Solidification/Stabilization of Sludge Waste from Thermal Power Plants Using Portland Cement

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***Abstract*- Shahid Rajaee Power Plant, located about 100 km west of Tehran, is one of the Iran's biggest thermal power plants. During the operation of the plant, different kinds of wastes are produced. Dewatered sludge waste from air heater washing wastewater treatment of the plant was subjected to investigation of the cement-based Solidification/Stabilization (S/S) experiments to reduce the mobility of heavy metals. By reviewing the production procedure of this waste, it can be conjectured that this waste probably contains a variable range of heavy metals such as V, Ni, Zn and Cr. In the present study, the S/S method was used to convert this waste into nonhazardous by using both Portland Cement Type I (CEMI) and standard sand (Ottawa Sand) as additive materials. The compressive strength of the samples with different amounts of waste was examined in order to study the changes in the bearing characteristic of the samples, in comparison with the control sample. Microscopic characteristics of both raw and solidified waste samples were observed using a Research Polarize Microscope (RPM). The compressive strength test results reported only about 30% decrease in the results of the samples with waste, comparing to control concrete sample without waste.**

***Keywords*- Thermal Power Plant; Hazardous Sludge Waste; Solidification/Stabilization; Environmental Engineering; Concrete**

I. INTRODUCTION

Solidification/Stabilization (S/S) method is a subset of physical-chemical treatment with its specific nature and process. S/S includes adding certain additives to the waste in order to minimize the contaminants leaching from waste to the environment. Adding additives would make chemical bonds change in the materials, resulting in confining the wastes [1]. Similarly, the physical properties of waste (which are known as engineering properties, including strength, durability, permeability, etc) will also be changed by adding certain additives [2]. Hence, S/S process decreases the amount of toxicity and leaching of the hazardous materials while improving their physical properties [3].

As a result of increased municipal consumption of natural gas and as a result of pressure loss during the late fall and winter, fuel oil is burnt to generate electricity in thermal power plants of Iran [4]. This is the case for Shahid Rajaee Power Plant. The heat produced in this process, being adjacent to a radiator network, is transferred to fluid container of network and electricity production process continues. Owing to the flow of burning fuel smoke, some materials are deposited on heat transfer surface which reduce the efficiency of heat transfer between fluid and outside air, affecting overall efficiency of the plant. Therefore, it is necessary to wash the air heater system surface regularly [5]. Resulting waste water from this process (air heater washing) contains different amounts of pollutants, especially heavy metals. Wastewater will then be treated through chemical precipitation processes which will result sludge containing those heavy metals in higher concentrations. Therefore, the sludge contains significant amounts of various heavy metals such as Chromium, Cadmium, Arsenic, Copper, Lead, Mercury, Nickel, Zinc, Selenium, and Vanadium that can be toxic and dangerous to the environment [6, 7]. The dewatered sludge should be classified as specific industrial waste which regardless of the quantity should be characterized in detail (i.e. toxicity leaching characteristics) under the specific waste management regulation of Iran [8]. Regarding Iranian codes, if the waste is categorized as hazardous, facility owners are not allowed to disperse or landfill it in the municipal waste landfills unless they are stabilized.

S/S has been extensively used as an effective technology for the treatment of hazardous wastes by many researchers [3, 5, 9-14]. Barth et al. (1990) showed that using cement and pozzolanic materials as binders in stabilization of heavy metals containing waste was effective in reducing the leaching of heavy metals. Others continued using cement-based binders for S/S of heavy metals in sludge waste. For instance, Sophia and Swiminathan (2005) have used different binders such as cement and fly ash for S/S of electroplating waste and reported that the use of cement has shown better results. They argued that alongside producing a solid mass, cement may make some changes in the chemical composition of the waste so as to reduce the toxicity of the compounds in the product [15].

In the present study, "Portland Cement" and "Sand-Cement" mixture has been used in order to investigate the leaching properties and mechanical resistance of the solidified waste materials [16]. Probable changes in the compressive strength and the leaching potential of the pollutants in the solidified materials are presented for different ratios of waste material and cement used in the study.

