

## Insights in Leaching Characteristic Assessment of Solidified Wastes Using Different Leach tests

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**ABSTRACT:** Solidified samples of fuel oil combustion bottom ash with two sets of Ordinary Portland Cement (OPC) and Pozzolan added OPC were investigated with three sets of chemical leaching tests. Toxicity characteristic leaching test (TCLP) results classified waste material and its solidification products as hazardous. Although Ni and Cr have over-leached, but their close examination with Sequential Chemical Extraction (SCE) test revealed new insights as follows. Nickel fixation in cement matrix has shifted over 20% of leachable Ni from first 4 fractions of SCE test to residual fraction with less likelihood of leaching. Chromium fixation in matrix has made shifts on leachable fractions that are not generally in favor of a successful fixation in matrix. In the case of Cd leaching, the only obvious finding from SCE test is that solidification processes have made a slight shift between fractions in bound to Iron and Manganese oxide and fraction in bound to carbonates. Compared to TCLP results for different mixtures, it can be concluded that Cd fixation has been done properly and significant change in leaching probability was not caused by solidification processes. Results of "Alkalinity, Solubility and Release as a function of pH" test indicate over regulation in the case of Pb and Cr leaching in different pHs. Results indicate need for more delicate interpretation of TCLP test results when several management scenarios are available and practical.

**Key words:** Cement, Solidification, Fuel oil combustion, Residue, TCLP, SCE, Alkalinity, Solubility, pH, Leach tests

### INTRODUCTION

Cement based solidification/stabilization process has long been used for different hazardous materials and have proven to be one of the most cost effective methods for handling of several waste types because of comparatively lower price of required material (cement, and water in the case of dry materials) than many other remediation technologies. Scope of utilization of this technology, as best practical, comprise sludge (Diet *et al.*, 1998; Asavapisita *et al.*, 2004; Coz *et al.*, 2004; Zain *et al.*, 2004; Tanapon *et al.*, 2005; Athanasios & Evangelos, 2006), mean radioactive wastes (Spence & Shi 2004, Zhoua *et al.*, 2006), low volume generating wastes (Jang & Kim, 2000), polluted soils (Jing *et al.*, 2004 & 2006). Differences are also in several binders and mixtures used in the cement- waste matrix (Shin *et al.*, 1995; Duchesne & Laforest, 2004; Shawabkeh, 2005; Sarvinder & Pant, 2006) but the governing assump-

tions of encapsulation and fixation of hazardous constituents in microscopic and macroscopic scale due to chemical and physical processes happening inside the mixtures remains relatively the same. Several different leaching characteristics of stabilized waste bodies has been reported elsewhere; some because of obviously different nature of waste being treated by cement matrix, and some because of unpredictable characteristics of final mixture of cement and waste. In almost all cases leach tests designed to evaluate hazard identification are just considered as predefined sets of regularly used leaching tests with assumptions not in accordance with the real management scenario.

Truth is that in recent years many evaluation processes on leaching characteristics of waste materials and their stabilization products have been conducted with less notice on real management scenario designated to that remedied wastes. Recently, international

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concerns on achieving efficient remedial actions and real evaluation of leaching condition of stabilization products is emerging and need for development of comprehensive characterization approaches is more and more revealed. Kosson (2002), in his paper on necessities of development of a case specific leaching framework for every waste management case, highlights that: "In evaluating the leaching potential of wastes based on a single, plausible worst-case mismanagement scenario via TCLP, the USEPA seeks to provide environmental protection for unregulated wastes. However, wastes are managed in many different settings, and under a range of conditions that affect waste leaching. The reliance of the USEPA on a single, plausible worst-case, management scenario for leach testing may be generally protective, but often at the cost of over regulation. It has also proven to be inadequately protective in some cases". That is exactly the reason why TCLP test has come to criticism by underlying assumption of municipal solid waste (MSW) co-disposal which does not happen in many cases. Moreover, Kosson emphasis that neither the TCLP nor any other test performed under a single set of conditions can provide an accurate assessment of waste hazards for all wastes. Importance in different interpretation of results reveals when researchers care about different assumptions on management scenarios. First, whether a single scenario is available for destination receptor environment or differences in scenarios have considerable effects on leaching condition of dumped materials. More importantly, whether regional parameters affecting leaching, or simplifying assumptions in developed leach tests have considerable effect on final assessment of solidification products. Assumptions such as: the fraction of the contaminant extracted during a batch extraction is equal to the fraction that will leach (USEPA 1986), or leachable fractions are divided in predefined sets of bounds in dumped material (Tessier *et al.*, 1979). The presumed leaching assessment approach must be consistent enough to appropriately assess leaching potentials (not necessarily exact measured amounts of release based on what test procedures define), and cover different conditions in possible management scenarios.

