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Stabilization of Metal-Laden Soil Using a Novel Combination of Cement with a Sintered Waste Additive

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Abstract — *Hazardous waste generating industries, which contain unsafe levels of organic and inorganic contaminants, should follow some routes to manage the waste. However, in most Asian countries like India, this management is relatively a very new concept. A major task to manage hazardous waste is to stop the leaching of the disposed wasted from polluting the underlying ground water. An attempt has been made to treat/stabilize hazardous wastes prior to disposal into a landfill using a specially prepared sinter "S" along with the conventional material like Fly ash, Cement & Lime. The experiments were carried out with 15 mixtures of cement, fly ash, sinter, and lime; each of these mixtures was blended with water. Characteristics of the stabilized/solidified product, including compressive strength and metal concentration in the leachate, were evaluated. The compressive strength of 6.9 N/mm^2 was attainable for solidification when the additives are added to the sludge and cured at 23°C for 28 days. The best mixes showed exceptionally high values of compressive strengths indicating the enormous success of the use of sinter for solidification. The optimal mixtures are effective in solidifying electroplating sludge (ETP sludge) and in reducing leachability to the required limits. The sinter obtained by a special process from ETP sludge and Water works sludge is found to replace cement to an extent of 45% in the Solidification/Stabilization process.*

Keywords*— *hazardous waste, heavy metals, leachate, solidification, stabilization, sinter,

1. INTRODUCTION

Rapid growth in Indian industries, owing to liberalization of economic policies, is observed in past forty years. Large amount of industrial wastes are produced every year by various industries. Metallurgical industries generate vast quantities of solid waste such as slag, ash, sludge, dross and tailings. Inappropriate disposal of these wastes causes contamination of surface water (runoff into surface water bodies), ground water (through seepage or leaching), biota (bioaccumulation), and soils (dust tracking and erosion); sediments (leaching into water bodies). Environmental pollution by heavy metals from industrial activities can become a very important source of contamination both in soil and water [1], [2].The presence of heavy metals produced during metal extraction in the aquatic environment is of major concern due to their toxicity to many life forms [3]-[5]. Any waste which has potential to cause irreparable damage to environment or incapacitate illness to humans is termed hazardous. This might be due to its biological, chemical, physical and infectious properties. It is a tossed out material whose nature makes it prospectively dangerous. Additionally being toxic, these wastes are corrosive, reactive and flammable. The hazardous effects are imposed extrinsically and intrinsically. Any material which can interfere with normal physiology, and is poisonous causing severe injury to animals and humans, is termed toxic. Hazardous waste generating industries, which contain unsafe levels of organic and inorganic contaminants, should follow some routes to manage the waste. However, in most Asian countries like India, this management is relatively a very new concept. India is handicapped by lack of technical and financial resources. Additionally, absence of regulatory control in the past led to the unscientific disposal of hazardous wastes. This problem of management is complicated by the non-homogeneity of the waste. Usually industries, tend to dispose the waste into a landfill, with/without treatment and stabilization; incinerate the waste with/ without pre-treatment, and ultimately dispose it into the landfills. Contamination of ground water by landfill leachate posing a risk to downstream surface waters and wells is considered to constitute the major environmental concern associated with the landfilling of the waste [6]. A major task to manage hazardous waste is to stop the leaching of the disposed wasted from polluting the underlying ground water. Of all the above mentioned options for management of hazardous waste, this study focused on treatment/stabilization of hazardous wastes prior to disposal into a landfill, with addition of cement binders, fly ash and lime. Several studies have been carried out on solidification/stabilization of metal laden soils. A stabilization process of mineral residue contaminated with heavy metals and organic compounds was attempted by Depelsenaire – Solvay [7] called the Novo sol process. Studies were carried out by different research teams from 1998 to 2001 using the strategy of incorporating it in concrete. Bachelor B [8] presented an overview of waste stabilization with cement. Wiles [9] reviewed stabilization and solidification technologies. Sobiecka [10] investigated "the chemical stabilization of hazardous waste material (fly ash) encapsulated in Portland cement. She suggested physico-chemical method as an effective stabilization method for hazardous waste. Her research explored the immobilization of metals in various mixtures of Portland cement and fly ash waste sampled from coal power plant in the province of Lodz, central Poland. Pritts et al. [11] studied stabilization of heavy metal containing hazardous wastes with by-products from advanced clean coal technology systems. Lasheen et al., [12] investigated the efficiency of metals immobilization in sludge using pozzolanic materials fly ash and cement clinker dust (CCD). Different leaching tests such as the standard European (EN) 12457-2 leaching tests; the toxicity characteristic leaching procedure; and the multiple extraction procedure test were used [13] to evaluate the efficiency of metals stabilization in sludge matrix, and they showed that the availability of metals leaching (Cd, Cu, Cr, Pb, Ni, Zn) from the stabilized sludge were lower than the permissible limit. Cinquepalmi et al. [14] studied reuse of cement-solidified municipal

