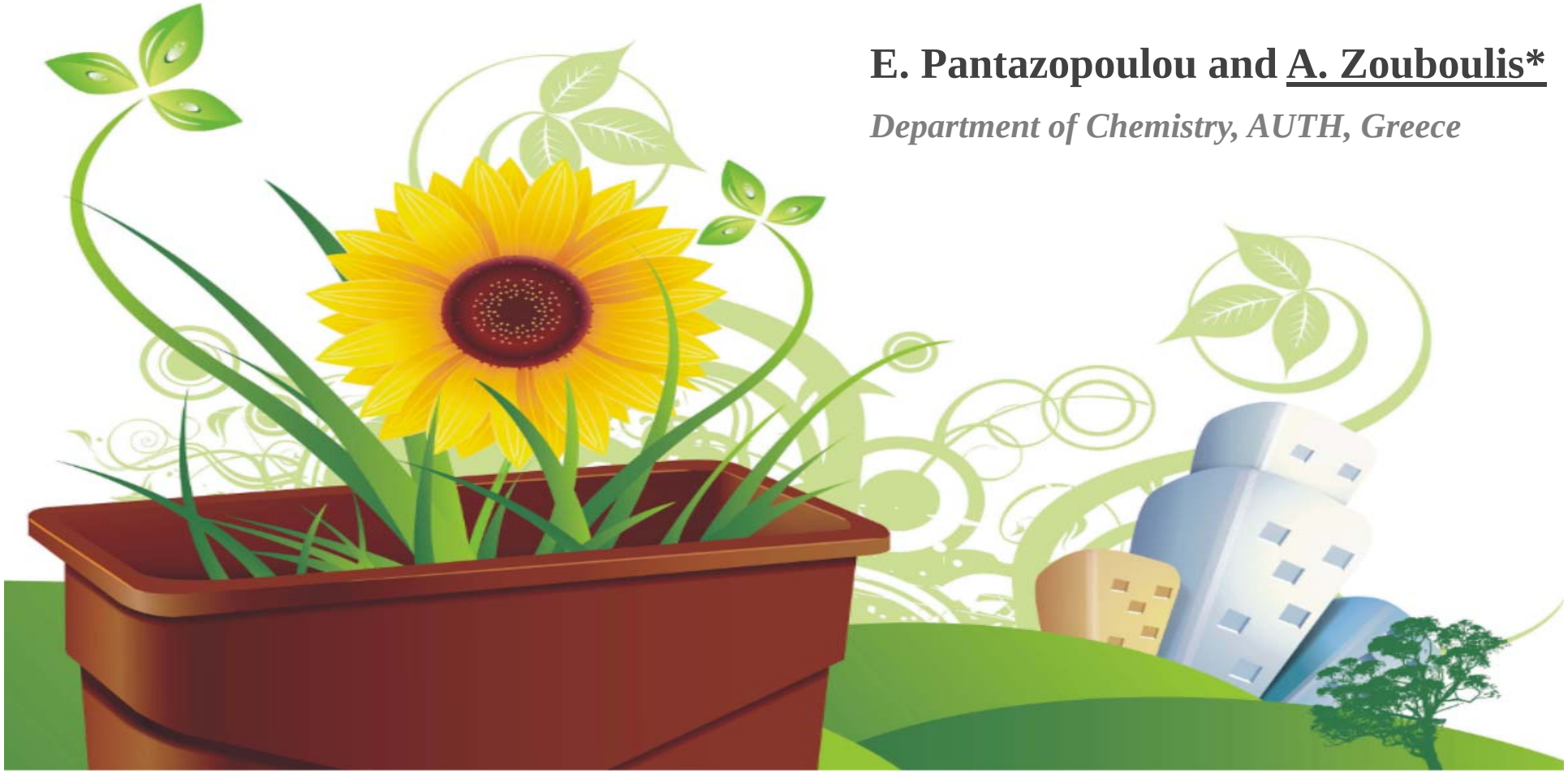
CYPRUS 2016

4th International Conference on
Sustainable Solid Waste Management

Chromium stabilization of tannery sludge by co-treatment with ladle furnace slag



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Outline

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Introduction

Industrial solid waste management in Greece

Stabilization

Tannery sludge

Stabilization additives (ladle furnace slag, organoclay)

Toxicity (chemical toxicity, ecotoxicity)