The most commonly fuel oil type used in Iran is Fuel oil. Characterization and stabilization of a thermal power plant air heater washing waste in Iran was carried out previously (Saeedi & Amini, 2007a; Saeedi & Amini, 2007b; Saeedi & Amini, 2008). Fuel oil combustion residues in Iran's thermal power have also been first characterized before (Saeedi & Rezaei Bazkiaei, 2008). Noticeable results were achieved in the case of heavy metal contents (Fe, Ni, Na<sub>2</sub>O, Cr<sub>2</sub>O<sub>3</sub>; 7.01, 6.02, 4.15, 2.14 % respectively), high loss on ignition or carbon content (36.76%), high Sulphur content (21.59 weight percent), high acidity (mean pH: 2.71), low mois-

ture content (2.02 weight percent), and more interestingly metal complexation formation in crude analyzed waste (controlling complex phase: Calcium Vanadium Oxide; CaO.17V<sub>2</sub>O<sub>5</sub>). It seems that compared to other studied residual waste forms in coal-fired thermal power plant wastes; bottom and fly ashes and MSW incineration residues (Ilham *et al.*, 2001; Asokan *et al.*, 2005; Dincer *et al.*, 2006; Jing *et al.*, 2006), our investigation of fuel oil combustion residue owns apparently different characteristics, thus far. USEPA TCLP test results on Oil Combustion Wastes (OCWs) in the category of bottom ash alleges characteristic of toxicity only infrequently in analyzed samples and that exceedences were spread across a relatively large number of sites (USEPA, 1999). USEPA results for elemental Cd (mean: 0.130 mg/L), Cr (mean: 0.387 mg/L), Pb (mean 1.23 mg/L), and Ni (mean: 30.7 mg/L) are noticeably less than leached amounts in our previous study (Saeedi and Rezaei Bazkiaei, 2008); Cd (mean: 5.55 mg/L), Cr (mean 38.54 mg/L), Pb (mean 19.3 mg/L), and Ni (mean: 472.5 mg/L). Although a comprehensive study on other thermal power plants in the characterization effort has not been conducted, but highly effective difference in concentrations was reasonable evidence on need for utilization of other test methods and case specific leaching assessment approaches, at least in particular waste management practices. Reportedly, the most common management scenario for OCW bottom ash wastes is mono-disposal in landfills or surface impoundments (USEPA, 1999), which is far from assumption of co-disposal with municipal wastes in development of worst case leaching scenario in TCLP test. This is what Kosson believes to serve as misrepresentation reason in many cases.

In the present investigation, a special combustion residue type waste material; fuel oil combustion bottom ash of a thermal power plant in Iran, was first undergone cement solidification process with two matrixes; Ordinary Portland Cement (OPC) and mixed OPC-Pozzolan matrixes, in different cement to waste ratios. Then a leaching assessment approach was designed to evaluate crude waste material and its cement solidification/stabilization products to assess efficiency of stabilization processes.

## MATERIALS & METHODS

In January 2006, 20 waste samples were taken from bottom ash of combustion furnace of Shahid Rajaei power plant in Qazvin Province, Iran. The collected samples were stored in a cool place in sealed bags until analysis. Four composite samples were prepared by homogenizing and combining every fifth sample. The samples were air dried at room temperature (<40°C) to constant mass before being divided and screened. The water content of samples used for leaching was

determined on a parallel sample by drying at 110°C overnight. Moisture content then was determined using ASTM 4254 (ASTM 2000). The natural pH of samples was determined using Cyber Scan PC510 pH meter. The chemical composition of dried samples was determined by X-ray fluorescence (XRF; Philips PW 2404) and X-ray Diffraction measurement was used to identify possible mineral phases in the waste sample. Two sets of solidification matrixes with OPC and pozzolan added OPC, with cement to waste ratio (C/W); 0.5, 0.75, 1, 3 and 5 were completely mixed with water based on ASTM-C109-90 standard mix design. Pozzolanic samples contained 5% weight pozzolan compared to cement amount in mixture. Prepared matrixes are then pored in 5×5×5 cm standard molds to form final stabilized samples, enough curing time in wet environment of sealed box is provided and samples were broken after 28 days. Required amounts of samples for analysis were gained from core of broken samples. XRF analysis was performed for determination of chemical composition of crude waste samples and resulting cementation products. XED analysis was executed on matrixes to identify possible cement hydration products, their variation in different matrixes and possible metal complexation with hydration products.