II. MATERIALS AND METHODS

Microscopic structure and compressive strength of raw and solidified samples were studied. By preparing thin sections of 30 μm thickness, RPM was used to observe the morphology of the raw and solidified/stabilized waste samples. A Zeiss RPM device was used and photography was taken by a Canon J5 scientific camera with size 150X.

Furthermore, ASTM-C109-90 method was employed to determine the compressive strength of the samples [17]. Also, load tolerance of the samples was measured by “ELE Elect-2000 Digital” instrument.

A. S/S Mix Design

Considering the studies provided in the literature and related discussions mentioned above, S/S of sludge, carried out using cement and sand-cement mixture. The samples were mixed, molded and demolded according to the procedure of ASTM-C109-90. This method is used to measure the compressive strength of sand-cement mortar cube samples with dimension of 50×50×50 mm, in which the ratio of sand/cement is 2.75 and water/cement is 0.485. Based on the ASTM-C778, the standard Ottawa sand which includes natural silica was used [18]. Mixing processes were performed according to the ASTM-C109-90, but instead of any metal tools, glass or plastic containers were used to remove possible influence of metal elements on compounds. In the case that sand-cement combination was used for stabilization, the process was exactly same as the above mentioned standard, but the ratio of water/cement was increased because of the lack of water due to the increase in waste content. Moreover, a part of the sand was replaced with certain amounts of cement and waste material. The practical process of preparing solidified/stabilized samples is described in the following section.

1) S/S with Sand-Cement:

The process of S/S with sand-cement mixture was performed based on ASTM-C109-90 standard method. Seven and fourteen day compressive strengths of samples have been tested to evaluate physical properties of the mixtures. Two samples for each mix design were prepared in order to increase the accuracy of results. With selected ratios of 5, 10, 15, 20, 25 % for waste/cement weight ratio, and having a control sample (for each of two mixtures, to make the results comparable and accuracy check purposes), 12 containers were totally used to make the samples. During this process 85 gr of cement was weighted for each sample at first. Then, according to the desired weight ratio for each sample, waste material was added to cement, except for the control sample. The waste material was placed in the stove at 64˚C for 24 hours to dry at first and then it was converted into a powder form in a special container and added to the cement with desired weight ratios that has been given in Table I. As shown in Table I, depending on the waste/cement ratio, the amount of waste in mixing design was calculated by keeping the cement constant.

TABLE I MIX DESIGN OF SAND-CEMENT SOLIDIFIED/STABILIZED SAMPLES

Waste/Cement Ratio (%)	Waste (gr)	Cement (gr)	Sand (gr)	Water (gr)
0	0	82.22	226.11	39.9
5	4.11	82.22	226.11	39.9
10	8.22	82.22	226.11	39.9
15	12.33	82.22	226.11	39.9
20	16.44	82.22	226.11	39.9
25	20.55	82.22	226.11	39.9

After adding powdered waste to the cement, it was mixed well in order to be homogeneous. Then, 226 gr of Ottawa standard sand (sand/cement ratio 2.75) was added to each sample and was mixed again to be completely homogeneous. Finally, according to the desired ratio of water/cement, 40 mL distilled water was added to each mixture. At this stage, molding of the samples was undertaken using clean and 50×50×50 mm molds. After pouring mortar samples into the molds, they were cured for 24 hours (at room temperature). Then the samples were immersed into the water completely to achieve a good processing condition. The samples were remained in water at least for seven days and then the first series of the samples were taken out for compressive strength testing. Second series of the samples brought out after fourteen days and related tests were performed on them.

2) S/S with Cement:

S/S process in the case of using only cement, as stabilizer material, is similar to the previous case. The only difference is that cement and powdered waste material were used instead of sand in the mixture. To reach a wider range of comparison between samples, the weight ratios of waste/cement were changed to 10, 20, 30, 40, and 50 %. Considering this fact that waste material in the compound is completely dry, the water/cement ratio equal to 0.485 seems inadequate, especially in combinations with weight ratios of 30, 40, and 50 %. So, the water/cement ratio was increased to 0.56 in order to ease mortar moving into the mold. The mix design is shown in Table II.

