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Chromium stabilization in tannery sludge using phosphogypsum

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Outline

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  - Tannery sludge
  - Phosphogypsum (PG)
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- Stabilization of tannery waste with PG
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Stabilization

- Stabilization converts hazardous substances to more stable chemical forms, which are much less soluble, mobile and toxic, using various additives, so that wastes can be safely disposed with minimum risk of releasing toxic substances, which could pollute water or groundwater resources.
- Various stabilizing agents, such as cement, hydrated lime, phosphoric compounds and pozzolanic materials, such as fly ash, have been used in stabilization/solidification processes
- The higher cost of traditional stabilizing additives prompt the development of alternative materials that are more cost-effective and less disruptive to the environment.

Stabilization

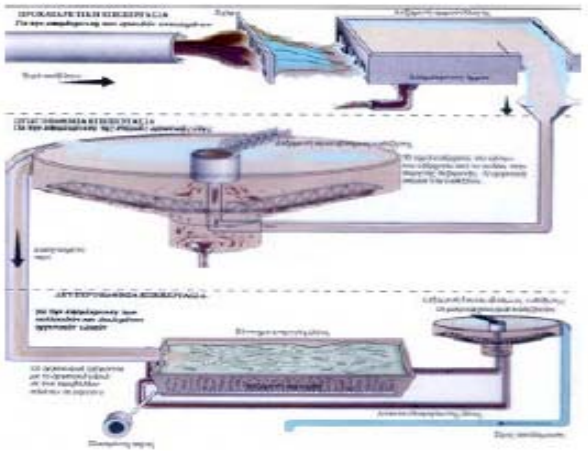
- Stabilizing additives decrease the leaching of trace elements by inducing various sorption processes:
  - adsorption to mineral surfaces,
  - formation of stable complexes with organic ligands and
  - surface precipitation and ion exchange.
- Precipitation as salts and co-precipitation can also contribute to the reduction of contaminant mobility.
- Physical encapsulation can be achieved by creating a solidified monolith and chemical inclusion through the incorporation of metals in binder hydration products.

Tannery Sludge

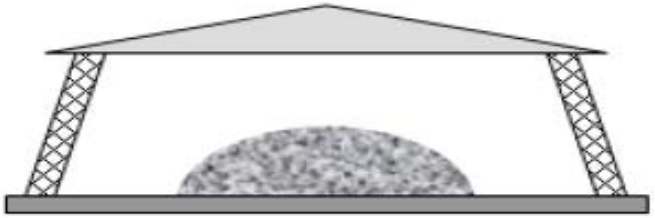
- Chromium salts, specifically the trivalent ones, are the most widely used chemicals in tanneries.
- Only 60 % of the chromium salts react with animal skin. The rest of chromium remains in the exhaust tanning bath and is subsequently discharged into the wastewater.
- The dissolved chromium and other spent chemicals in the wastewater are mainly removed through the chemical precipitation technique before the wastewater is allowed to enter the biological treatment process.
- The precipitated chromium along with some other co-precipitated organic compounds is finally discharged as sludge.

Tannery Sludge

Tannery



Wastewater Treatment Plant



Tannery sludge

Phosphogypsum

- An acidic by-product resulting from phosphate industrial activities in wet-process fertilizer plants.
- Arises as a waste in the manufacture of phosphoric acid from calcium phosphate ore, $Ca_{10}(PO_4)_6F_2$ and sulfuric acid.
- Composed mainly of gypsum and the phosphorus content is usually < 1 %.
- About 5 tons of PG is produced for every ton of phosphoric acid manufactured.
- Only 15 % of world PG production is recycled as building materials, agricultural fertilizers or soil stabilization amendments and as set controller in the manufacture of Portland cement.

Phosphogypsum

- PG is usually dumped in large stockpiles exposed to weathering processes.

Stockpile of PG in Industrial Park of Schistos.

Characterization of Tannery Waste

- **EN 13657**: Digestion with aqua regia (partial digestion of the solid waste leaving the silicate matrix intact).
- Elementary analysis with AAS and GF.