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incinerator fly ash in cement mortars as an artificial aggregate. Porosity, compressive strength, leaching behavior of these specimens was tested. Relatively high compressive strength (up to $36 N/mm^2$) and low leaching rates of heavy metals (Cr, Cu, Pb and Zn) were reported. Malviya and Chaudhary [15] conducted experiments on leaching behavior and immobilization of heavy metals in solidified/ stabilized products. Solidification/stabilization (S/S) of hazardous sludge from steel processing plant has been studied. Mechanical strength and leaching behavior test of solidified/stabilized product was performed. Mechanical strength decreases with increase in waste content. Pb, Zn, Cu, Fe and Mn could be considerably immobilized by the solidification/stabilization process.

2. MATERIALS AND METHODS

The objective of the study was also to compare the novel binder "S" with other conventional binders. In this study the conventional binders like Fly ash, Cement & Lime has been utilized alone and also with the Sinter "S" to check the efficiency of stabilization. Hence an experimental study has been carried out with the selected samples by varying the proportion of these four binding agents alone and in combinations as shown in Table 1. The effects of operational parameters such as dosage of the stabilizer, curing time and combination of stabilizers on efficiency of mobilization were investigated to reach the criteria of hazardous waste disposal on secured landfill site. The samples were collected from representative regions in clean polyethylene bags and preserved. A significant amount of soil/sludge is mixed well and dried in the oven at 60˚C for 24 hours. The sample was crushed using a crusher to remove the boulders and is sieved to get a homogenized sample having particle size less than 1 mm. A representative sample of the soil was characterized in the laboratory as per standard procedure. The procedure followed in this research is; *(1)* Determination of optimal mixtures based on the compressive strength of the prepared samples (2)Determining the leaching characteristics of the samples to identify the optimum mixture (of cement and additives. to the metal laden soils.) that satisfies the criteria for disposal on to landfills. *(3)* Finally, the optimal mixtures based on the compressive strength consideration and leachability considerations were preserved for study of their microstructure. ETP sludge waste samples collected from various locations were utilized. Five kg each of electroplating sludge and waterworks sludge was taken and analyzed for physical and chemical properties. Stabilization agents like cement, fly ash, lime, and a sintered waste(S) additive was analyzed for CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO, loss on ignition etc. Leach resistance tests were conducted by varying the proportion of stabilizing agents. Studies on characterization of these agents and extracted stabilized samples were done and concentrations of heavy metals were measured. Changing the operational parameters like dose of stabilizers, combinations of stabilizers and their ratios and curing time (3, 7 and 28 days), the optimum operational conditions were arrived at.

2.1 Preparation of cylindrical specimens

100 gm of the metal laden soil was taken and mixed with predetermined weights of cement, and solidification additives (fly ash, lime and sinter "S") by adding distilled water. The mixtures of samples were then placed into 2.5 cm diameter by 7.5 cm long PVC moulds for 24-hour hardening and cured for 3, 7 and 28 days in a controlled temperature/humidity room (23 °C, 95 % relative humidity). All dosages are listed in Table 1.