Different leaching tests utilized for a comprehensive coverage of waste and stabilization products leaching characteristics. These are tests in which interpretation of leached amounts based on close examination of different conditions can provide insights on several possible management scenarios and site specific conditions. Detailed specifications of tests are as follows:

**a) Toxicity Characteristic Leaching Procedure (TCLP)** (USEPA, 1992) a commonly used leaching procedure to identify waste characteristic under a specific supposed worst case field condition; Acetic acid as leachant in pH 2.88 ± 0.05 over Liquid to Solid (L/S) ratio 20/1 and tumbling in an end-over-end fashion for 18 hours.

**b) Sequential Chemical Extraction;** According to (Tessier *et al.*, 1979); elements can be classified into the following five operationally defined fractions: 1) exchangeable: The sample was extracted for 5 h with 0.5 M MgCl<sub>2</sub> at pH 7.0 and a L/S ratio of 8; 2) bound to carbonates: The solid residual from step (1) was extracted with 1M NaAc at pH 5 and a L/S ratio of 8 for 5 h; 3) bound to iron and manganese oxides: The residual from step (2) was extracted with 0.04 M NH<sub>2</sub>OH.HCl in 25% (v/v) HAc for 6 h at 96°C. The L/S ratio was 20; 4) bound to organic matter and sulfides: The residual from step (3) was extracted with 30% H<sub>2</sub>O<sub>2</sub> for 6 h at 85°C, then extracted with 3.2 M NH<sub>4</sub>Ac in 20% (v/v) HNO<sub>3</sub> with continuous agitation for 30 min;

and (5) residual: this fraction was calculated from digestion of remnant of step (4)

**c) Alkalinity Solubility and Release as a function of pH** (Kosson *et al.*, 2002) ; The equivalents of acid or base are added to a combination of deionized (DI) water and the particle size reduced material (<2mm), with Nitric acid solution 2N in situation where natural pH of samples is to be reduced or Potassium Hydroxide solution 2N where natural pH is to be raised, to cover desirable range of pH values which may occur under different field conditions, with final L/S ratio 10 in an end-over-end fashion for 24 hours to identify leaching characteristics of samples over a broad range of possible pH value (2 to 12) and in fact more realistic conditions over different plausible management scenarios. Performing the tests, elemental concentrations of Ni, Fe, Cr, Pb and Cd in eluates from different tests were determined using Atomic Absorption Spectrometry (Buck Scientific 210 VP model).

## RESULTS & DISCUSSION

Crude waste and solidification products with Cement to Waste ratio (C/W) 0.5, 3 and 5 are subjected to XRF analysis. Results illustrated in Table 1. indicate high concentrations of elemental Fe, Ni, Cr respectively. Constituents with concentrations less than 0.01 % has been under detection limits of XRF apparatus and has not been reported though, but as it is stated in TCLP test results, elemental Cd and Pb concentrations has leached to eluate solution indicating presence of these elements in lower amounts than 0.01 % fraction in crude waste. Leaching results for solidification products are predictably lower than concentrations in crude waste; depletion of concentrations is nearly in ratio of dilution with cement and water. One of important features of characterized waste is its comparatively high carbon content. Reported carbon content in same origin wastes (combustion residue type wastes) have shown notably lower weight percent carbon content than 23.5 in this case (Asokan *et al.*, 2005; Dincer *et al.*, 2006; Jing *et al.*, 2006).

Results of TCLP leach test are presented in Table 2. The very first conclusion from results is identification of both waste material and solidification products as hazardous in almost all samples and in the case of all elements except for Cd in all samples. Compared to hazard limit for Pb in TCLP test (5 mg/Lit), only cement samples with C/W ratios 1, 3 and 5 has met regulatory leaching limits. In the case of Cr, with TCLP leaching limit 5 mg/L, the only sample meeting the threshold is pozzolanic sample with C/W ratio 5. Nickel concentrations in all samples are above limits posed by EPA based on 100 times safe potable water concentration; equal to 10 mg/L (EPA, 2003). Till this step of characterization procedure, regardless of other characteris-