	%
Moisture	10.8
Loss at 500°C	57.6
Loss at 800°C	63.6
Al	0.33
K	0.08
Na	0.73
Ca	9.1
Mg	1.3

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

ND: Not Detected

Characterization of PG

- **EN 13657**: Digestion with aqua regia (partial digestion of the solid waste leaving the silicate matrix intact).
- Elementary analysis with AAS and GF.

	%
Moisture	2.4
Loss at 500°C	2.2
Loss at 800°C	4.8
Al	0.04
Na	0.07
Ca	28
Mg	0.004

	mg/kg of dry substance
As	24
Ba	313
Cd	0.4
Cr total	45
Cu	ND
Hg	ND
Mn	ND
Ni	12
Pb	4
Sb	0.8
Se	ND
Zn	255

ND: Not Detected

Radiochemical results of PG

Radionuclides	Bq/kg
U-235/Ra-226	51.2
U-238	693
Cs-137	9.7
K-40	24.5
Total	778.4

- PG is highly radioactive (778.4 Bq/kg) and its radioactivity originates mainly from ^{238}U.
- The USEPA has classified PG as "Technologically Enhanced Naturally Occurring Radioactive Material" (TENORM).
- PG, which exceeds 370 Bq/kg of radioactivity, has been banned from all uses by the EPA since 1992.

Stabilization of tannery waste with PG

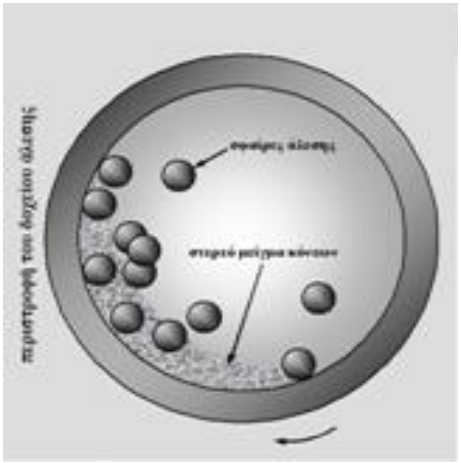
Tannery waste

+

PG

dry weight ratio 50:50

Homogenization
Ball mill ~ 20 min



Immediately, after
7, 15 and 30 days

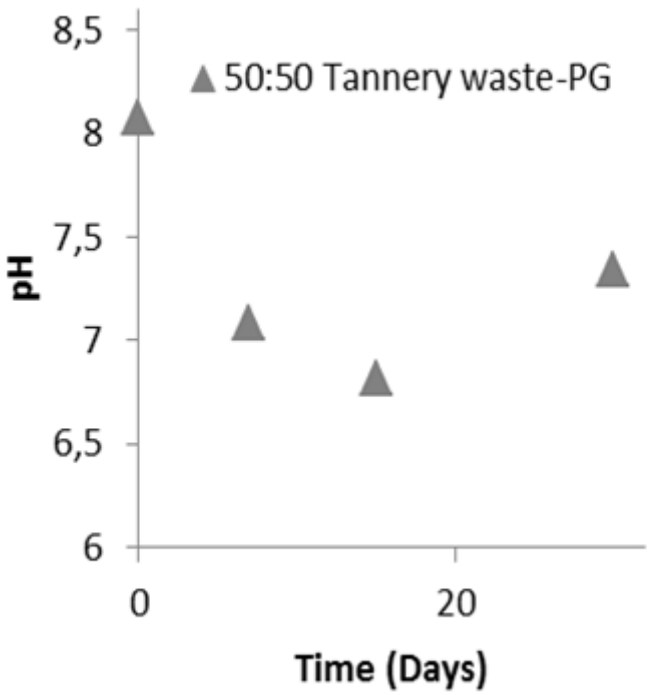
Standard leaching test EN ELOT 12457-2

Standard leaching test EN ELOT 12457-2

- Mass of sample, 100g
- Liquid/Solid ratio, 10 L/kg
- Time, 24 h
- Way of mixing, rotational 10 rpm
- Leaching solvent, deionized water in pH 4 with HNO_3