Table 1 Proportions & combinations of the stabilizing agents

Sl.No	Additives Cement Ratio	Quantity (gm)				
		ETP Sludge	Additives + Cement (40gm)			
			Additives			Cement
			Sinter	Fly Ash	Lime	
1	20::80	60	1/3	1/3	1/3	
			8/3=2.67	8/3=2.67	8/3=2.67	32
2	20::80	60	2/3	0	1/3	
			8x2/3=5.33	0	8/3=2.67	32
3	20::80	60	2/3	1/3	0	
			8x2/3=5.33	8/3=2.67	0	32
4	30:70	60	1/3	1/3	1/3	
			4	4	4	28
5	30:70	60	2/3	0	1/3	
			8	0	4	28
6	30:70	60	2/3	1/3	0	
			8	4	0	28
7	40::60	60	1/3	1/3	1/3	
			5.33	5.33	5.33	24
8	40::60	60	2/3	0	1/3	
			10.66	0	5.33	24
9	40::60	60	2/3	1/3	0	
			10.66	5.33	0	24
10	50::50	60	1/3	1/3	1/3	
			6.66	6.66	6.66	20
11	50::50	60	2/3	0	1/3	
			13.33	0	6.66	20
12	50::50	60	2/3	1/3	0	
			13.33	6.66	0	20
13	60::40	60	1/3	1/3	1/3	
			8	8	8	16
14	60::40	60	2/3	0	1/3	
			16	0	8	16
15	60::40	60	2/3	1/3	0	
			16	8	0	16

Table 2 Characteristics of the sludge samples used

Parameter	Instrument/ Method Used	ETP Sludge	Water Works Sludge
Physical State	Visual Observation	Solid	Solid
Colour	Visual Appearance	Deep Brown	Brown
Texture	Visual Appearance	Granular	Clayey
Specific Gravity	Pycnometer Method	2.72	2.85
Calorific Value (KCal/kg)	Bomb Calorimeter	287.6	8.95
Loss On Drying (%)	Oven Drying Technique	12.3	67
Loss On Ignition (%)	Furnace Volatilization Technique	7.84	10.33
pH	pH Meter	8.36	8.16

2.2 Analysis

After the predetermined specific curing period, the samples were tested for unconfined compressive strength (UCS) using a Universal Testing Machine. Each sample formulation was measured in duplicate. The UCS test was completed on a cylindrical sample of the stabilized/solidified matrix. After measuring the UCS of the cured sample, the hydrated samples were crushed to prepare them for the following Toxicity Characteristic Leaching Procedure (TCLP) test.

2.3 TCLP test

100 g of the sample and 2000 ml of the specified concentration of acetic acid solution were placed in polyethylene bottles. The samples were agitated and removed from the agitator after 18 hours and filtered through a 0.6 to 0.8 mm Millipore filter. Then the pH of the leachate was measured. The filtered leachate was acidified with nitric acid to pH 2 to measure the metal concentration by ICP-OES.

Table 3 Heavy metal concentration in samples

S. N	Sample	Heavy Metal Concentration (ppm)								
		Cu	Cr	Fe	Mn	Ni	Pb	Zn	Co	Cd
1.	Raw ETP Sludge	315	150	19,890	1059	81	14	196	14.3	BDL
2.	Water Works Sludge	76	44	566	23.8	2.9	0.4	8.4	0.1	BDL
3.	Sinter "S"	355	162	20,122	1044	73	14	187	13.9	BDL
4.	SLF Disposal Limits	10	0.5	-	-	3	2	10	-	0.2

3. RESULTS AND DISCUSSIONS

A novel combination of cement, fly ash, and lime with a sintered waste was used in these experiments to solidify the metal-laden soils and reduce the heavy metal concentration in the leachate before it has been disposed on to a secured landfill. The solidification and stabilization studies were performed at laboratory scale. The experiments were conducted by varying the dosage of the binders at different combinations and duration (i.e., curing time). The samples, obtained from ETP sludge were collected. The samples which contain heavy metals were subjected to preliminary studies to know about the basic characteristics. Specific studies were done on different parameters viz., Specific gravity, calorific value, Loss on Drying (LOD), Loss on Ignition (LOI), pH, etc., of the samples as mentioned in the methodology chapter. Also the heavy metal concentrations of the samples were studied using ICP-OES to know its initial heavy metal concentration. The Table-2 shows the basic characteristics, whereas the Table-3 shows the heavy metal concentration in the samples from the table 3, it can be observed that the electroplating sludge from the common effluent treatment plant is found to contain large quantities of Fe, Mn, Ni, Cu, Cr, Zn, Pb and Co. The waterworks sludge used to prepare the sinter "S" contained high concentrations of Fe, Cu, Cr and Mn. From the tables 4, it is clear that all the mix designs of ETP sludge satisfy the criteria for disposal to SLF from the point of view of unconfined compressive strength (being > 0.34 N/mm^2). The Unconfined compressive strengths of all 15 mix designs for ETP sludge were determined in a Universal Testing Machine. The UCS values were measured after a curing period of 3, 7 and 28 days. (Number of UCS tests carried out was 15*2 = 30). It was observed in all the cases that a mere 3 day curing period was sufficient to attain the minimum secured landfill disposal criteria value of 0.34 N/mm^2.

