Stabilization of tannery waste using ferronickel sludge

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Keywords: tannery sludge, stabilization, ferronickel slag, organoclay
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Abstract

The current global trend towards increasingly stringent environmental standards and efforts for efficient utilization and re-use of available by-products and/or wastes, favor the use of low-cost sorbent materials for the treatment of heavy metal-contaminated solid wastes. In this study, the stabilization of tannery sludge, produced from the physicochemical and biological treatment of tannery wastewaters, was examined by the addition of ferronickel slag (FS) and/or organoclay in different proportions. Characterization of the tannery sludge leachates showed high amounts of chromium which exceeded the acceptable level for disposal in non-hazardous waste landfills, while the dissolved organic carbon (DOC) concentrations exceeded the limits for disposal in landfills for hazardous wastes, according to the EU Decision 2003/33/EC. Leachates of the tannery sludge stabilized with FSat a ratio of 40:60 presented chromium and DOC concentrations below the regulation limits for disposal in landfills for non-hazardous wastes. Moreover, mixing tannery sludge with FS and organoclay resulted in a stabilized waste accepted for disposal in landfills for non-hazardous wastes with the addition of only 5% organoclay.Apart from the obvious benefit for the environment, such as reduced environmental impact of hazardous tannery sludge, the proposed stabilization process decreases also the treatment cost, as well as the disposal cost of tannery sludge.

1. Introduction

According to the results of the survey on the generation and treatment of solid wastes, carried out by the Greek Statistical Institute, the quantity of industrial wastes generated in 2010 amounted to 70,433,000 tonnes approximately, of which about 292,000 tonnes are hazardous wastes, representing 0.5% of the total amount and 26 kg of hazardous wastes per inhabitant. In Greece, 58,520,000 tonnes of solid wastes were disposed or deposited in designated sites or landfills, 6,415,000 tonnes were used for embankment and fill applications, 5,308,000 tonnes were recycled or used for energy and substance recovery, 126,150 tonnes were incinerated for energy recovery and 21,300 tonnes were simply incinerated. However, there are considerable amounts of solid wastes temporarily stored in areas next to industrial sites, as well as illegally disposed of in several other sites, thus posing serious environmental risks. Consequently, there is a demand for an efficient process that can allow the disposal of the produced solid wastes using an environmentally sound and low cost method.

Leather tanning involves the transformation of animal skin to leather. The predominant tanning method is based on chromium salts; specifically trivalent chromium salts are the most widely-used chemicals in tanneries [1, 2]. Of the total amount of chromium applied during the tanning process, about 60% is consumed during the processing of raw materials (animal skin). Residual chromium remains in the tanning bath and is subsequently discharged into the wastewater. Dissolved chromium and other spent chemicals present in the wastewater, are mainly removed by chemical precipitation before the wastewater is allowed to enter the biological treatment process. Precipitation is induced through pH adjustment usually by lime and the addition of inorganic coagulants. The precipitated chromium along with other co-precipitated organic compounds is discharged as sludge [3]. Tannery sludge contains trivalent chromium, organic matter, proteins, fats, and salts such as chlorides, sulfates and carbonates [4]. Concentrations of trivalent chromium and organic compounds in the tannery sludge are considerably high and it cannot be accepted even at landfills for hazardous wastes, which in turn signalizes the demand for its stabilization [5].

Using various additives, stabilization aims to convert hazardous substances to more stable chemical forms that are much less soluble, mobile and toxic. Therefore stabilized wastes can be safely disposed into the environment with minimal risk of leaching toxic substances and polluting surface water or groundwater resources [6]. 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 current global trend towards increasingly stringent environmental standards and efforts for the efficient utilization and re-use of available by-products and/or wastes, favor the use of low-cost sorbent materials for the co-treatment of heavy metal-contaminated solid wastes.The higher cost of traditional stabilizing additives prompt the development of alternative materials that are more cost-effective and less disruptive to the environment.