TABLE II MIX DESIGN OF CEMENT SOLIDIFIED/STABILIZED SAMPLES

Waste/Cement Ratio (%)	Waste (gr)	Cement (gr)	Water (gr)
0	0	301.50	146.20
10	30.15	301.50	150.80
20	60.30	301.50	155.30
30	90.45	301.50	159.80
40	120.60	301.50	164.30
50	150.75	301.50	168.80

In this case, there were also five different combinations and a control sample that contains only cement and water. Two samples of each combination were prepared to improve the accuracy of the results. The measurements for compressive strength of samples were undertaken at seven and fourteen-day curing age. The processing method was same as previously described. Therefore, samples were demolded and immersed into the distilled water. First series of samples brought out after seven days and second series were taken out after fourteen days to conduct desired chemical and physical tests on.

III. RESULTS AND DISCUSSION

A. Physical and Chemical Characteristics

The physical characteristics of the raw and solidified/stabilized waste samples are presented in Table III. C stands for cement samples, and SC denotes Sand+Cement samples. The pH of all solidified/stabilized samples is more than 12.0. This shows the effect of cement in the samples and the basic properties from this material which has completely desolated the acidic properties of the raw waste. Density results from the raw waste shows that this waste is lighter than cement and sand, so it is expected that the density decreases in samples with higher waste content (Table III). It is obvious that in solidified/stabilized samples, as the waste/cement ration increase, the density of the product decreases. Chemical composition of raw and solidified/stabilized waste samples determined by XRF method is presented in Table IV. As we were concerned on presence of heavy metals in this study, all the related components have been determined and presented. The main constituent of waste is Fe_2O_3. The percentile of Fe2O3 in Shahid Rajaee power plant wastes is much higher than reported magnetite content of some other waste types in previous studies [19, 20]. Mean concentration of some trace elements such as Cr, Ni, V, and Zn in raw waste is in the upper range which makes them more noticeable, but some other elements such as As, Cd, and Hg have lower concentrations. As it is seen in Table IV, fuel oil related metals (V, Ni, Zn, Sr, Cr, and Ba) have high concentrations in the waste.

TABLE III PHYSICAL CHARACTERISTICS OF THE RAW AND SOLIDIFIED/STABILIZED SAMPLES

	Sample Code	Waste/Cement Ratio (%)	Density (kg/m^3)	pH
Mean Raw Waste	–	–	1879	6.31
Cement Solidified/Stabilized	Control (i)	0	2061	13.32
	C1	10	2028	13.12
	C2	20	1976	12.86
	C3	30	1916	12.87
	C4	40	1988	12.89
	C5	50	1847	12.89
Sand+Cement Solidified/Stabilized	Control (ii)	0	2084	12.63
	SC1	10	2077	12.91
	SC2	20	2062	12.66
	SC3	30	2042	12.88
	SC4	40	2020	12.51
	SC5	50	2000	12.85

B. Microscopic Imaging

Microscopic photos of both raw and solidified/stabilized samples have been presented in this section in order to analyse the effect of pollution presence on the micro-structure of samples. Figure 1, which is related to the raw waste microscopic structure, shows amorphous mass with many open pores in the waste clearly. With a little closer and more accurate watch to Figures 1-a and 1-c, some compounds of wet oxidized ferrous can be seen that are most likely Fe_3O_4, FeOOH or Fe_2O_3+H_2O colored reddish dark brown. Figures 2 and 3 illustrate microscopic structure of samples solidified/stabilized by cement and sand–cement mixture with different ratios of waste to cement, respectively. In sand–cement solidified/stabilized samples quartz and sand grains are quite visible and the cement paste matrix that created adhesion between the grains is visible. Existence of waste mass in the samples increases the surface of waste materials in comparison to total microscopic surface. As the waste/cement weight ratio is increased, more areas can be found with brown color. Also, homogeneous matrix structure of cement or sand–cement is reduced with more fracture and discontinuity.