Table 1. Results of XRF analysis for crude waste and matrixes

C/M or Raw material	Parameters															
	L.O.I	SO <sub>3</sub>	V <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>	Ni <sub>2</sub> O	Na <sub>2</sub> O	Cr <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO	TiO <sub>2</sub>	MnO	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	Others
<b>0.5</b>	23.5	12.8	10.3	4.3	3.75	2.56	1.35	1.15	1.23	0.53	0.2	<0.01	<0.01	<0.01	<0.01	<0.01
<b>1</b>	17.59	10.8	9.3	3.52	2.74	2.1	1.05	0.65	0.86	0.35	0.17	<0.01	<0.01	<0.01	<0.01	<0.01
<b>3</b>	9.21	5.65	4.32	1.45	1.58	0.85	0.67	0.57	0.38	0.21	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
<b>5</b>	6.33	4.25	2.65	1.35	0.95	0.75	0.58	0.18	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
<b>Crude Waste</b>	37.67	21.59	17.12	7.01	6.27	4.15	2.14	1.73	1.68	0.87	0.3	<0.01	<0.01	<0.01	<0.01	<0.01
<b>Cement</b>	-	1.51	<0.01	3.41	<0.01	<0.01	<0.01	19.72	66.75	3.48	3.48	0.47	0.18	<0.01	0.87	<0.01
<b>Pozzolan</b>	-	<0.01	<0.01	3.83	<0.01	3.31	<0.01	66.21	5.69	15.15	1.59	0.68	<0.01	0.27	3.07	<0.01

Table 2. Concentration of constituents of interest in TCLP test and percent removal in mixtures compared to crude waste leached concentration

	Cement samples (mg/L)					Pozzolan samples (mg/L)				
	0.5	0.75	1	3	5	0.5	0.75	1	3	5
<b>C/W ratio</b>	0.5	0.75	1	3	5	0.5	0.75	1	3	5
<b>Ni</b>	153.9	171.5	227.8	185.9	132.5	209.5	137.3	156.4	122.5	87.2
<b>% Removal</b>	62.52	58.23	44.52	54.72	67.73	48.92	66.56	61.61	70.15	78.56
<b>Cr</b>	10.1	9.87	10.35	8.65	6.65	10.48	8.85	9.3	6.4	4.2
<b>% Removal</b>	73.22	73.84	72.62	77.12	82.41	72.28	76.59	75.4	82.01	88.89
<b>Pb</b>	7.6	5.7	2.3	3.6	1.5	5.3	4.65	4.98	5.35	4.12
<b>% Removal</b>	61.22	70.92	88.27	81.63	92.35	72.96	76.28	74.58	72.7	78.47
<b>Cd</b>	0.25	0.2	0.18	0.15	0.11	0.38	0.35	0.24	0.19	0.16
<b>% Removal</b>	95.41	95.27	96.70	97.25	97.25	93.03	93.58	95.60	96.51	97.06

tics of samples, all these samples must be rejected for co-disposal with municipal solid wastes in landfills, but examination of percent removal of elements compared with leached amounts in natural waste can provide clues for future practices. With close consideration of removal percents in all samples, strange behavior of matrixes from C/W ratios 0.5 to 1 is revealed. In both cement and pozzolanic samples, leached amounts increase with increase in cement content of mixture till the ratio of 1 and thereafter in ratio 3 and 5 leached amounts has decreased. It may be contributed to high percentage of carbon in natural waste material where its hindering effect on hydration processes may have caused difficulties on generation of Calcium Silicate Hydrate (C-S-H) gels. Considering the fact that with increase in cement content of mixture, required water content also increases, it can be concluded that cement addition till ratio 1, not only has not helped the mixture to improve its leaching characteristics, but also has caused more release because of presence of necessarily higher water content in the mixture. Till C/W 1, solidification products were a mixture of not completely formed or enough generated hydration products and waste material with no satisfactory bound to cement hydration products. But after C/W 1, it seems that hindering effect of carbon has been weakening by higher cement hydration products and leaching characteristics have improved in mixtures with C/W 3 and 5. Although measures with higher C/W ratios was not carried out in this practice because of time limits, but it seems that with increase in C/W ratios to about 10 many samples may meet regulatory leaching criteria of TCLP test. Here stands one of trivial but important features of a successful waste management practice with cement mixtures; choose reasonably adequate range of matrixes to cover unpredictable range of observations in practice.

Changes in hydration processes and formed crystals in XRD analyses of cement samples with C/W 0.5, 3 and 5 ascertain our assumption of hydration products. As it is depicted from XRD analysis, the most observable crystal phases formed in 0.5 sample are just some isolated phases of cement hydration; Calcium Sulfate Hydrate, Gypsum, and Bassanite. XRD analysis reveals samples with C/W 3 and 5, crystal phases formation with elemental Aluminum and Manganese are reported; Calcium Magnesium Aluminum Oxide Silicate. This can be evidence on better hydration processes in cement ratios 3 and 5. Although the XRD results does not contain a weight percent evaluation of different mineral phases in the mixture but this extent qualitative interpretation of results can also be of help to better conclude on real occurring phenomenon in mixtures.