Table (4) Unconfined compression strength of ETP sludge laden samples

Batch No.	3rd Day Unconfined Compressive Strength	7th Day Unconfined Compressive Strength	28th Day Unconfined Compressive Strength
	(N/mm^2)	(N/mm^2)	(N/mm^2)
1.	2.12	3.59	5
2.	2.41	4.1	6.66
3.	2.06	3.49	5.78
4.	2.29	3.86	6.27
5.	2.36	3.98	6.47
6.	2.18	3.69	6.08
7.	2.12	3.51	5.68
8.	2.23	3.7	5.98
9.	2	3.33	5.39
10.	1.92	3.13	5
11.	1.94	3.21	5.19
12.	1.82	3.05	4.9
13.	1.69	2.7	4.52
14.	1.79	2.88	4.82
15.	1.53	2.57	4.12

Also, as expected logically, longer curing periods made the samples attain higher compressive strengths, reaching a phenomenal maximum of 6.6 N/mm^2 which is nearly 18 times the SLF criteria value. Conduction of the leach ability studies yielded the concentrations of the individual heavy metals present in the leachates extracted from the 15 mix design batches ETP sludge samples. It clearly indicate the extent of the stabilization achieved for each metal as it can be compared with the minimum criteria value of each metal specified for the disposal into a secured landfill. The batches exceeding the criteria value are the ones which are the batches whose mix designs have failed to stabilize the sludge with respect to that particular heavy metal. The table 5 shows these results (i.e. The Heavy Metal Stabilization effectiveness) concisely.

4. CONCLUSIONS

These solidification/stabilization technologies using cementitious materials have been used for many years as a final treatment step prior to the disposal of hazardous wastes.

Table (5) Heavy Metal Stabilization Effectiveness in the ETP sludge mix design batches

Mix Design Batch No.	Additive: Cement Ratio	Metal concentrations in leachates in ppm								
		Cu	Cr	Fe	Mn	Ni	Pb	Zn	Co	Cd
		Criteria Conc (ppm)								
		10	**0.5**	**-**	**-**	**3**	**2**	**10**	**-**	**0.2**
1.	20.:80	7.85	0	0	2.75	2.8	0	6.81	1.07	0
2.	20.:80	7.12	0	0	2.3	2.16	0	6.33	1.05	0
3.	20.:80	7.54	0	0	2.58	2.51	0	6.74	1.05	0
4.	30:70	7.93	0	0	3.64	2.95	0	7.25	2.53	0
5.	30:70	7.71	0	0	3.26	2.7	0	6.91	2	0
6.	30:70	7.82	0	0	3.43	2.84	0	7.16	2.33	0
7.	40.:60	8.95	0	0	3.92	2.71	0	8.9	3.22	0
8.	40.:60	8.27	0	0	3.74	2.52	0	8.23	2.89	0
9.	40.:60	8.69	0	0	3.81	2.63	0	8.61	2.93	0
10.	50.:50	9.92	0	0	4.69	2.89	0	9.84	3.41	0
11.	50.:50	9.75	0	0	4.41	2.65	0	9.77	3.23	0
12.	50.:50	9.8	0	0	4.62	2.77	0	9.71	3.33	0
13.	60.:40	19.88	0	0	4.79	5.6	0	11.88	4.09	0
14.	60.:40	17.2	0	0	4.53	5.31	0	11.65	3.9	0
15.	60.:40	18.9	0	0	4.78	5.32	0	11.8	4.01	0

Note: Data underlined exceed limits

This project work aims to find a novel waste additive "S" added to cement to stabilize metal laden soils. The research carried out using this additive yielded promising results in reducing the cost of disposal of metal laden sludge. The data presented above reveal a number of trends and lead to some significant conclusions regarding S/S practice. The following conclusions were made based on the results of the present study: 1) All the sinter stabilized mix design samples proved to be very effective for solidification as their Unconfined Compressive Strength (UCS) values were much greater than minimum criteria value prescribed for disposal on to Secure Landfill i.e. 0.34 N/mm^2. 2) From the study, it can be derived that Sinter "S" provides a better reduction in the concentration of metals along with cement than the other conventional binders like fly ash and lime.

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