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Stabilization of tannery waste using ferronickel slag

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Athens

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OPERATIONAL PROGRAMME
EDUCATION AND LIFELONG LEARNING
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Stabilization of tannery waste

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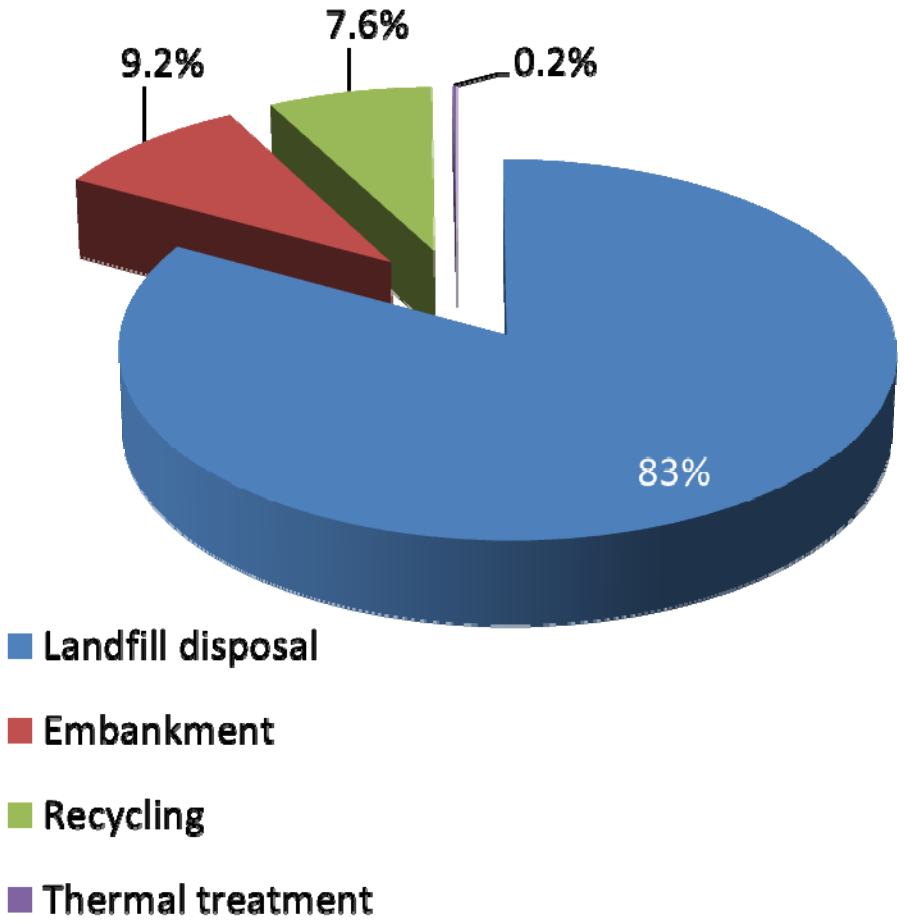
Introduction