The principle of the Sequential Chemical Extraction test is that a series of increasingly more aggressive extraction solutions are applied successively. Ideally, only the metal from a particular matrix should be released and other forms of metal should remain in the solids. However, these assumptions may not be true in practical systems (Li *et al.*, 2001). Although SCE test was originally developed for sediments and its application for S/S-treated wastes needs further study (Li *et al.*, 2001), but in a wise assessment framework for waste management practices, results of this test can help to achieve a more efficient final strategy. This method may be of help in determination of likelihood of presence of an element in easily leachable fraction or in hard bounds. It can help on decision making when practical technologies have noticeable operational cost differences. Results can also provide researcher with supplementary insights on interpretation of results of other leach tests. Results of SCE test for all samples are depicted in Table 3. Close examination of results for solidification matrixes and natural waste reveals some clues on how solidification processes have exchanged leachable amounts of elements between different fractions.

In the case of Ni fixation, more than 65% weigh fraction of total leachable Ni in all samples is present in last fraction (Residual fraction) where based on Tessier assumption is the least likely leachable fraction of element. Highest percent in this fraction belongs to samples with C/W ratio 1 and 3 in both cement and pozzolanic matrix. Compared to this amount in crude waste, 57% weight percent, solidification processes have shifted about 20% of leachable Ni from first 4 fractions to residual fraction. Although leaching amounts of Ni in TCLP test have not shown compliance with regulatory limits, but it is likely that with addition of cement to higher ratios, this trend may help to more definite fixation of Ni in matrix.

Results for Cr are more interesting, solidification process has made shifts on leachable fractions that are not generally in favor of a successful fixation in matrix. Results for crude waste show that about 57.5% of total leachable amount of Cr is present in residual fraction of test and remaining are relatively evenly distributed between bounded to carbonates (12.57%), bounded to Iron and Manganese oxides (12.2 %) and bound to organic matter and Sulfides (11.98%). Results for cement matrix show that leachable amount has shifted more from residual fraction to fraction 2 and 3 where between 19.9 % to 30.78% of Cr has shown to be in bound to carbonates (fraction2) and amount of Cr in residual fraction has reduced to even 39.24 % in sample with C/W 3. Generally, about 10% of leachable amount of Cr has shifted from residual form to other 4 more easily leachable fractions, and this trend

Table 3. Percent of constituents of interest in different fractions of SCE test for all samples

Fraction	% Ni in Cement matrixes (numbers are C/W ratios)					% Ni in Pozzolanic matrixes (numbers are C/W ratios)					% Ni in Waste				
	0.5	0.75	1	3	5	0.5	0.75	1	3	5	0.5	0.75	1	3	5
1	0.57	1.09	1.29	0.73	3.48	1.38	1.53	1.90	3.49	5.93	1.81				
2	18.2	12.23	3.42	4.99	7.50	17.55	9.80	3.47	3.74	5.03	22.31				
3	11.75	8.61	6.41	5.95	5.14	12.30	9.24	6.31	5.08	4.14	15.94				
4	2.60	2.15	2.38	2.70	2.21	2.37	2.58	2.98	2.14	1.77	2.87				
5	66.87	75.82	86.5	85.63	81.69	66.42	76.84	85.34	85.55	83.14	57.04				
Total	100	100	100	100	100	100	100	100	100	100	100				
	% Cr in Pozzolanic matrixes (numbers are C/W ratios)														
	% Cr in Cement matrixes (numbers are C/W ratios)														
	% Cd in Pozzolanic matrixes (numbers are C/W ratios)														
	% Cd in Cement matrixes (numbers are C/W ratios)														
	% Ni in Waste														
Fraction	0.5	0.75	1	3	5	0.5	0.75	1	3	5	0.5	0.75	1	3	5
1	5.35	3.13	5.01	6.44	1.99	2.70	6.09	4.14	5.91	2.97	5.79				
2	19.95	17.48	22.91	29.10	30.78	2.54	22.50	13.31	10.22	16.49	12.57				
3	17.40	18.71	19.99	17.35	16.16	18.21	19.41	27.88	25.90	26.97	12.20				
4	6.78	7.06	9.86	7.97	6.59	7.10	5.38	12.20	8.10	6.14	11.98				
5	50.52	53.62	42.23	39.24	44.40	49.45	46.62	42.47	49.98	47.52	57.44				
Total	100	100	100	100	100	100	100	100	100	100	100				
Fraction	0.5	0.75	1	3	5	0.5	0.75	1	3	5	0.5	0.75	1	3	5
1	9.53	17.65	18.1	21.83	20.04	14.17	22.01	25.74	21.55	28.36	24.19				
2	19.18	18.33	23.29	18.32	23.08	15.63	11.41	7.44	20.26	24.52	10.56				
3	53.22	43.80	43.75	40.46	34.88	40.10	42.59	41.24	35.91	26.23	43.57				
4	3.96	5.39	3.41	11.15	15.56	14.06	4.16	6.51	12.15	13.86	13.68				
5	14.11	14.82	11.42	8.24	6.44	16.04	19.46	19.07	10.13	7.04	7.88				
Total	100	100	100	100	100	100	100	100	100	100	100				