TABLE IV CHEMICAL COMPOSITION OF RAW AND SOLIDIFIED WASTE SAMPLES

		Sample											
	Mean Raw Waste	**Cement Solidified**						**Sand + Cement Solidified**					
		Blank	**1**	**2**	**3**	**4**	**5**	**Blank**	**1**	**2**	**3**	**4**	**5**
Waste/Cement Ratio (%)	–	0	10	20	30	40	50	0	5	10	15	20	25
Compound		Concentration											
Na_2O (%)	0.50	0.35	0.29	0.43	0.35	0.38	0.40	0.27	0.36	0.28	0.36	0.34	0.28
MgO (%)	1.76	–	–	–	–	–	–	–	–	–	–	–	–
Al_2O_3 (%)	2.59	3.92	3.08	3.79	3.46	3.77	3.81	3.71	3.75	3.82	3.80	3.78	3.82
SiO_2 (%)	5.91	25.82	21.14	22.71	21.63	21.75	21.83	37.53	40.60	34.69	39.41	37.99	34.69
P_2O_5 (%)	3.39	0.062	0.130	0.429	0.414	0.544	0.691	0.078	0.114	0.165	0.219	0.240	0.165
Fe_2O_3 (%)	68.88	2.21	7.23	9.91	11.24	12.96	14.89	5.11	4.13	5.06	5.70	6.62	5.06
MnO (%)	0.46	0.087	0.075	0.102	0.103	0.110	0.116	0.073	0.074	0.079	0.083	0.079	0.079
K_2O (%)	0.17	0.47	0.49	0.65	0.51	0.49	0.50	0.41	0.54	0.38	0.48	0.45	0.38
CaO (%)	2.64	61.49	63.56	61.81	58.96	56.77	55.97	49.46	48.61	51.04	45.46	46.14	51.04
TiO_2 (%)	0.08	3.115	1.849	2.851	2.709	2.845	3.065	3.861	3.593	4.062	3.886	3.583	4.062
V (mg/kg)	64413	11	234	505	563	689	815	41	93	164	213	268	164
Ni (mg/kg)	17375	21.9	1038.6	2158.7	2504.7	2978.0	3416.1	182.1	474.3	825.8	980.3	1279.7	825.8
Zn (mg/kg)	1511	51.6	47.8	73.3	91.9	110.2	118.3	82.2	93.4	64.5	122.0	104.9	64.5
Sr (mg/kg)	627	182	199	202	201	208	203	104	114	113	114	116	113
Cr (mg/kg)	6236	16	328	641	714	845	1011	52	115	204	252	336	204
Cd (mg/kg)	1	0.50	0.07	0.05	0.23	0.38	0.05	0.08	0.19	0.08	0.16	0.10	0.08
Co (mg/kg)	129	3.45	6.83	21.12	24.36	28.38	33.04	5.38	7.77	9.85	11.20	13.35	9.85
Hg (mg/kg)	1	0.039	0.291	0.273	0.263	0.216	0.255	0.086	0.069	0.074	0.078	0.080	0.074
Mo (mg/kg)	36	2.71	2.89	2.95	3.07	3.44	3.10	1.91	1.60	1.98	1.61	1.88	1.98
Ag (mg/kg)	–	0.036	0.201	0.170	0.130	0.065	0.197	0.243	0.176	0.195	0.162	0.179	0.195
Bi (mg/kg)	–	0.230	0.110	0.012	0.060	0.010	0.030	0.420	0.580	0.410	0.570	0.460	0.410
Pb (mg/kg)	229	22	22	22	22	22	22	22	22	22	22	22	22
Sb (mg/kg)	–	38.17	17.49	21.91	22.46	27.06	19.81	29.52	39.39	32.79	39.79	32.75	32.79
Sc (mg/kg)	–	110.53	86.85	101.55	99.81	97.98	100.12	78.76	77.58	82.83	75.33	78.04	82.83
Sn (mg/kg)	–	98.15	5.24	32.38	37.80	54.10	12.63	54.50	108.14	74.90	98.74	72.37	74.9
W (mg/kg)	–	1.53	1.04	1.88	0.46	1.52	0.62	0.38	0.55	0.30	0.55	0.38	0.3
Cu (mg/kg)	–	23	24	43	46	54	60	20	26	27	28	33	27
La (mg/kg)	–	26.59	21.23	9.59	35.48	17.94	22.38	14.34	4.84	4.99	6.52	6.96	2.99
Rb (mg/kg)	–	11.1	8.2	8.7	9.3	8.9	9.8	11.6	10.6	13.0	12.1	11.6	13
Zr (mg/kg)	–	64	66	62	62	63	58	62	51	60	53	48	60
Ba (mg/kg)	467	627	629	630	630	631	631	623	631	624	619	625	624
As (mg/kg)	7	7.26	7.26	7.28	7.25	7.23	7.23	7.24	7.24	7.25	7.24	7.24	7.25