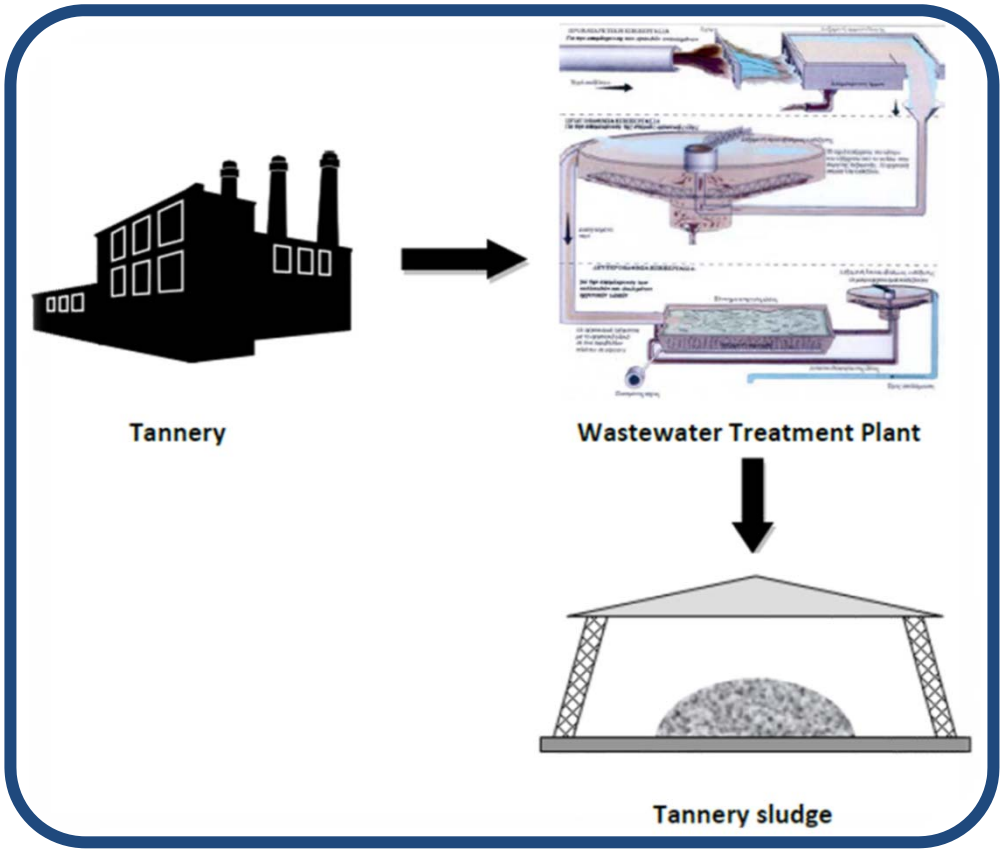
Industrial solid waste management in Greece



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 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 for the co-treatment of heavy metal-contaminated solid wastes.

Tannery sludge



- Leather resistance is achieved through tanning.
- Only 60% of Cr (III) salts used in tanneries, i.e. $Cr_2(SO_4)_3$, react with animal skin.
- Tannery sludge is produced by chemical precipitation technique before the 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 plant and is shipped abroad for landfilling.
- The most common management practice: Stabilization using cement and/or FA.
- Proposed management methods: Stabilization using other wastes, as well as through vitrification and recovery of Cr.

