RECOVERY AND DISPOSAL OF PHOSPHATE SLUDGE FROM AUTOMOTIVE INDUSTRY

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Abstract. Turkish automotive sector constitutes one of the major powers of the Turkish Industry with its importance as one of the most-advanced branches of the Turkish manufacturer industry. There are 15 automotive main industry companies which manufacture trailers, trucks, light lorries, pick-ups, passenger cars, buses, minibuses, midibuses. Main hazardous waste originated from automotive industry is phosphate sludge. Phosphate sludge coming from automotive sector often contains heavy metals and a variety of other hazardous substances which can cause soil and ground water pollution. This sludge is classified as hazardous waste at the European Waste Catalogue as adopted in Council Decision 2000/532/CE. This work attempts to better understand the physical and chemical characteristics of these sludges, by studying on samples taken from automotive manufacture plant in Marmara Region of Turkey. Chemical composition and leaching characteristics are given, together with disposal and recovery methods.

Keywords: hazardous wastes, soil pollution, water pollution, wastes disposal.

1. Introduction

Phosphating and metal coloring operations are generally used to obtain a good substrate for further painting and deposition of organic agents in order to provide corrosion protection. For example, anodizing is an electrolytic process that converts the metal surface into an insoluble oxide coating, which confers corrosion protection [1, 2].

Phosphating is a chemical/electrochemical process, in which thin, microcrystalline and water insoluble phosphates are produced on metal surfaces from phosphoric acid solutions in a dipping or spraying process. Because they originate from a chemical reaction with the underlying metal, the pale to dark grey colored metal phosphate coatings are firmly anchored to the metal surface and have numerous

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cavities and capillaries. This property gives the phosphate layers an optimum absorption capacity for oils, waxes, coloring pigments, and paints, so that they have proved their worth as corrosion protection and as a good surface for coats of coloring and paint.

A further property of the phosphate coating is the ability to reduce friction (as arises for example in deformation, drawing or sliding processes). So, as well as an improvement in the surface properties of the peaces treated, in prolonged use of the tools the work rate can be fundamentally increased.

Phosphate sludges are often classified as hazardous wastes by environmental agencies (e.g., European Union Commission Decision 2001/573/EC). In the hazardous waste list, phosphate sludge is assigned as (11) "Wastes From Chemical Surface Treatment and Coating of Metals and other Materials; Non-Ferrous Hydrometallurgy", (11 01) "wastes from chemical surface treatment and coating of metals and other materials for example galvanic processes, zinc coating processes, pickling processes, etching, phosphating, alkaline degreasing, anodizing" *(11 01 08* phosphating sludges).*

The hazardous character and toxicity is related to the high concentration of leached species, such as heavy and/or transition metals, such as Zn and Ni. Removal of those species depends on their ultimate equilibrium form and, particularly, on the pH values of the surrounding environment [3]. Here, toxicity characteristics are assessed from leaching tests. Leaching tests in distilled water (DIN 38414-S4) indicate that the leaching levels of Ni and Zn are not directly predictable by the solubility of corresponding hydroxides, since the mobility is mainly related to the composition of the residue [4].

2. Characterization

Samples were dried at 105°C to constant mass before eluting and the water content determined.

The heavy metal composition of dried samples was determined by X-ray fluorescence spectroscopy.

Leaching tests were performed according to DIN-38414-S4 (EN 12457) in order to determine pollutants' mobility under neutral conditions at the beginning using distilled water over 24 h. The liquid (water)/solid ratio was 10 L/kg. Pictures were taken as dimension of 1 μm and 100 nm by using Scanning Electron Microscope and given Fig. 2.1.