FS is produced during the production of stainless steel. FS is the slag of the electric arc furnace, a by-product of metallurgical processing generated by rapid cooling, which represents about 80–90% of the feeding material [7]. FS is a pozzolanic material due to its high content in SiO_2, as it contains more than 25% (about 40%). Apart from its high content in SiO_2, it is very rich in iron and alumina.Organoclay derives from a natural clay mineral by exchanging the original interlayer cations with organic cations (typically quaternary alkylammonium ions); an organophilic surface is generated,consisting of covalently linked organic moieties.

FS was investigated as an alternative material for stabilization of tannery waste with additional benefits. Specifically, the objective of this study was to examine the possible co-treatment of tannery sludge with FS in order to both stabilize chromium and organic compounds. Additionally, the influence of organoclayaddition on stabilization of organic compounds was also examined.

2. Materials and Methods

Tannery sludge was collected from the central wastewater treatment unit of tanneries cluster in the industrial area of Thessaloniki (Northern Greece), where it is temporary stored in the backyard of the site, forming large piles. The air-dried sludge was collected and was abbreviated as chromium-rich tannery waste (Cr-RTW).

FS is produced at the LARCO S.A. ferronickel plant in Greece; 30% of it is used in the cement industry whilst the remaining volumes are disposed of in a nearby bay causing several environmental problems [8].Table 2 shows a typical analysis of FS in the form of oxides.Organoclay is a commercial product produced by CETCO. It is a semi-granular adsorption media effective in removing oils, greases and other high molecular weight/low solubility organics.

Table 2 Typical analysis of FS [9]

% 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

The standard leaching test EN 12457-2 (liquid per solid ratio - L/S 10) was selected to characterize the Cr-RTW leachates. To investigate the stabilization process, Cr-RTW and FS were mixed in weight ratios of 50:50, 40:60, 30:70 and 20:80, while Cr-RTW, FS and organoclay were mixed in weight ratios of 55:40:5, 50:45:5, 50:40:10 and 40:50:10. The homogenized mixtures were then subjected to the standard leaching test EN 12457-2. Classification of the examined wastes was based on the European Decision 2003/33/EC, regarding the acceptance of wastes at landfills [10].

3. Results and Discussion

The chemical composition of Cr-RTW is presented in Table 1. Cr-RTW contains 8.6% wt. chromium, 9.1% wt. calcium (most of which in $CaCO_3$ form), and 22.6% wt. carbon, due to the content of organic matter.

Table 1 Typical chemical analysis of Cr-RTW

% wt. dry substance							
Al	C	Ca	Cr	K	Mg	N	Na
0.3	22.6	9.0	8.6	0.04	1.3	1.7	0.7
mg/kg dry substance							
As	Ba	Cu	Mn	Ni	Pb	Zn	
62	100	61	120	110	11	373	