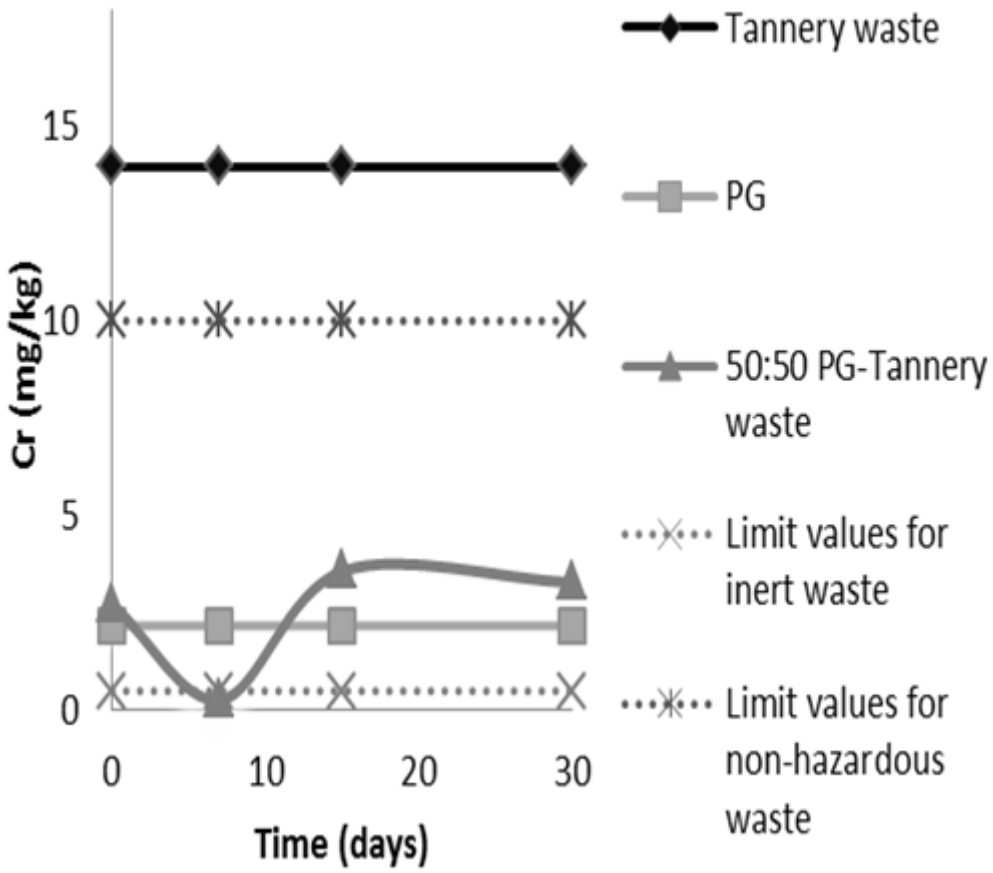
✓ Measurements of pH and concentrations of total chromium and dissolved organic carbon (DOC) were carried out in the leachates.