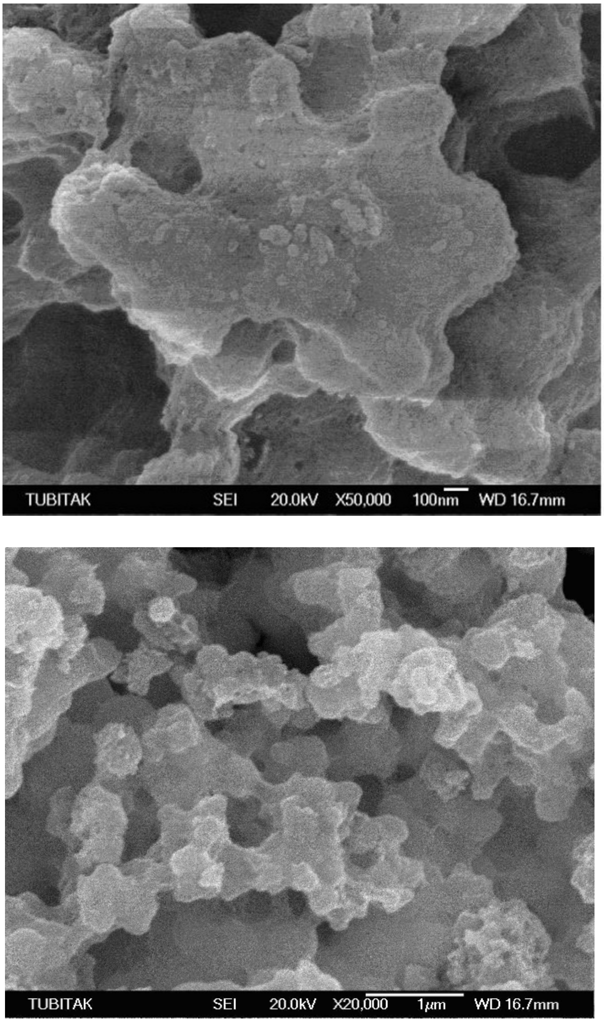

Fig. 2.1. Pictures of phosphating sludge by using SEM.

Chemical composition and leaching characteristics are given Tables 2.1 and 2.2.

Table 2.1. Chemical composition of phosphating sludge determined by XRF.

Elements					
Fe	Na	Ni	Zn	P	O
22.552	0.008	0.85	12.30	20.93	41.28

Table 2.2. Concentration of phosphate sludge of eluate.

Eluate criteria L/S = 10 L/kg	Phosphate sludge (mg/L)	Wastes to be processed as inert waste (mg/L)	Wastes to be processed as non-hazardous waste (mg/L)	Wastes to be processed as hazardous waste (mg/L)
As (Arsenic)	0.142	≤0.05	0.05–0.2	<0.2–2.5
Ba (Barium)	0.026	≤2	2–10	<10–30
Cd (Cadmium)	0.002	≤0.004	0.004–0.1	<0.1–0.5
Cr (Chromium)	<0.001	≤0.05	0.05–1	<1–7
Cu (Copper)	0.04	≤0.2	0.2–5	<5–10
Hg (Mercury)	<0.0005	≤0.001	0.001–0.02	<0.02–0.2
Mo (Molybdenum)	0.0027	≤0.05	0.05–1	<1–3
Ni (Nickel)	120	≤0.04	0.04–1	<1–4
Pb (Lead)	0.097	≤0.05	0.05–1	<1–5
Sb (Antimony)	0.016	≤0.006	0.006–0.07	<0.07–0.5
Se (Selenium)	0.058	≤0.01	0.01–0.05	<0.05–0.7
Zn (Zinc)	650	≤0.4	0.4–5	<5–20
Chloride	133	≤80	80–1,500	<1,500–500
Fluoride	134	≤1	1-15	<15–50
Sulphate	115	≤100	100–2,000	<2,000-5,000
DOC (Dissolved Organic Carbon)	24	≤50	50–80	<80-100
TDS (Total Dissolved Solids)	7,250	≤400	400–6,000	<6,000–10,000
Phenol Index	<0.05	≤0.1		
Criteria for original sample		(mg/kg)	(mg/kg)	(mg/kg)
TOC (Total Organic Carbon)	3,250	≤30,000 (3%)	50,000 (5%)–pH ≥ 6	60,000 (6%)
BTEX (Benzene, toluene, ethylbenzene and xylenes)	1.6	6		
PCBs	<0.01	1		
Mineral oil	7,200	500		
LOI (Loss of Ignition)	24			10,000 (10%)

Particle size distribution is given in Fig. 2.2.

Table 2.3 shows the main mineralogical phases in sludge after calcination at 950°C. Structure of the sample before calcinations was mostly amorphous. SHIMADZU XRD-6000 instrument coupled with Cu-X Ray tube (л = 1.5405 Angstrom) was used for determination of components.