Table 4. Leached amounts from samples in eluates from "Alkalinity, solubility and release as a function of pH" test

Analyzed sample	All concentrations in mg/L											
	pH	2	3	4	5	6	7	8	9	10	11	12
Crude waste	Cr	22.5	18.5	8.25	7.22	6.21	5.51	5.32	2.51	1.65	1.52	1.25
	Pb	8.65	8.98	7.65	5.3	5.21	4.68	3.65	3.14	2.53	2.15	1.24
C/W=0.5	Cr	5.25	5.12	4.56	3.38	3.51	2.81	1.65	1.51	1.22	1.14	1.45
Cement matrix	Pb	6.65	5.4	5.1	4.65	4.2	4.6	4.12	3.74	2.62	1.95	1.58
C/W=1	Cr	6.28	5.45	5.38	4.6	4.75	3.68	2.22	1.63	1.28	1.12	0.98
Cement matrix	Pb	8.85	8.33	6.25	6.1	5.87	3.35	5.5	1.98	1.73	1.93	2.1
C/W=3	Cr	8.65	7.38	7.15	6.52	6.37	6.13	4.25	3.2	1.58	0.86	0.45
Cement matrix	Pb	2.95	2.74	2.63	2.35	2.22	2.19	2.30	2.43	1.98	1.65	1.25

is observed in almost all samples. Results are interesting when compared with TCLP. Although some samples (Pozzolanic C/W 5, 4.2 mg/L) has met regulatory leaching limit (5 mg/L), and some (Cement C/W 5, 6.65) has leached near the limit, but considering likelihood of presence of Cr in more leachable fractions with addition of cement can not definitely meet the regulatory compliance under only the assumption of landfilling of solidified samples. It is likely that with change in management scenario, real condition of ambient environment is likely to leach more easily leachable fraction of bound to carbonate, where it seems to be one of important features of TCLP test that brings it to criticism.

In the case of Cd leaching, the only obvious finding from SCE test is that solidification processes have made a slight shift between fraction in bound to Iron and Manganese oxide and fraction in bound to carbonates. Weight percent of Cd in bound to Iron and Manganese oxides has shifted from 43.57 % to about 26% in Pozzolanic sample with C/W 5 and remaining has shifted to fraction 2 and 4. In other samples also fraction shifting has shown main changes between fractions in bound to carbonate, bound to Iron and Manganese oxides and slight shift to fraction in bound to organic matter and Sulfides but this change is not as considerable as in fraction 2 and 3. Compared to TCLP results where all samples have met regulatory leaching limits for Cd, it can be concluded that Cd fixation has been done properly and significant change in leaching probability is not made by different mixture formulas. The Alkalinity, Solubility and Release as a function of pH test with its wide range of environmental pH can help to better simulate actual environmental condition of final dump site. In this investigation the test is executed just for 4 samples; crude waste, and cement samples with C/W ratio of 0.5, 1 and 3. Results are shown in Table 4. Released amounts in all samples have shown decrease with increase in alkalinity of samples but change rates differ from sample to sample. In the case of crude waste, release has reduced from 22.5 mg/L for Cr and 8.65 mg/L for Pb in pH 2, to 1.25 and 1.24 in pH 12 respectively. Leached amounts are interestingly lower than 100 times potable water limits (10 mg/L) - a criteria to evaluate harm posed by non-regulatory hazardous classified material that are supposed to pose human harm (EPA, 2003) - for Cr in all eluates with pH more than 3. This situation for Pb was just met in pH 12 where leached amount (1.24 mg/L) is lower than 100 times potable water limits (1.5 mg/L). Considerable changes in leached amounts are observed in pH 3 and after that decrease in leached amounts has more rapid rate. In other samples, the leaching decrease rates are relatively the same as in crude waste with exception of considerably lower leached concentration in acidic

pHs. This can indicate effective impact of acid attack in leaching of crude waste where with addition of cement hydration products with high buffer capacity this acid attack has shown comparatively lower effect. Utilizing result of test in different managerial scenarios can definitely cover overdesign parameters gained from conservative results of TCLP test.