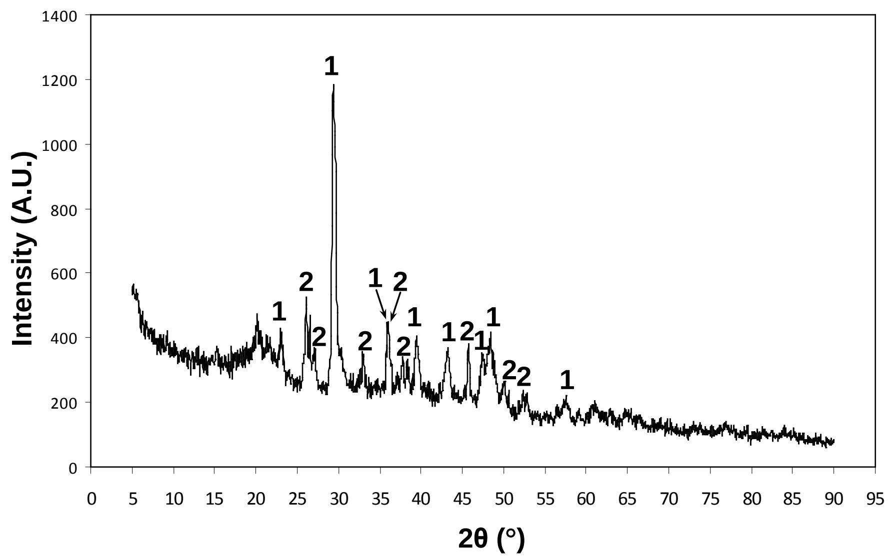

Figure 1 XRD diagram indicating that the main crystalline phase present in Cr-RTW is $CaCO_3$ that is found in the form of calcite (1)and aragonite (2)

When water passes through solid wastes, some ingredients are dissolved. The degree of dissolution depends on various factors such as pH, chemical characteristics, metal speciation, morphology and solubility of the solid waste, and the presence of organic matter. Leaching test methods are frequently used to assess: (a) whether land disposal of a specific waste is an appropriate management method, (b) the effectiveness of the waste treatment process, and (c) the environmental impact of the wastes.

The evaluation of Cr-RTW leachates is presented in Table 3. As shown in the table, the leached concentration of chromium (40.2 mg Cr/kg) from Cr-RTW is higher than the maximum permitted level of 10 mg Cr/kg for disposal in non-hazardous waste landfills.Moreover, the DOC concentration of leachates was 2,400 mg/kg, which is much higher than the regulation limit for disposal in hazardous waste landfills according to Council Decision 2003/33/EC. Consequently, Cr-RTW cannot be accepted in landfills for hazardous wastes, which in turn indicates the need for its stabilization.

Table 3 Cr-RTW leaching characteristics determined using the EN 12457-2 standard leaching test

	Cr-RTW	**Detection limit**	**Regulation limits**		
			Inert waste	**Non-hazardous waste**	**Hazardous waste**
pH	8.5	-	-	-	-
EC (mS/cm)	3.2	-	-	-	-
Redox (mV)	+146	-	-	-	-
mg/kg					
As	0.42	0.01	0.5	2	25
Ba	nd	1	20	100	300
Cd	nd	0.001	0.04	1	5
Cr total	13.5*	0.01	0.5	10	70
Cu	1.1	0.5	2	50	100
Ni	2.2	0.01	0.4	10	40
Pb	0.075	0.01	0.5	10	50
Sb	0.015	0.01	0.06	0.7	5
Se	0.045	0.01	0.1	0.5	7
Zn	0.80	0.2	4	50	200
Chloride	3,310	50	800	15,000	25,000
Fluoride	nd	0.1	10	150	500
Sulphate	6,640	100	1,000	20,000	50,000
DOC	2,400*	5	500	800	1,000
TDS	32,000	50	4,000	60,000	100,000

nd: not detected

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

According to the redox potential Eh–pH diagram, at pH > 3.5 hydrolysis of Cr(III) yields trivalent chromium hydroxy species such as $Cr(OH)_3$. Specifically at around neutral pH and under reducing conditions Cr has a composition corresponding to Cr (III) hydroxide hydrates, which obtained byprecipitation with alkali of $Cr_2(SO_4)_3$ and are usuallyformulated as $Cr(H_2O)_3(OH)_3$with a bright bluish green color [11].

Figure 2 shows Cr and DOC values at the leachates for each proportion of Cr-RTW with FS, while Figure 3 shows Cr and DOC values at the leachates for each proportion of Cr-RTW with FS and organoclay. Mixing Cr-RTW with FS in 40:60 ratio resulted in the production of a stabilized waste acceptable in non-hazardous waste landfills according to the EU regulation limitfor Cr total and DOC (Cr 10 mg/kg and DOC 800 mg/kg), i.e Cr 1.7 mg/kg and DOC 795 mg/kg. On the other hand, mixing Cr-RTW with FS and organoclay in 55:40:5ratio resulted in a stabilized solid waste which fulfils regulation limit for disposal at non-hazardous waste landfills, i.e. DOC 783 mg/kg and Cr 0.7 mg/kg.More specifically, Cr leaching potential decreased over 90% in both cases, while DOC leaching potential about 20% in both cases, beyond the expected reduction of the dilution of the mixing.