Table 2.4 gives the relevant physical characteristics of the sludge. As expected, sludge has very high moisture concentration as 65% and the particle size distribution is mainly varied between 2–50 μm and average particle size is 10 μm (Fig. 2.2).

Chemical composition of phosphating sludge determined by means of Atomic Absorption Spectrometry is given in Table 2.5. Concentrations of Ni, Zn, Fe, and Na are 7,415 mg/kg, 94,000 mg/kg, 186,000 mg/kg, and 27,000 mg/kg, respectively.

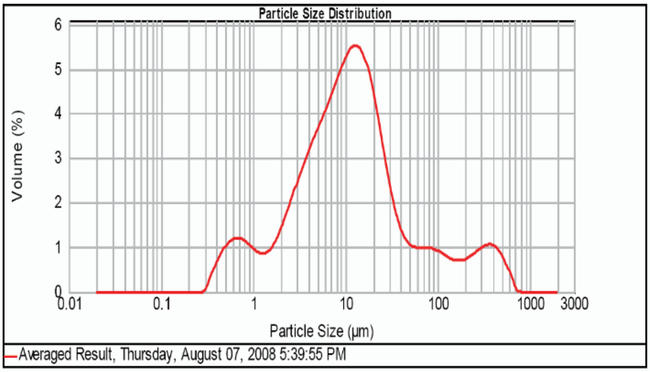

Fig. 2.2. Particle size distribution of phosphating sludge.

Table 2.3. Main mineralogical phases in sludge after calcination.

Compounds	Formulation of compounds	Composition rate (%)	Dust diffraction number
Iron Phosphate	$Fe_7(PO_4)_6$	44	49–1088
Zinc Phosphate	$Zn_2P_2O_7$	50	34–1275
Sodium Iron Phosphate	$NaFeP_2O_7$	6	36–1454

Table 2.4. Physical characteristics of the sludges.

	Particle size distribution (%)		
Moisture Content (%)	0.3–2 (μm)	2–50 (μm)	50–1,000 (μm)
65	10	80	10

Table 2.5. Chemical composition of sludge.

Composition (mg/kg)				
Ni	Zn	Fe	Na	Total P
7,415	94,000	186,000	27,000	150,400

3. Stabilization/solidification of phosphating sludge

With ever-increasing emphasis on the environment and the decrease in available landfill capacities as well as within the frame of harmonization of EU directives with Turkish regulations, the generation and disposal of phosphate sludge has become a challenge in automotive industry in Turkey. The general application for waste disposal in Turkey is landfilling due to economical considerations. Eluate concentration of pollutants after the Hazardous Waste Control Regulation should not be exceeded in order to dispose of the waste on landfill sites. But, eluate concentrations of Ni and Zn in the leaching test of phosphating sludge exceed the limits set in the Regulation. For this reason, another opportunity for recovery and disposal of phosphating sludge is stabilization and solidification processes before landfilling. The solidification/stabilization technology can be applied to the phosphating sludge classified as hazardous wastes. In the process, some binders and additives such as cement, zeolite, and bentonite can be used, which are non-hazardous and inexpensive in Turkey.

An effective procedure for stabilization/solidification of phosphating sludge was developed and verified. The sludges containing some toxic heavy metals are detoxified and made non-hazardous by solidification/stabilization technology.

After S/S process using cement, zeolite and bentonite as binder, the product is analyzed by using SEM, XRF and XRD in order to determine the structure and composition of the material. S/S process is realized by mixing of binders and additives in different proportions. According to the result, the properties of the material can well define whether it is hazardous or non-hazardous. The solidified materials are also analyzed by using elute and extract procedures, and the hazard characteristics of the waste are determined based on the regulation by means of leaching test methods (DIN 38414-S4 Test).

A solidification/stabilization process was realized by mixing of binders and additives as cement, sand and sludge in different proportions. Twenty-eight days retention time was applied for maturation of concrete. The leaching test was realized by using distilled water according to standard method. Ni and Zn are analyzed by means of standard methods after receiving extract and eluate. Results of leaching tests are given in Figs. 3.1 and 3.2.