Characterization of tannery waste

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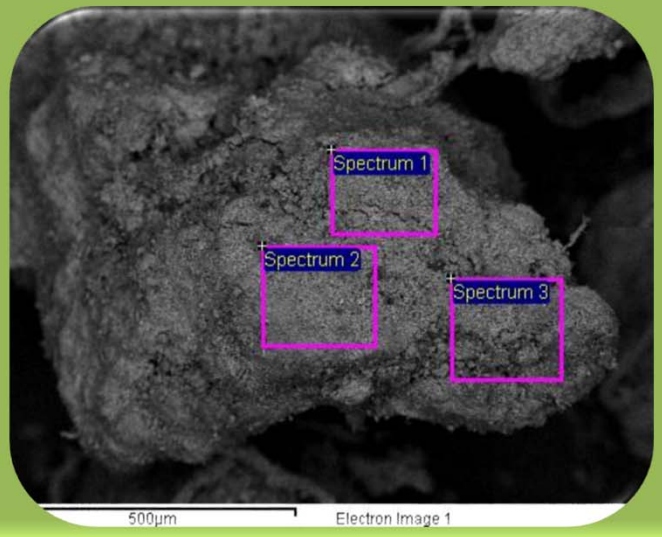
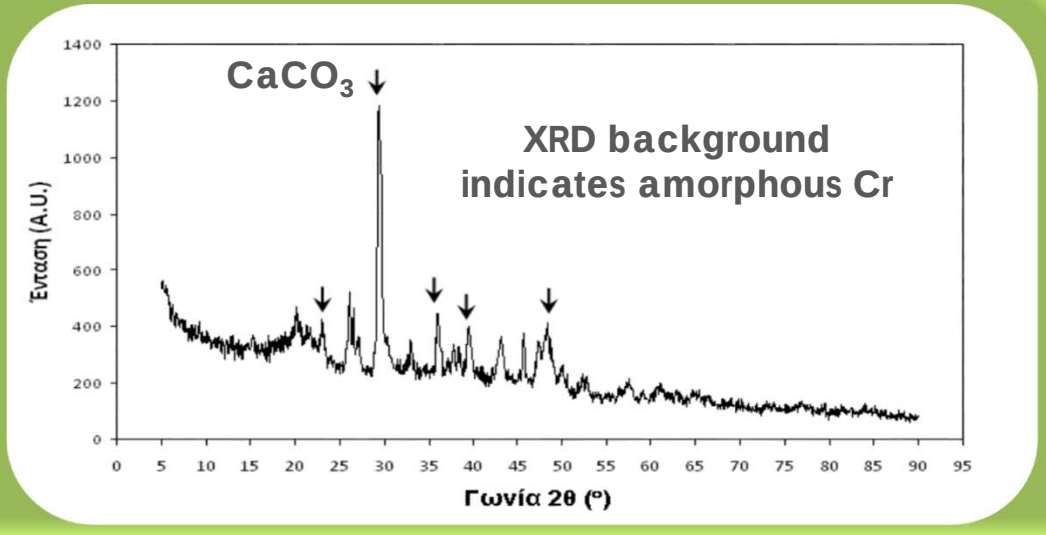
%										
Moisture	**Mass loss**		**Al**	**K**	**Na**	**Ca**	**Mg**	**Fe**	**C**	**N**
	500°C	**800°C**								
10.8	57.6	63.6	0.3	0.08	0.7	9.1	1.3	0.2	22.6	1.7

mg/kg of dry substance										
As	**Ba**	**Cd**	**Cr total**	**Cu**	**Mn**	**Ni**	**Pb**	**Sb**	**Se**	**Zn**
62	100	nd	86100	61	120	110	11	1	1	373

nd: not detected

EN 13657
Digestion with aqua regia





Characterization of tannery waste

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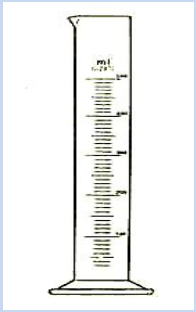
Tannery waste



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 1000 mg/kg)

	mS/cm	mV			%			
pH	**EC**	**Redox**	**K**	**Mn**	**Na**	**Ca**	**Mg**	**Fe**
8.3	3.2	+146	0.01	nd	0.4	0.15	0.05	1.5

	mg/kg of dry substance														
Al	**As**	**Ba**	**Cd**	**Cr ολικό**	**Cu**	**Ni**	**Pb**	**Sb**	**Se**	**Zn**	**F^-**	**Cl^-**	**SO_4^{2-}**	**DOC**	**TDS**
5	0.4	nd	nd	40.2	1.1	2.2	0.08	0.02	0.05	0.8	nd	3310	6640	2400	34000

nd: not detected

Ferronickel slag

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- FS is produced in electric arc furnaces during laterite processing for ferronickel production
- Content in SiO_2 40% wt., FeO 34% wt. and Al_2O_3 8.5% wt. (pozzolanic material)
- Annual production of FS in Greece, approximately 1.7 million t
- FS can be accepted for disposal in non-hazardous waste landfills

% wt. of dry FS										
Al_2O_3	CaO	Cr_2O_3	FeO	Fe_2O_3	MgO	MnO	SiO_2	C	Ni	S
8.55	5.36	2.70	33.7	2.86	5.78	0.38	39.9	0.17	0.14	0.17

- About 450,000 t is used in sandblasting operations, in the cement industry and as substitute for aggregates in road construction.
- A small quantity is sold to industries that produce construction materials, such as fire-resistant bricks, ceramic tiles and anti-slippery pavement tiles.

