

Comparison of Two Leaching Tests to Assess the Effectiveness of Cement-Based Hazardous Waste Solidification/Stabilization

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Abstract

The Turkish Hazardous Waste Control Regulation (THWCR) recognizes solidification/stabilization (S/S) as a promising new technology for the safe disposal of hazardous wastes. In this study, the effectiveness of S/S in terms of the reduction of contaminant mobility was evaluated through two different leaching procedures. Heavy metal enriched mining residue was used as hazardous waste. For the S/S of mining waste, Portland cement as a binding agent was mixed with mining waste at different ratios (10 and 20%). Solidified samples were crushed into two different fractionation sizes (between 1 and 2 mm and greater than 2 mm) and subjected to the toxicity characteristic leaching procedure of the U.S. Environmental Protection Agency and the distilled water leaching procedure of the THWCR. The leaching test results showed that generally S/S produced efficiencies greater than 90% for the retention of metals in the solidified mass.

Key words: Heavy metals, Leaching, Mining waste, Portland cement, Solidification/stabilization.

Introduction

Solidification/stabilization (S/S) is a treatment technology used to reduce the hazard potential of hazardous waste by converting the contaminants into their least soluble, mobile or toxic form with the addition of a binding agent. S/S is designed to either improve waste handling and physical characteristics, decrease the surface area across which pollutants can transfer or leach, or limit the solubility of or detoxify the hazardous constituents (Wiles, 1987). S/S also refers to techniques that attempt to prevent the migration of contaminated material into the environment by forming a solid mass (Hinsenveld, 1998).

Cement-based S/S generally uses Portland cement. Portland cement is made by firing a mixture of limestone and clay (or other silicate) in a kiln at high temperatures (LaGrega *et al.*, 1994). A typical

chemical composition of Portland cement is given in Table 1 (Glasser, 1997).

Table 1. Chemical composition of Portland cement.

Oxides	Chemical composition of Portland cement (% , by weight)
CaO	61-67
SiO ₂	17-24
Al ₂ O ₃	3-8
Fe ₂ O ₃	1-6
MgO	0.1-4
Na ₂ O + K ₂ O	0.5-1.5
SO ₃	1-3

When Portland cement is mixed with water, heat is evolved and the mixture becomes strongly alkaline. However, the reaction slows after a few minutes and the period, known as the induction

period, or dormant period, normally lasts several hours. During the first minutes of the reaction, the anhydrous clinker grains become coated with a nearly-amorphous precipitate, which acts as a semi-protective film and slows the reaction during the induction period. Towards the end of the induction period, breakdown of the film marks the onset of rapid hydration. This onset also initiates the development of a continuous but initially tenuous gel network linking the particles, with the result that physical stiffening occurs. Then, as the gel continues to stiffen and densify, strength gain commences. Typical modern Portland cement achieves about two-thirds hydration in 28 days (Glasser, 1997). The main chemical that is considered in hydrated cement is colloidal calcium silicate hydrogel, known as C-S-H, and this gel product is formed at the cement particle surfaces (Cocke, 1990). C-S-H has important implications for the mechanisms of fixation during solidification (Hills *et al.*, 1996) and is principally responsible for strength development (Cartledge *et al.*, 1990).

Leaching tests are used to examine or predict the chemical stability of treated wastes when they are in contact with aqueous solutions. The procedures demonstrate the degree of contaminant immobilization and are indicators of the potential environmental effects of the treated waste (Martin and Johnson, 1987).

Extraction (batch) leaching tests are performed on crushed waste material. The mass is broken and a larger surface area is exposed to the leaching agent. Therefore, these tests simulate the worst-case scenario. One example of common extraction tests is the toxicity characteristic leaching procedure (TCLP) (Sharma and Lewis, 1994). TCLP is the most widespread test and is also the U.S. Environmental Protection Agency's (EPA) procedure for as-

sessing the potential for hazardous wastes to leach into the groundwater from a landfill (Parsa *et al.*, 1996).

The Turkish Hazardous Waste Control Regulation (THWCR) accepts S/S technology, but does not provide any technical criteria based on its effectiveness.

The major objective of this study was to investigate the effectiveness of the Portland cement-based S/S technology for the safe disposal of hazardous waste containing high levels of toxic metals. The effectiveness of S/S in terms of reduction of contaminant mobility was evaluated through TCLP of the EPA and the distilled water leaching procedure DWLP of the THWCR.