FS manages to maintain the pH values of the stabilized wastes at about 8.5. In this optimum pH, heavy metals solubility is minimized. It is well known that pH is the primary factor controlling the leachability of heavy metals in wastes. Very low and high pH values favour more intense reactions which, in turn, increase transportation of dissolved constituents from the solid phase into the leachates.The amorphous ferro-aluminosilicate glass material of FS has a surface of variable charged groups, where specific adsorption of metal cationsmay take place. Furthermore, silica and alumina react with free lime, originating from FS, forming cementitious hydrates CAH and CSH compounds.It is most likely that chromium is transformed to calcium–chromium minerals, or immobilized in the stable calcium silicate hydrate phase (CSH) by the applied stabilization treatment [12].If chromium is co-precipitated with iron hydrous oxides, which are presenting low mobility and bioavailability in solids, it is likely to remain stable for longer time [13].

Theorganophilic surface of organoclay is consisted of covalently linked organic moieties.The adsorptive capacity of organoclayreduces the required cap thickness compared to in-situ sand caps. This adsorptive capability provides a sub-aqueous chemical isolation of contaminated sediment mitigating organic contaminant transport into the water.

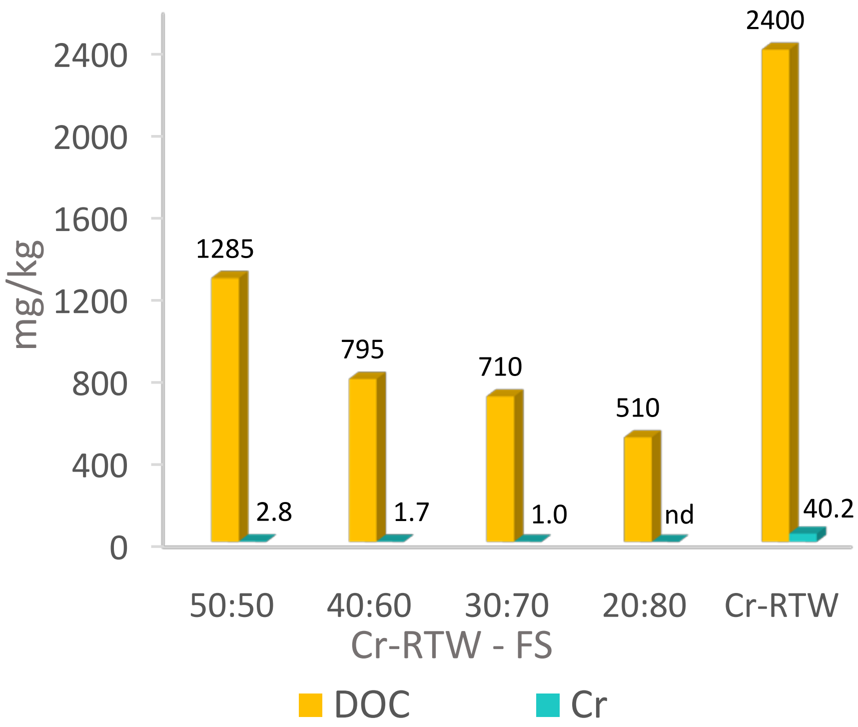

Figure 2 Influence of FS addition on Cr and DOC leaching from Cr-RTW

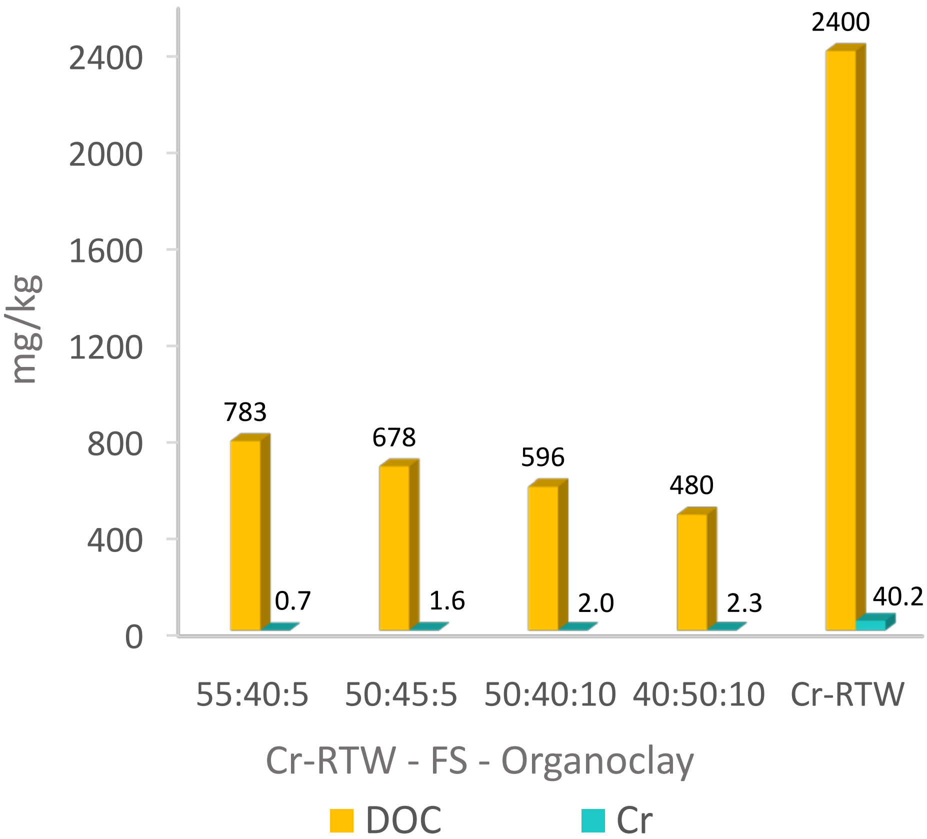

Figure 3 Influence of organoclay and FS addition on Cr and DOC leaching from Cr-RTW