The remaining quantities are disposed of either in landfills or in the sea

Stabilization process

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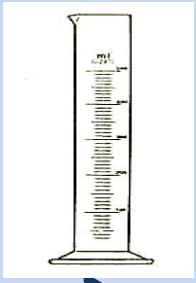
Ferronickel slag

Deionized water

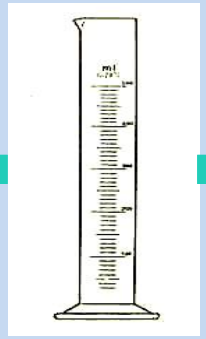


EN 12457-2

Tannery waste

Determination of Cr & DOC

Organoclay



Deionized water

Ferronickel slag

Stabilization - Results

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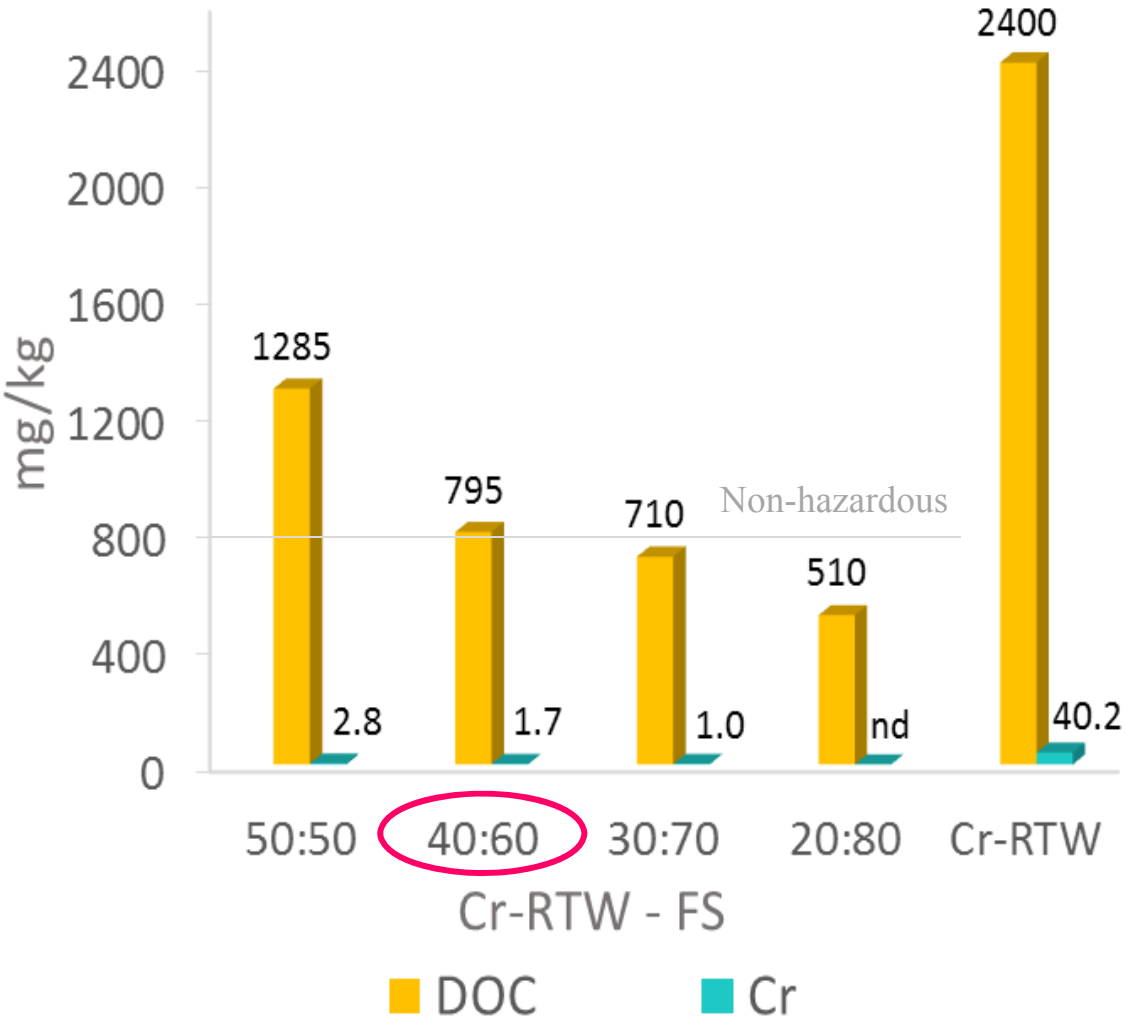