Characterization of tannery waste

Toxicity evaluation

Chemical toxicity

Ecotoxicity

Conclusions

Introduction

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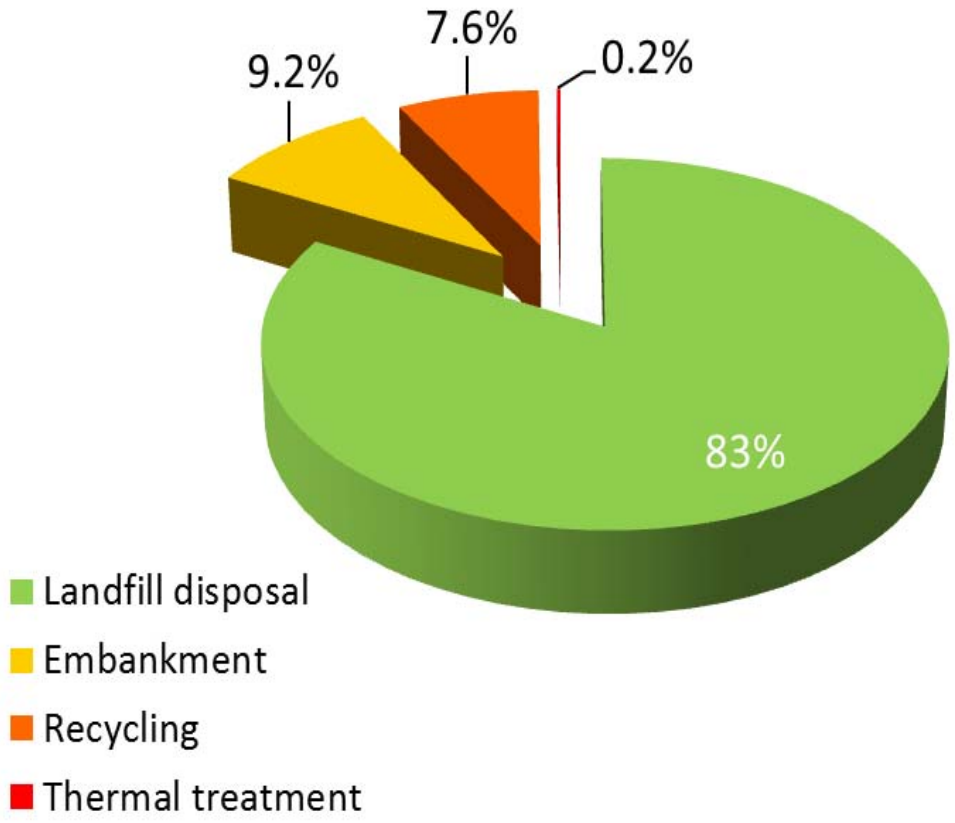
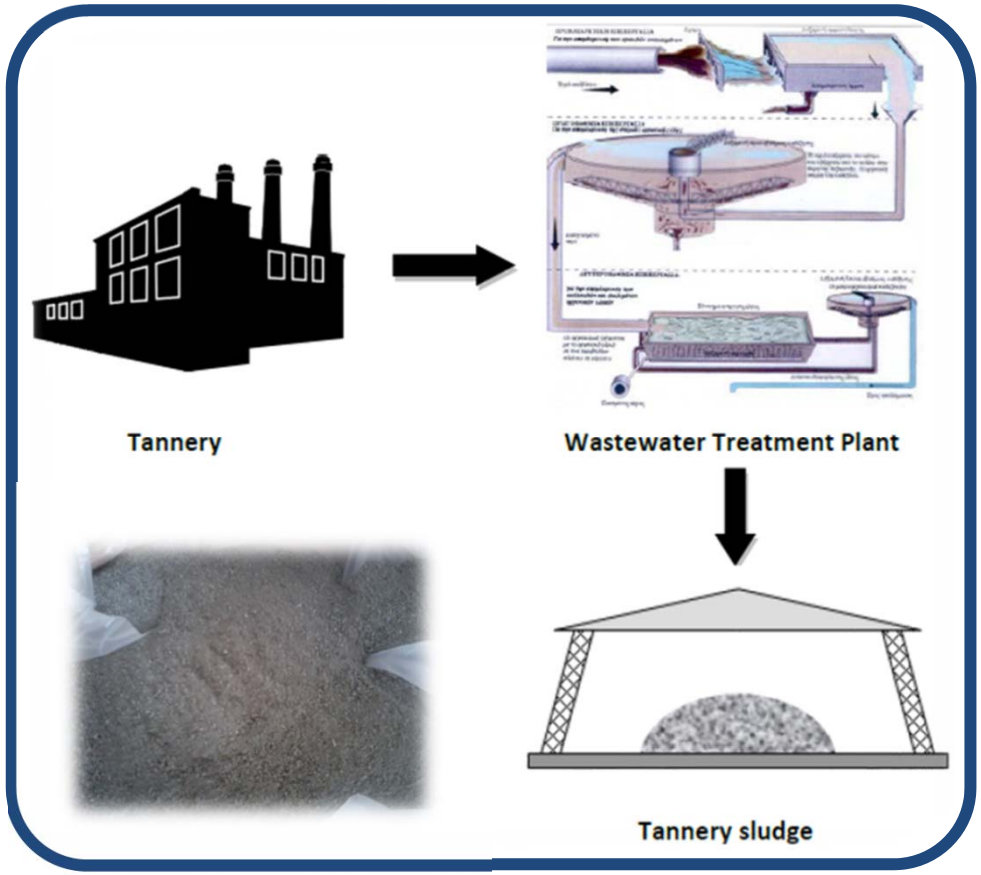
Industrial solid waste management in Greece