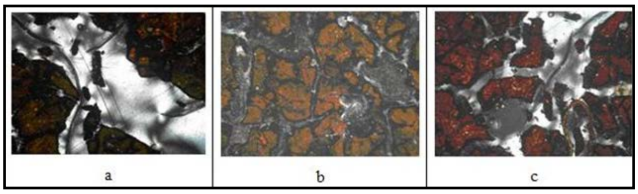

Fig. 1 RPM photography of raw waste

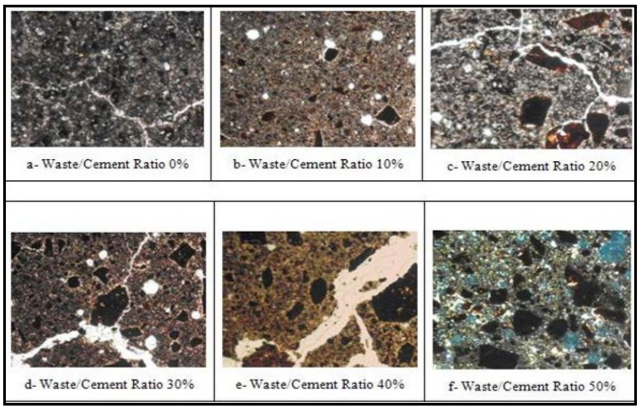

Fig. 2 RPM photography of cement solidified samples

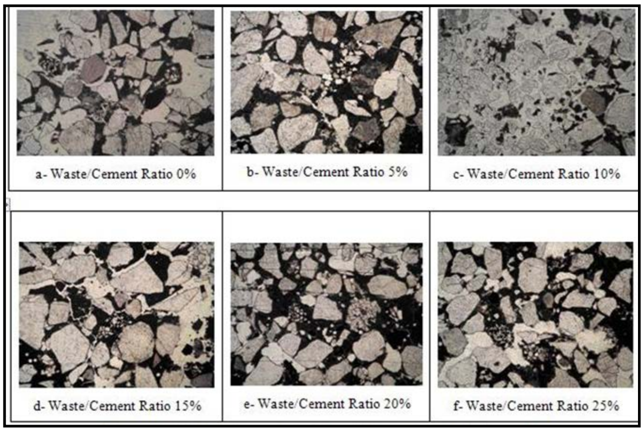

Fig. 3 RPM photography of sand-cement solidified samples

C. Compressive Strength of Concrete Samples

One of the most important physical properties desired in the present study is the compressive strength changes of the cement and sand–cement concrete samples by adding waste to the composition. As already explained, preparing process of samples and measuring their compressive strength were performed according to the ASTM-C109-90. The compressive strength tests were conducted on two series of seven-day and fourteen-day samples to examine the variations of compressive strength in the processing period. The results have been presented in Table V. 7C and 7SC denote seven days Cement and Sand-Cement solidified/stabilized samples, respectively. While 14C and 14SC represent fourteen days Cement and Sand-Cement solidified/stabilized samples, respectively.

TABLE V COMPRESSIVE STRENGTH TEST RESULTS OF SOLIDIFIED SAMPLES

		Sample Code	**Waste/cement (%)**	**Compressive Strength (N/mm^2)**
7 Days samples	**Solidified with Cement**	Control	0	255.25
		7C1	10	182.85
		7C2	20	180.64
		7C3	30	145.38
		7C4	40	129.5
		7C5	50	120.78
	Solidified with Sand-Cement	Control	0	131.96
		7SC1	5	95.05
		7SC2	10	92.09
		7SC3	15	77.24
		7SC4	20	69.37
		7SC5	25	58.81
14 Days samples	**Solidified with Cement**	Control	0	380.88
		14C1	10	268.22
		14C2	20	210.98
		14C3	30	174.44
		14C4	40	154.4
		14C5	50	139.01
	Solidified with Sand-Cement	Control	0	163.31
		14SC1	5	134.65
		14SC2	10	129.63
		14SC3	15	127.35
		14SC4	20	121.17
		14SC5	25	99.93