- In all proportions, Cr total is below the limit value for wastes acceptable in non-hazardous waste landfills (10 mg/kg).
- DOC is below the limit value for non-hazardous waste landfills (800 mg/kg) above 60% addition of FS.
- Cr leaching potential decreased over 86%, beyond the expected reduction of the mixing dilution, while DOC leaching potential decreased approximately as the expected reduction of the mixing dilution.

Influence of other wastes

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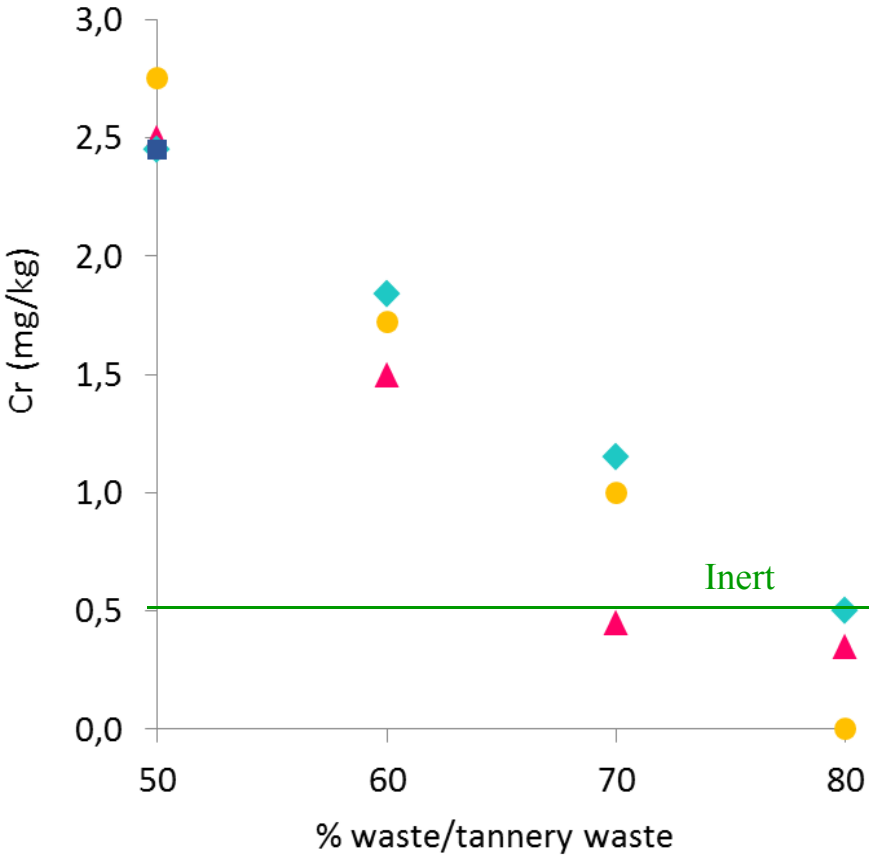
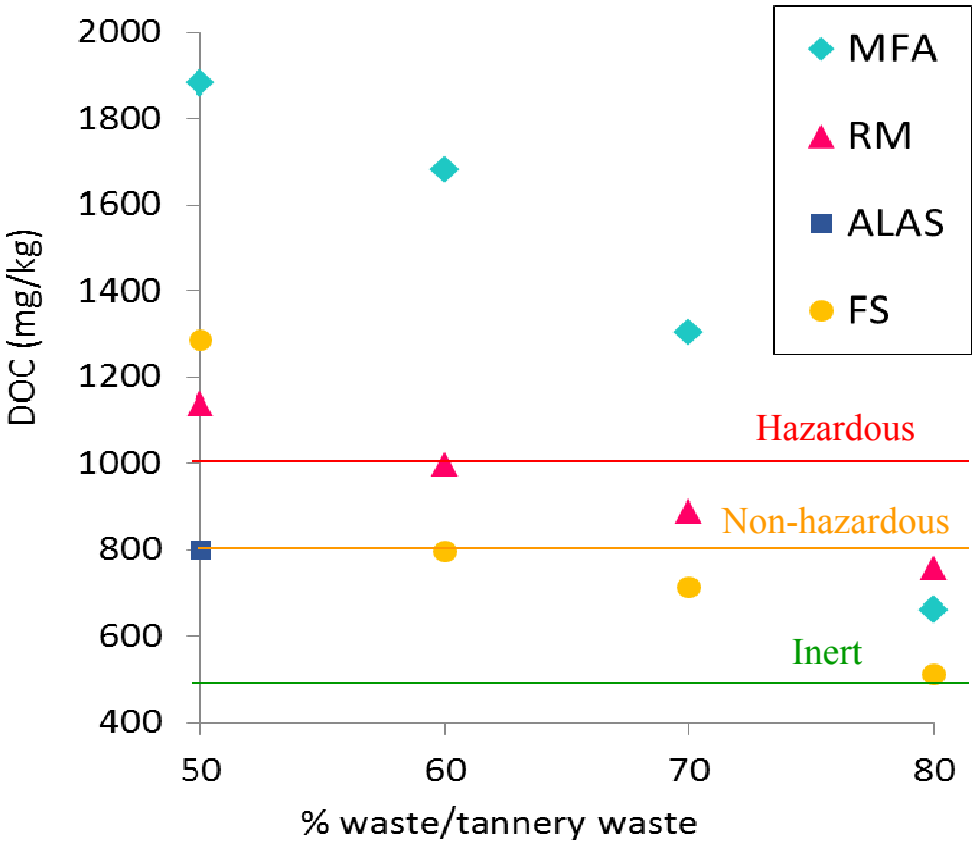
- Megalopolis Fly Ash (MFA), Red Mud (RM) and Aluminum Anodizing Sludge (ALAS) were also used for tannery waste stabilization.
- Cr total is below the limit value for non-hazardous waste landfills (10 mg/kg) in all cases, while DOC is below the respective limit value (800 mg/kg) at 50% addition of ALAS and 60% FS.