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

- Stabilization converts hazardous substances to more stable chemical forms, so that wastes can be safely disposed off with minimum risk of releasing toxic substances.
- The current global trend for the efficient utilization and re-use of available by-products and wastes, favor the use of low-cost sorbent materials (or other industrial wastes) for the co-treatment of heavy metal-contaminated solid wastes.

Tannery sludge



- Leather resistance is achieved through tanning. The tanning process is producing several wastes.
- (Among them) tannery sludge is produced by the chemical precipitation technique before tanning wastewater is allowed to enter the biological treatment.
- The air-dried sludge (tannery waste) contains Cr(III), organic matter, as well as proteins, fats, and salts, such as chlorides and sulfates.
- It is classified as hazardous waste and its direct landfilling is not permitted.

- Tannery sludge is temporary disposed near the wwt plant and is shipped inland or abroad for further treatment and disposal.
- The most common management practice: Stabilization by using cement and/or Fly Ash.
- **Proposed management method: Stabilization using other waste, i.e. ladle furnace slag.**

Stabilization process

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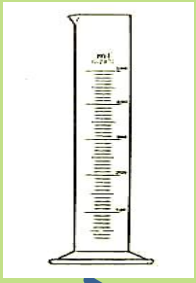
Ladle furnace slag

Deionized water

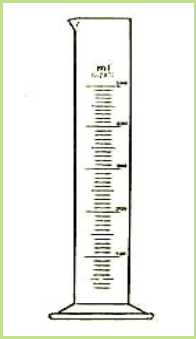


EN 12457-2

Tannery waste

Determination of Cr & DOC

Organoclay



Deionized water

Ladle furnace slag

Stabilization additives

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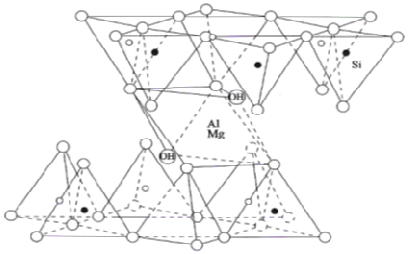
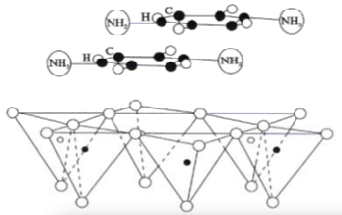
Ladle furnace slag (LFS)

- LFS is produced as a by-product in the final stage of steelmaking, i.e. during steel refining in ladle furnaces.
- Annual European production of LFS, approximately 4 million t.
- LFS is dumped mostly in specific landfills.

% wt. of dry LFS						
Al_2O_3	CaO	Fe_2O_3	MgO	MnO	SiO_2	LOI
9.0	55.0	5.5	7.0	2.0	17.0	4.5





Organoclay

- Organoclay derives from a natural clay mineral by exchanging the original interlayer cations with organic cations (quaternary alkylammonium ions).
- Organoclay has an organophilic surface and a high capacity for interactions with low-soluble organic compounds.