## CONCLUSION

Differences in final results of leaching tests and their underlying assumptions necessitate development of case specific leaching test schemes in criteria of waste management activities. In this way, TCLP test has been commonly used as main leaching test to assess effectiveness of almost all solidification/stabilization processes internationally. Approach in this investigation was to develop and use a leach testing framework consisting of different leach tests for special thermal power plant waste, fuel oil combustion residue. TCLP has been used as core leaching test and other two sets of tests were used to evaluate its effectiveness. Results express deficiencies of TCLP test for final evaluation of these type waste management practices where actual final scenario does not necessarily match assumption of co-disposal with MSW in TCLP test. Results of two other designed tests, SCE and "Alkalinity, solubility and release as a function of pH", has shown inadequacy of TCLP test for interpretation of actual condition of leaching of elemental Ni, Cr, Pb, and Cd. Comprehensive understanding of real conditions of dump site are the factors that just considering simultaneously can provide decision makers with more cost-effective and not just over-designed waste management scenarios. Conditions like actual pH of surrounding soil or other synthetic material, drainage condition leading to evaluation of actual Liquid to Solid ratios, actual leachant with respect to type of soil, practical particle size of final products, and so on are of the factors should be considered in choosing the best leach test in each case. It depends on how important this matter will be in future with looming higher waste generation problem world wide.

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## REFERENCES

- ASTM (2000). Standard Test Methods for Minimum Index and Unit Weight of Soils and Calculation of Relative Density, D4254. American Society for Testing and Materials, Conshohoken, USA.
- ASTM (1990). Standard Test Method for Compressive strength of Hydraulic cement Mortars (Using 50-mm Cube