Stabilization of tannery waste with PG



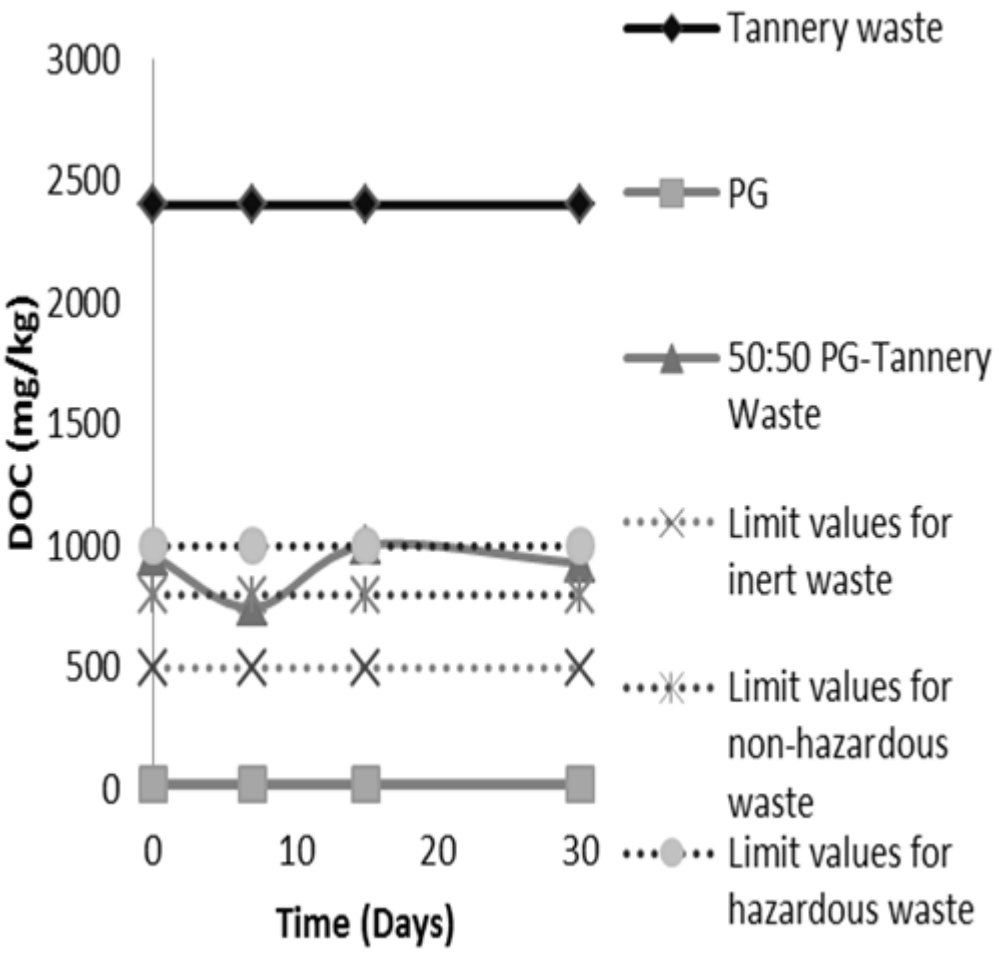
- pH of tannery waste leachate 8.5 and PG 3.5
- PG is an acidic by-product, which enables it to be a good amendment material for stabilization of chromium.
- pH is the primary factor which controls the leachability of heavy metals in the stabilized wastes.
- Very low and high pH values favor more intense reactions and can favor the transportation of dissolved constituents from the solid phase in the leachates.

Stabilization of tannery waste with PG



- The total chromium of the tannery waste's leachates is below of the limit values for wastes acceptable at landfills for hazardous wastes (70 mg/kg).
- Stabilization with PG resulted in the reduction of chromium leaching potential of tannery waste.
- The total chromium in the leachates of the stabilized tannery waste with PG is less than that mentioned in the Council Decision 2003/33/EC for non-hazardous wastes.

Stabilization of tannery waste with PG



- The characterization of the tannery waste's leachates revealed that this waste cannot be accepted at landfills for hazardous wastes, because of high DOC values, while PG can be accepted at landfills for non-hazardous wastes.
- Stabilization with PG resulted in the reduction of organic compounds leaching potential of tannery waste.
- Mixing tannery waste with PG resulted in the production of a stabilized tannery waste acceptable in hazardous waste landfills.

Radiochemical results of stabilized tannery waste

Radionuclides	Bq/kg
U-235/Ra-226	23.8
U-238	304
Cs-137	4.9
K-40	7.7
Total	340.4

- The storage of PG without any prior treatment requires large land areas and can cause serious environmental contamination of soils, water and the atmosphere.
- Mixing tannery waste with PG in 50:50 ratio, resulted in a product with reduced radioactivity (about half) in comparison with the single PG (778 Bq/kg).

Conclusions

- The mixing of tannery sludge with PG (50:50 ratio) results in a stabilized product with:
  - Chromium concentration values in the leachates below the limit values foreseen for disposal at landfills for non-hazardous wastes and
  - DOC values below from the respective values for hazardous wastes.
- The stabilized tannery waste can be accepted in hazardous waste landfills according to the Council Decision 2003/33/EC.

Acknowledgements

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