Stabilization - Results

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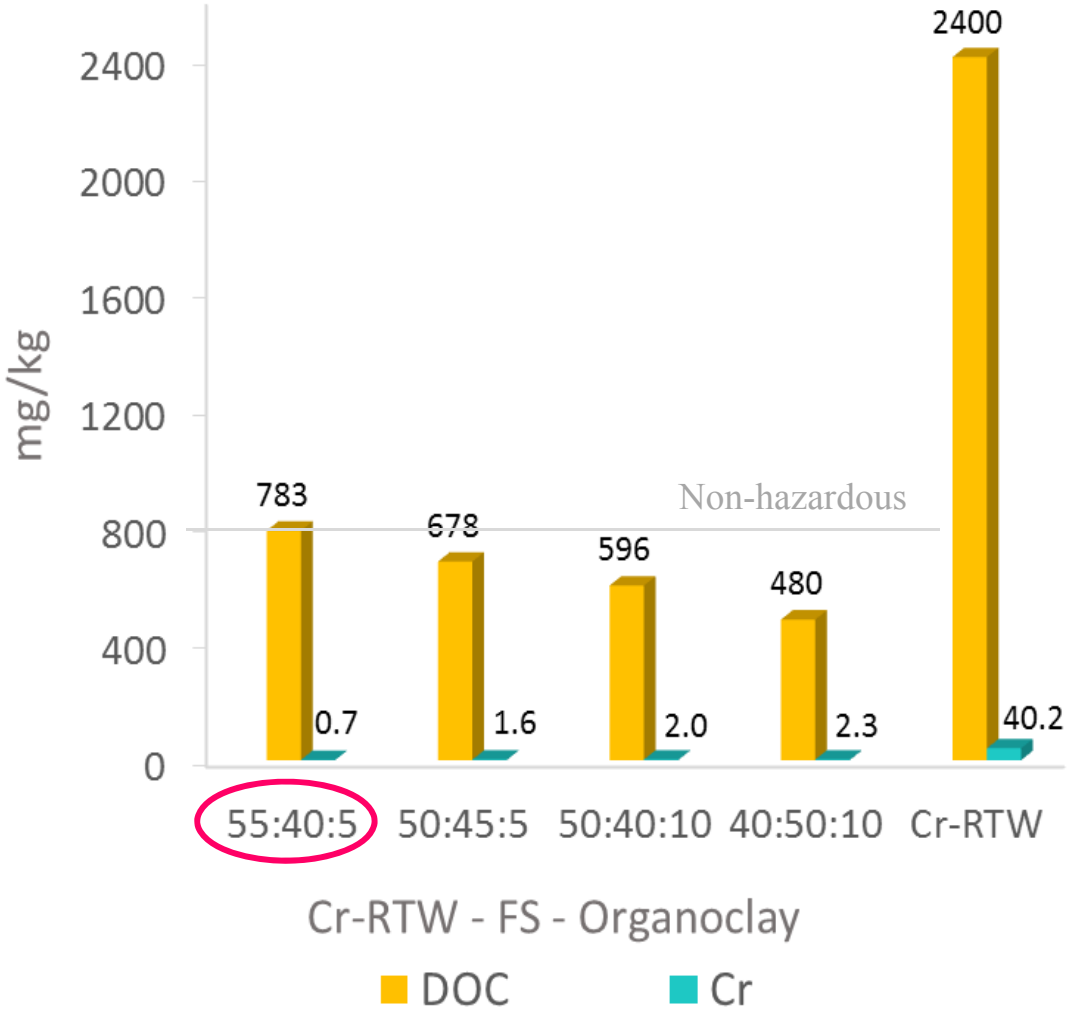

- Cr total and DOC are below the limit values for wastes acceptable in non-hazardous waste landfills.
- Cr leaching potential decreased over 85%, while DOC between 40-50%, beyond the expected reduction of the mixing dilution.
- pH of the stabilized wastes at about 8.5, in which heavy metals solubility is minimized.
- The ferro-aluminosilicate FS has a surface of variable charged groups, where metal adsorption may take place, while SiO_2 and Al_2O_3 react with CaO forming cementitious hydrates CAH and CSH compounds.