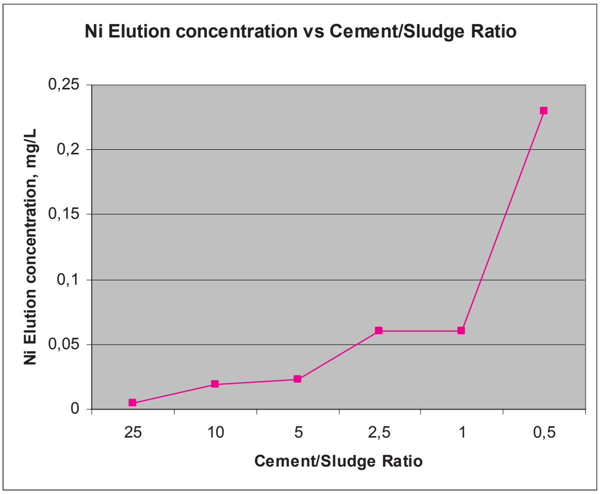

Fig. 3.1. Ni elution concentration of solidified sludge.

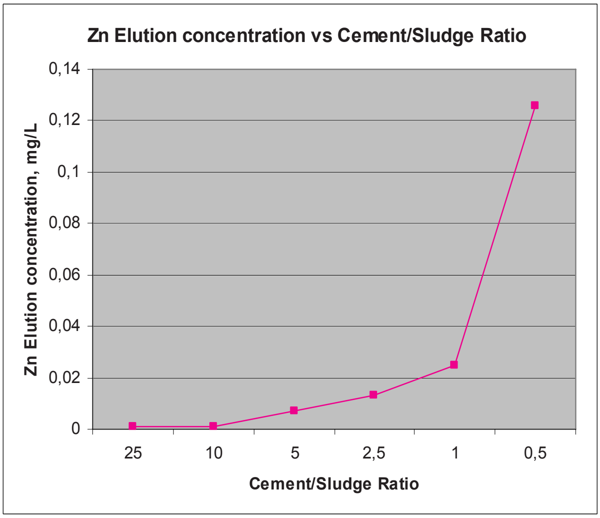

Fig. 3.2. Zn elution concentration of solidified sludge.

According to the results, Ni concentration of elution was reduced from 120 mg/L (original sample) to 0.005, 0.019, 0.023, 0.06, 0.06, 0.23 mg/L by mixing ratio of cement/sludge 25, 10, 5, 2.5, 1, 0.5 , respectively. Zn concentration of elution varied from 650 mg/L (original sample) to 0.001, 0.001, 0.007, 0.013, 0.025, 0.126 mg/L by mixing ratio of cement/sludge 25, 10, 5, 2.5, 1, 0.5, respectively (Table 3.1). Increasing the cement content of the mixtures decreases the elution rates of the heavy metals.

Table 3.1. Leaching test result according to sludge and cement mixing ratio.

Sample no.	Sludge (%)	Cement (%)	Sand (%)	Elution concentration of Ni (mg/L)	Elution concentration of Zn (mg/L)
1	100	–	–	120	650
2	50	25	25	0.230	0.126
3	25	25	50	0.060	0.025
4	10	25	65	0.060	0.013
5	5	25	70	0.023	0.007
6	2.5	25	72.5	0.019	0.001
7	1	25	74	0.005	0.001

Additionally, compressive strength tests should also be conducted in order to determine the usability of solidified concrete waste as bricks or other construction materials.

4. Conclusion

The automotive sector manufacturing vehicles and its spare parts is called as 'the locomotive' of the economy in industrialized countries. It is labeled as the locomotive sector because of its close relations with many industrial branches and other sectors of the economy.

Turkish automotive sector represents one of the major powers of the Turkish Industry with its importance as one of the most-advanced branches of the Turkish manufacturer industry. In Turkey, the automotive sector presents a rapid-rising performance inside the general Turkish economy.

As a recovery and disposal methods, solidification and stabilization processes are very important considering the limited number of hazardous waste disposal sites.

Additionally, economical consideration is also very important to encourage the Turkish industry especially automotive industry by improving feasible disposal and recovery processes. In that point, to find both technical and economical feasible disposal method for phosphating sludge originated from automotive industry and to implement this method to all automotive industry in Turkey is essential to encourage them and to eliminate one of the environmental problems that can be a challenge for the development of this sector.

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