Toxicity evaluation

Chemical toxicity

The standard leaching test (EN 12457-2) is used in order to assess:

a) whether land disposal (or landfilling) of the wastes is an appropriate method of management,

b) the effectiveness of applied waste treatment process, and

c) the (overall) environmental impact of wastes.

Ecotoxicity

- Microtox is an in vitro testing system that uses bioluminescent bacteria to detect toxicity.
- ***Vibrio fischeri*** are non-pathogenic, marine, luminescent bacteria that are sensitive to a wide range of toxicants.
- Microtox can be considered as a primary test to quickly determine which compounds yield certain risks for the environment.

Ecotoxicity

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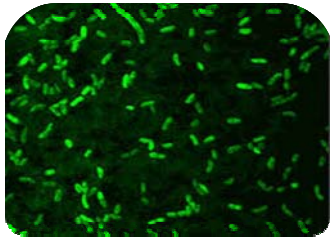
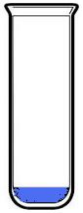
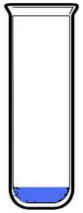
MicrotoxOmni software

- Microtox test is based on the use of luminescent bacteria, *Vibrio fischeri*, which produce light as a by-product of cellular respiration.
- Any inhibition of normal metabolism, exposure to toxic substances, results in a decreased rate of bioluminescence.
- ↑ level of toxicity, ↑ inhibition of light production.
- Microtox M500 analyzer maintains the activated bacteria and the samples at 15ºC and detect the light intensity at 490 nm, the wavelength emitted by the bacteria. The reduction in intensity of light emitted from the bacteria is measured.



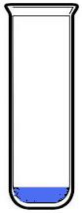


Measure of bioluminescence



Add sample

After 5, 15 & 30 minutes for the leachate



Measure of bioluminescence

Characterization of tannery waste

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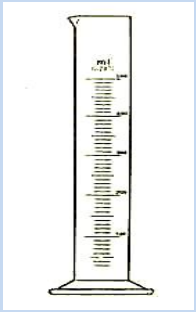
Tannery waste



Deionized water

EN 12457-2
Standard
leaching test

L/S 10 L/kg
10 rpm
24 h

Tannery waste cannot be accepted in hazardous waste landfills (DOC limit value 1,000 mg/kg)

pH	EC (mS/cm)	Moisture (%)
8.5	4.1	10

mg/kg of dry substance

As	Ba	Cd	Cr total	Cu	Mo	Ni	Pb	Se	Zn	F^-	Cl^-	SO_4^{2-}	DOC
0.02	2.5	nd	42	0.8	0.09	1.9	nd	nd	2.3	nd	6,050	9,450	3,700

nd: not detected

Characterization of ladle furnace slag

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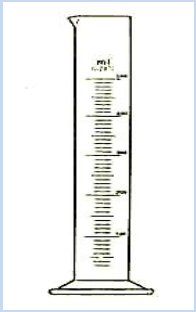
Ladle furnace slag



Deionized water

EN 12457-2 Standard leaching test

L/S 10 L/kg
10 rpm
24 h

LFS can be accepted in non-hazardous waste landfills

pH	EC (mS/cm)	Moisture (%)
12.8	10.5	1.5

mg/kg of dry substance

As	Ba	Cd	Cr total	Cu	Mo	Ni	Pb	Se	Zn	F^-	Cl^-	SO_4^{2-}	DOC
0.04	30	0.02	1.7	nd	0.06	0.03	nd	0.05	0.2	25	90	185	50

nd: not detected

Stabilization - Results

- In all proportions, Cr total is below the limit value for waste acceptable in non-hazardous waste landfills (10 mg/kg).
- Cr leaching was found to decreased with the increase of slag content.
- LFS was successfully used to stabilize Cr, while it cannot stabilize organic matter.
- DOC remains above the limit value for hazardous waste landfills (1,000 mg/kg).