Influence of organoclay addition

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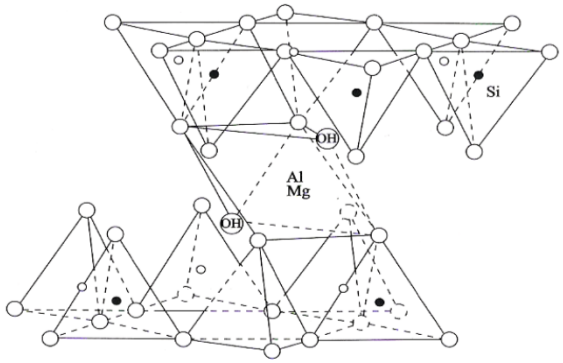
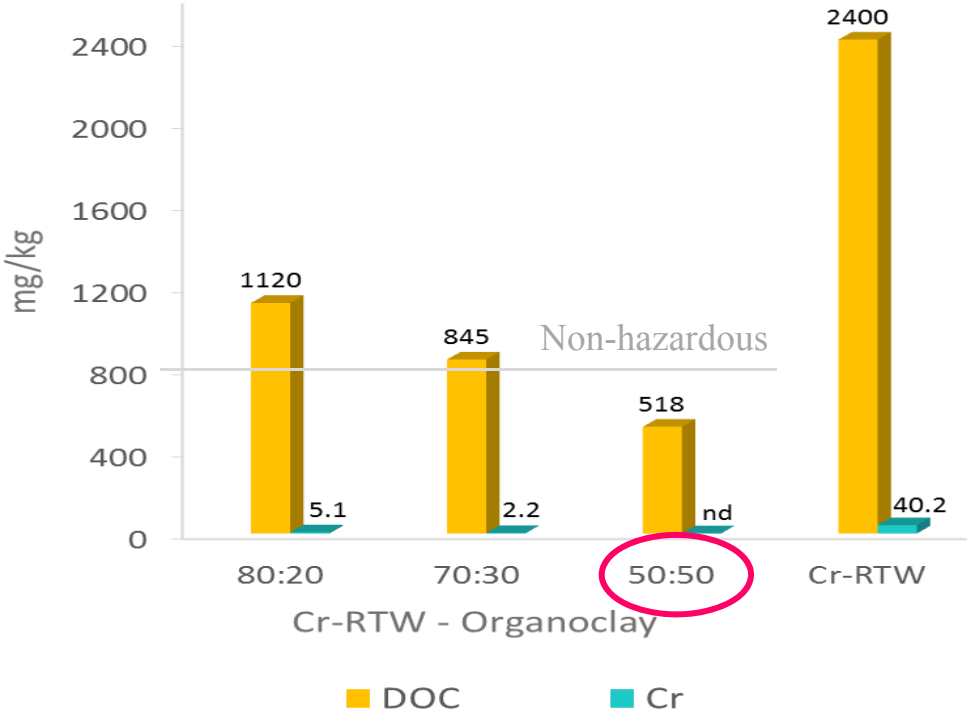
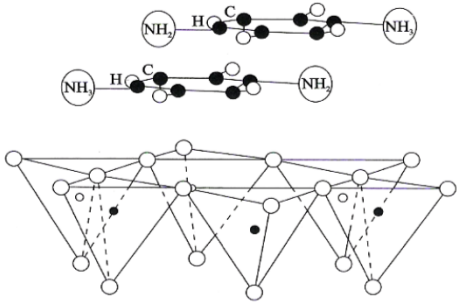
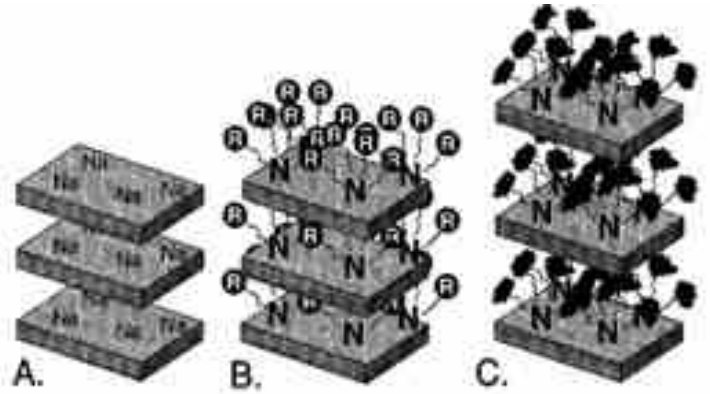
- Organoclay derives from a natural clay mineral by exchanging the original interlayer cations with organic cations (typically quaternary alkylammonium ions).
- Organoclay has an organophilic surface , consisting of covalently linked organic moieties.
- Organoclays have a high capacity for low-soluble organic compounds and are specialty sorbents of organic molecules.









Conclusions

- Mixing tannery waste with FS in 40:60 ratio resulted in the production of a stabilized waste acceptable for disposal in non-hazardous waste landfills.
- When using organoclay, mixing tannery waste with FS in 55:40 ratio and the addition of 5% organoclay resulted in the production of a stabilized waste acceptable in non-hazardous waste landfills.
- FS is an effective agent for Cr immobilization due to its pozzolanic properties, while due to organoclay's organophilic surface, making organoclay attractive to organic molecules.
- Apart from the obvious benefit: reduced environmental impact of hazardous tannery waste, the proposed stabilization process decreases the treatment cost, as well as the disposal cost of tannery waste.

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