FS can be used as effective agent for immobilization of heavy metal-contaminated solid wastes and it is suitable for stabilization/solidification, due to its pozzolanic properties. Conclusively, FS can be considered a relatively efficient additive for Cr-RTW stabilization as it manages to bind Cr and organic compounds.Organoclays havea high capacity for low-soluble organic compounds and are specialty sorbents, due to their organophilic surface, making them attractive to organic molecules with extended life and reduced cost.

4. Conclusions

About 450,000 tonnes of FS are used in sandblasting operations, in the cement industry and as substitute for aggregates in road construction [7]. A small quantity is sold to industries that produce construction materials, such as fire-resistant bricks, ceramic tiles and anti-slippery pavement tiles. Although considerable research focused on commercial uses for FS, the utilization of FS as an alternative material for waste stabilization needs further investigation. In the proposed process, FS, i.e. a solid industrial waste, was used to stabilize Cr-RTW. This mixing resulted in the production of a stabilized waste acceptable for disposal in non-hazardous waste landfills according to the EU regulation limits, since Cr and DOC leaching concentrations were below the limit valuesof non-hazardous wastes for 40:60 Cr-RTW/FS ratio, while when using organoclay, for 55:45 Cr-RTW/additives ratio with the addition of 5% organoclay. Apart from the obvious benefit for the environment, such as reduced environmental impact of hazardous Cr-RTW, the proposed stabilization process decreases also the treatment cost, as well as the disposal cost of Cr-RTW.

Acknowledgements

This research has been co-financed by the European Union (European Social Fund - ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: THALES: Reinforcement of the interdisciplinary and/or inter-institutional research and innovation.

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