Influence of organoclay addition

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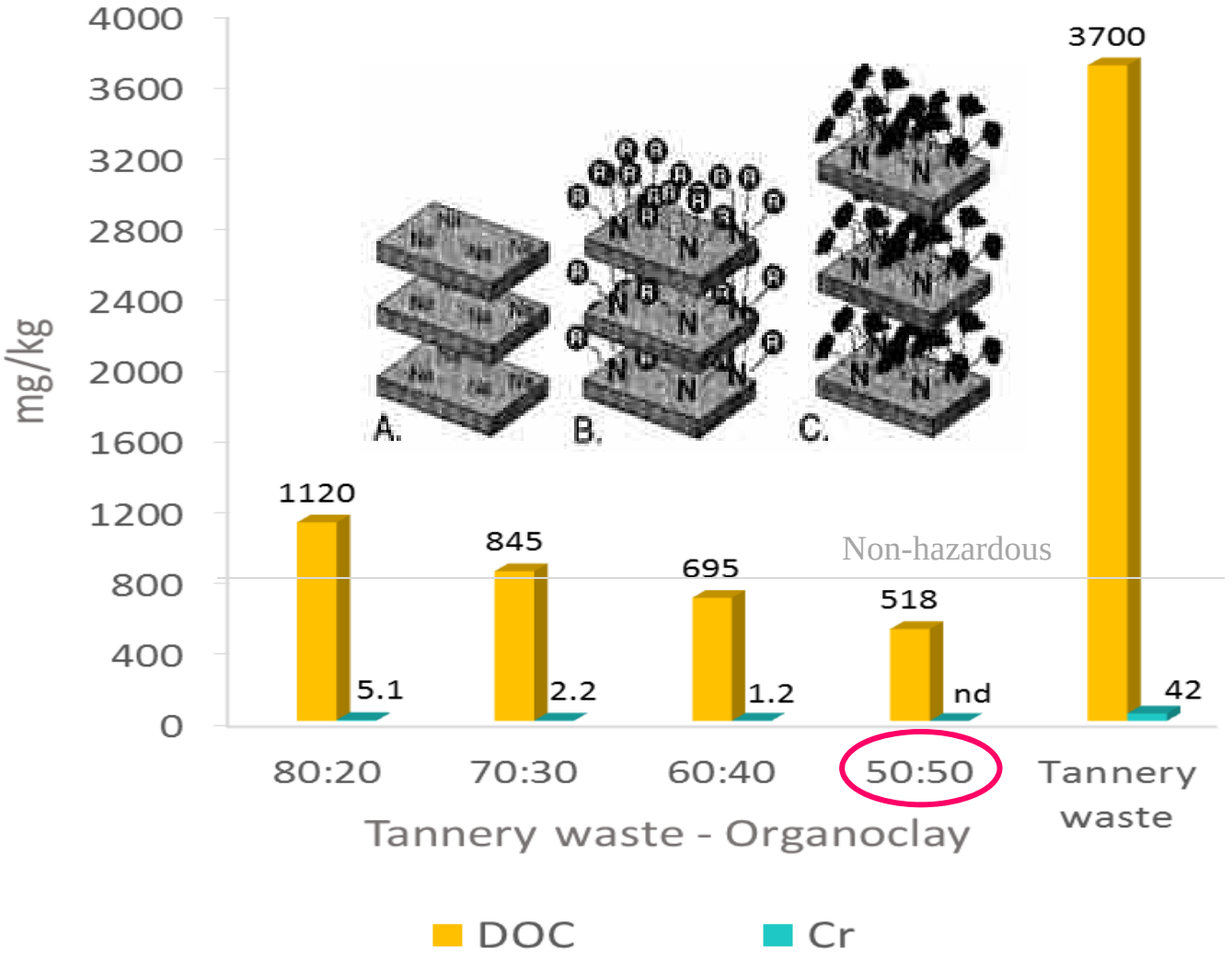
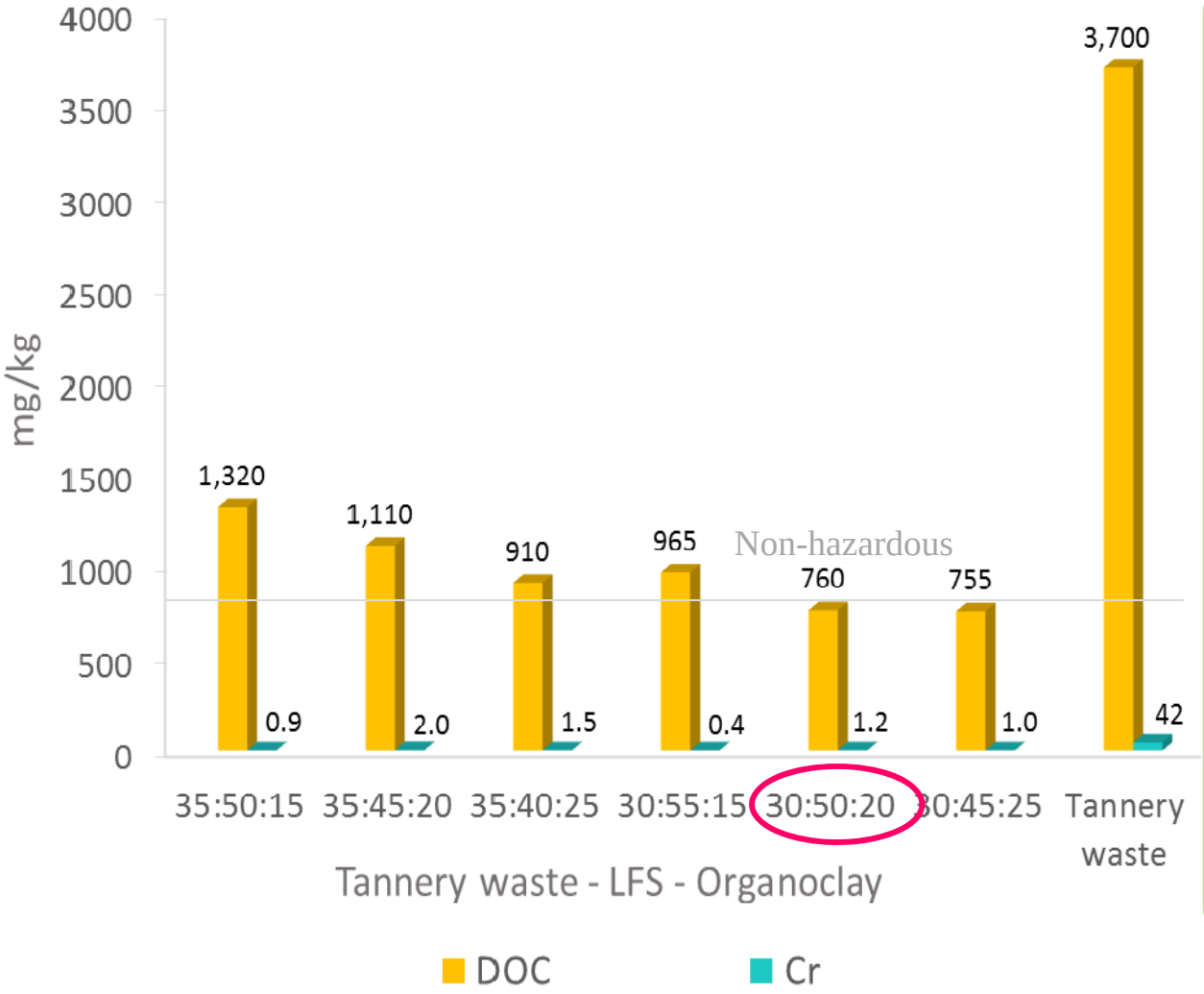