As can be observed, the results indicate that when the waste material is added to the control sample, compressive strength is reduced. This may be resulted from the amorphous texture of waste materials existed in the samples. In fact, by adding waste to cement and making mortar, amorphous tissue of waste material is replaced with the tissue of contiguous and crystalline of cement or sand-cement links. Reducing these crystal links density, means more amorphous combinations were replaced with cement or sand-cement links and therefore the compressive strength of concrete is decreased. Figures 4a and 4b corroborate that when processing of cement or sand-cement samples is done properly, the fourteen-day compressive strength of samples are generally higher than the seven-day compressive strengths.

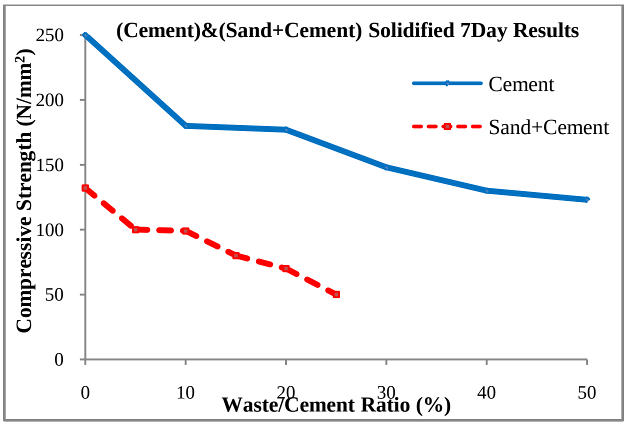

Fig. 4a Changes in Compressive Strength of 7-Day Solidified Samples

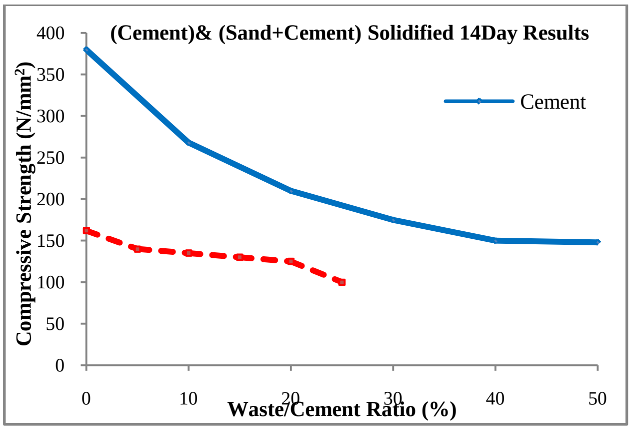

Fig. 4b Changes in Compressive Strength of 14-Day Solidified Samples

As shown in Figures 4a and 4b, the compressive strength of fourteen-day concrete has been about 25% and 50% more than compressive strength of seven-day concrete when sand-cement and cement were employed as additive, respectively.

IV. CONCLUSIONS

In this study, cement-based solidification/stabilisation has been used as an applied method to treat hazardous wastes generated from thermal power plants. For this purpose, compressive strength tests were conducted on concrete samples to examine the changes of resistance characteristics. The results demonstrated that by replacing cement with sludge waste in concrete mixture design, the compressive strength of concrete is reduced. However, the maximum loss of resistance is less than 30% for the most of examined waste/cement ratios. So, it proves high capacity of these solidified/stabilized products in practical applications, which can be studied in further researches.

It is noteworthy that the reported method of solidification/stabilisation is not just for this particular waste material and is applicable for the treatment of all types of hazardous wastes containing heavy metals, especially for wastes from industrial units.

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1. Abessi, O., Saeedi, M., Zaker., N. H., Kheirkhah Gildeh, H., "Flow Characterization Dilution in Surface Discharge of Negatively Buoyant Flow in Stagnant and Non-Stratified Water Bodies" J. of Water and Wastewater Eng., May 2010.

2. Abessi, O., Saeedi, M., Zaker., N. H., Kheirkhah Gildeh, H., "Waste Field Characteristics, Ultimate Mixing and Dilution in Surface Discharge of Dense Jets into Stagnant Water Bodies" J. of Water and Wastewater Eng., Aug. 2010.

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