- Specimens), C 109. American Society for Testing and Materials, Conshohocken, USA.
- Asavapisita, S., Nakrichum, S. and Wong N. H. W. (2004). Strength Leachability and Microstructure Characteristics of Cement- Based Solidified Plating Sludge. *Cement & Concrete Res.*, **35**, 1042-1049.
- Asokan, P., Saxena, M. and Asolekar, S. R. (2005). Coal Combustion Residues Environmental Implications and Recycling Potentials. *Resources, Conservation & Recycling*, **43**, 239-262.
- Athanasios, K. K. and Evangelos A. V. (2006). Release of Zn, Ni, Cu, SO<sub>4</sub><sup>2-</sup> and CrO<sub>4</sub><sup>2-</sup> as a Function of pH from Cement-Based Stabilized/Solidified Refinery Oily Sludge and Ash from Incineration of Oily Sludge. *J. Hazardous Materials*, **85**, 225–239.
- Coz, A., Andres A., Sorianom S. and Angel I. (2004). Environmental Behavior of Stabilized Foundry Sludge. *J. Hazardous Materials*, **B109**, 95-104.
- Diet, J.N., Moszkowicz, P. and Sorrentino, D. (1998). Behavior of Ordinary Portland Cement During the Stabilization/Solidification of Synthetic Heavy Sludge: Macroscopic and Microscopic Aspects. *J. Hazardous Materials*, **18**, 17-24.
- Dincer, A.R., Yalcin G. and Nusret K. (2006). Coal-Based Bottom Ash (CBBA) Waste Material as Adsorbent for Removal of Textile Dyestuffs from Aqueous Solution. *J. Hazardous Materials*, **141**, 529-535.
- Duchesne, J. and Laforest, G. (2004). Evaluation of the Degree of Cr Ions Immobilization by Different Binders. *Cement & Concrete Res.*, **34**, 1173–1177.
- Ilham, D., Randall, E. H. and Philips, J. D. (2001). Formation and Use of Coal Combustion Residues from Three Types of Power Plants Burning Illinois Coals. *Fuel*, **80**, 1695-1673.
- Jang, A. and Kim, I. S. (2000). Solidification & Stabilization of Pb, Zn, Cd & Cu in Tailing Wastes Using Cement & Fly Ash. *Minerals Engineering*, **13**, 1659-166.
- Jing, C., Meng, X. and Korfiatis, P. (2004). Lead Leachability in Stabilized / Solidified Soil Samples Evaluated with Different Leaching Tests. *J. Hazardous Materials*, **B114**, 101-110.
- Jing, Ch., Liu, S., Korfiatis, G. P. and Meng, Xi. (2006). Leaching Behavior of Cr(III) in Stabilized/Solidified Soil. *Chemosphere*, **64**, 379–38.
- Jing, Z., Matsuoka, N., Jin, F., Hashida, T. and Yamasaki, N. (2006). Municipal Incineration Bottom Ash Treatment Using Hydrothermal Solidification. *Waste Management*, **27**, 287-293.
- Kosson, D.S., Van der Sloot, H.A., Sanchez, F. and Garrabrants, A.C. (2002). An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials. *Environ. Engineering Sci.*, **19**, 159-204.
- Li, X.D., Poon, C.S., Sun, H., Lo, I.M.C. and Kirk, D.W. (2001). Heavy Metal Speciation and Leaching Behaviors in Cement Based Solidified/Stabilized Waste Materials. *J. Hazardous Materials*, **82**, 215- 230.
- Saeedi, M. and Amini, H. R. (2007a). Characterization of a Thermal Power Plant Air Heater Washing Waste: A Case Study from Iran. *Waste Management & Res.* **24**, 1-4.
- Saeedi, M. and Amini, H. R. (2007b). Chemical, Physical, Mineralogical, Morphology and Leaching Characteristics of a Thermal Power Plant Air Heater Washing Waste. *Int. J. Environ. Res.*, **1**, 74-79.
- Saeedi M. and Rezaei Bazkiaei, A. (2008). Characterization of thermal power plant fuel oil combustion residue. *Res. J. Environ. Sci.*, **2**, 116-123.
- Sarvinder, T. and Pant, K. (2006). Solidification / Stabilization of Arsenic. Containing Solid Waste Using Portland Cement, Fly ash, and Polymeric Materials. *J. Hazardous Materials*, **131**, 29-36.
- Shawabkeh, R. A. (2005). Solidification and Stabilization of Cadmium Ions in Sand–Cement–Clay Mixture. *J. Hazardous Materials*, **B125**, 237–247.
- Shin, H.S and Jun, K.S. (1995). Cement Based Solidification/ Stabilization of Organic Contaminated Hazardous Wastes Using Bentonite and Silica Fume. *J. Environ. Sci. & Health, Part A, Environ. Sci. & Engineering*, **30**, 651-658.
- Spence, D. and Shi, C. (2004). *Stabilization and Solidification of Hazardous, Radioactive and Mixed Wastes*. CRC Publishers Inc., Florida, USA.
- Tanapon, P., Taha F. M. and Manaskorn R. (2005). A SEM and X-ray Study for Investigation of Solidified/Stabilized Arsenic–Iron Hydroxide Sludge. *J. Hazardous Materials*, **B118**, 185–195.
- Tessier, A., Campbell, P.G.C. and Blisson, M. (1979). Sequential Extraction Procedure for Speciation of Particulate Trace Metals. *Analytical Chemistry*, **51**, 844-851.
- USEPA (1986). *Hazardous Waste Management System, Land Disposal Restrictions: Final Rule*, Federal Register, Part II, Vol. 40. United States Environmental Protection Agency, Washington D.C., USA.
- USEPA (1992). *Test Methods for Evaluating Solid Waste Physical/Chemical Characteristics*, SW-846. United States Environmental Protection Agency, Washington D.C., USA.
- USEPA (1999). *Wastes from the Combustion of Fossil Fuels, Vol. 2, EPA 530-R-99-010: Methods, Findings, and Recommendations*, Office of Solid Waste and Emergency Response. United States Environmental Protection Agency, Washington DC, 20460, USA.
- USEPA (2003). *Guidance on the Use of Stabilization/Solidification for the Treatment of Contaminated Materials*. United States Environmental Protection Agency, Washington DC, 20460, USA.
- Zain, M. F. M., Islam, M. N., Radin, S. S. and Yap, S. G. (2004). Cement-Based Solidification for the Safe Disposal of Blasted Copper slag. *Cement & Concrete Composites*, **26**, 845–851.
- Zhoua, Q., Milestone, N.B. and Hayes, M. (2006). An Alternative to Portland Cement for Waste Encapsulation—The Calcium Sulfoaluminate Cement System. *J. Hazardous Materials*, **136**, 120–129.