Stabilization - Results



- Cr total is below the limit value for waste acceptable in non-hazardous waste landfills, while DOC is below this limit value for 30:50:20 mass ratio.
- Cr leaching potential decreased about 90%, while DOC up to 32%, beyond the expected reduction of mixing.
- Aluminosilicates and Fe oxides from LFS possess variable charge surfaces for metal adsorption.
- CAH and CSH compounds are formed, due to the reaction of SiO_2 and Al_2O_3 with CaO at alkaline pH.

Stabilization - Results

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- Stabilized tannery waste (tannery waste: LFS: organoclay, 30: 50: 20 mass ratio)

pH	EC (mS/cm)
12.7	8.2

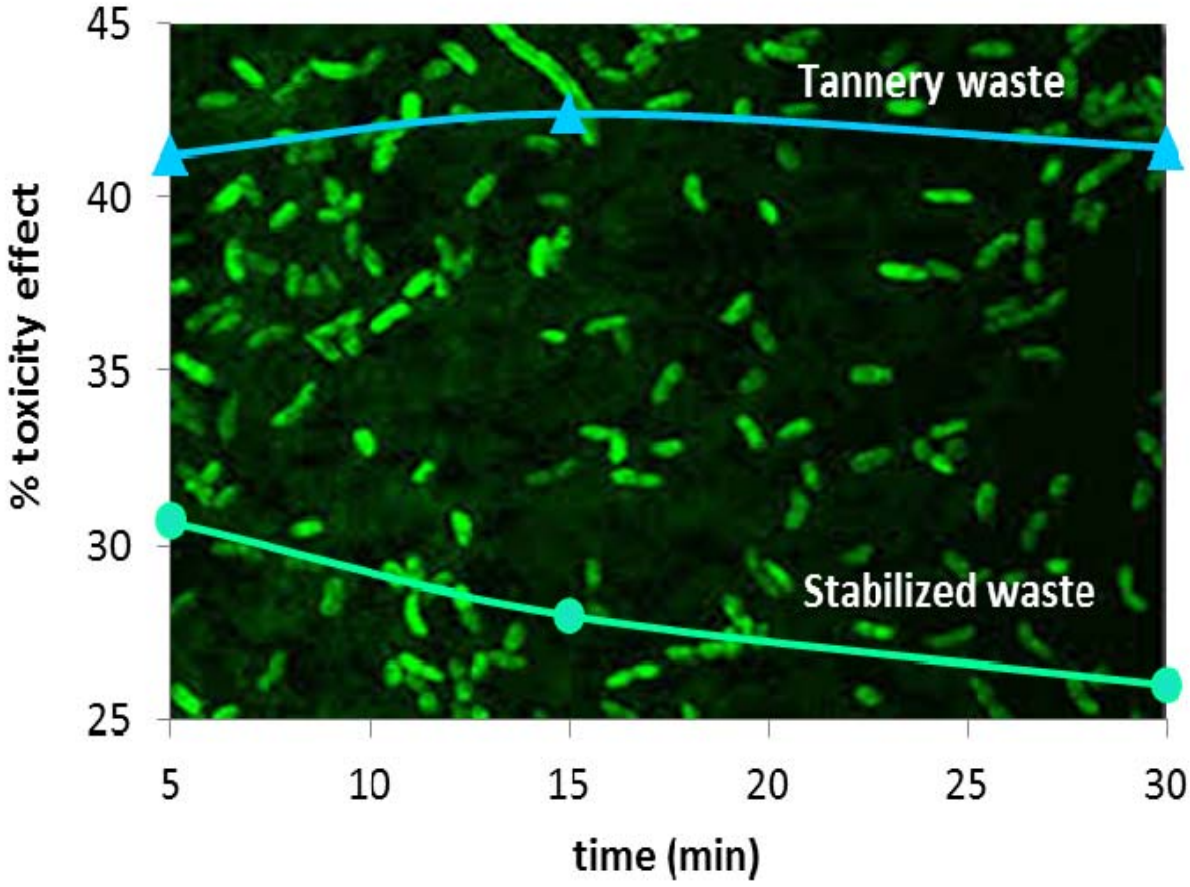
Toxic metals in the leachate (L/S 10 L/kg)

Stabilized tannery waste can be accepted in non-hazardous waste landfills

mg/kg of dry substance								
As	**Ba**	**Cd**	**Cu**	**Mo**	**Ni**	**Pb**	**Se**	**Zn**
0.02	1.7	nd	2.4	0.03	1.5	nd	nd	0.25

nd: not detected

Ecotoxicity



- Bioluminescence inhibition of tannery waste leachate reached 43%.
- Stabilized waste (tannery waste: LFS: organoclay, 30: 50: 20 mass ratio): Bioluminescence inhibition of the leachate did not exceed 31%.
- Typical curve of many heavy metal compounds: % toxicity effect is reduced during time.

Conclusions

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- Tannery waste cannot be accepted in hazardous waste landfills according to the EU Decision 2003/33/EC. DOC is much higher than the regulation limit for disposal in hazardous waste landfills (1,000 mg/kg).
- Mixing tannery waste with LFS and organoclay in 30:50:20 resulted in the production of a stabilized waste acceptable in non-hazardous waste landfills.
- LFS is an effective agent for Cr immobilization, due to its pozzolanic properties, while due to the organoclay's organophilic surface, this material is attractive to stabilize organic molecules (DOC stabilization).
- The toxicity effect of tannery waste leachate on ***Vibrio fischeri*** was up to 43%, while that of the respective stabilized waste was found between 26 to 31% (within the initial 30 min of contact time).

Thank you for your attention

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