Waste Material

For the solidification of waste material and encapsulation of contaminants, Portland cement as a binding agent was mixed with metal mining waste at different ratios (10 and 20%). Metal mining waste was obtained from gold mining residue (tailings). The obtained waste material was not actually subjected to mineralogical processes to extract the gold, but it was ground down to the particle sizes appropriate for the application of the mineralogical processes and for the planned waste disposal practice of paste backfilling and/or S/S. The waste material used in this study can be viewed as the representative waste material obtained from most metal mining processes (e.g., gold, copper, cadmium, chromium, lead) with respect to both physical characteristics and metal contaminant composition. The physical characteristics of the metal mining waste used in this study are given in Table 2.

Table 2. Physical characteristics of metal mining waste.

Physical characteristics	Value
Dry density (g/cm ³)	1.77
Optimum moisture content (%)	15
Liquid limit (%)	28
Plastic limit (%)	18
Plasticity index (%)	10
Soil classification	ML (silt-low plasticity)
Specific gravity	2.72
Particle size distribution	18% clay; 55% silt; 27% sand

Although the waste material had a relatively high heavy metal content, in order to better assess the performance of S/S, the mining waste material was spiked with much higher metal concentrations. The added salts were chromium nitrate, cadmium nitrate, lead nitrate, copper sulfate and zinc sulfate. Both the initial (before spiking with metal salts) and final (after spiking with metal salts) metal composition of mining waste are given in Table 3. It was seen that after the addition of the metal salts, the metal concentrations of waste material reached the desired high levels. For some metals, the increase in the concentration was around 1000 mg/kg.

Since cement, as a binding agent, was mixed with waste material, the metal composition of the cement was also determined in order to observe any contribution to the metal content of the waste. The results of the total metal analyses for cement are given in Table 4. According to this table, the main constituents of the Portland cement used in this study were calcium, magnesium, aluminium and iron, as expected.

For the mining waste, two samples representing fine and coarse particle size distribution were prepared. In order to prepare the coarse particle size distribution, sand was added to the waste. The mixing ratio of sand to (waste + cement + moisture) was 1:1.

Portland cement was added to fine and coarse mining waste samples at two different ratios: 10% and 20%. The samples were prepared for the 28-day cure to solidify by compacting the desired waste:cement mixture at the optimum moisture content to the corresponding maximum dry density in cylindrical molds with a height of 71 mm and a diameter of 36 mm. After compaction, the cylindrical

samples were removed from the molds and placed in a humidity room for 28 days. The cure period was 28 days for the S/S of mining waste samples because Portland cements achieve about two-thirds hydration in that time (Glasser, 1997). At the end of the 28-day cure period, prior to the performance of the leaching tests, the solidified samples were crushed and passed through sieves for fractionation to sizes greater than 2 mm and between 1 and 2 mm.

As well as the initial metal composition of mining residue and Portland cement, total metal analyses of waste samples at the end of the 28-day cure period were performed in order to obtain the chemical composition of these waste samples before the leaching tests. The results are given in Table 5. According to this table, the metal concentrations of the coarse waste samples were diluted due to the addition of sand, which shifted the texture of the mining waste from silt (fine) to sand (coarse). Moreover, since 20% Portland cement containing coarse mining waste contained less original mining waste than 10% Portland cement containing it, the lowest total metal concentration was observed in 20% Portland cement containing coarse mining waste. Due to the high concentrations of Fe, Al, Ca and Mg in Portland cement, mining waste samples also have very high concentrations of these metals.

Leaching Tests

The effectiveness of a process in terms of the reduction of contaminant mobility is evaluated through leaching tests (Albino *et al.*, 1996). In this study, the TCLP of the U.S. EPA, Method 1311 of SW-846, (U.S. EPA, 1996) and the DWLP of the THWCR (Turkish Official Gazette, 1995) were used.

Table 3. Metal concentrations of mining waste before and after metal salts addition.

Metal	Metal concentrations of mining waste before metal salts addition (mg/kg)	Metal concentrations of mining waste after metal salts addition (mg/kg)
Cd	40	970
Cu	2410	3640
Cr	350	1410
Pb	3480	4380
Zn	2380	3760
Fe	29,700	32,210
Al	30,890	30,090
Ca	440	640
Mg	1150	1570

The methods were modified as follows to allow a smaller amount of material to be used. At the end of 28 day-cure-period, prior to the performance of the leaching tests, the samples were crushed and then passed through sieves for fractionation to sizes greater than 2 mm and between 1 and 2 mm. Then TCLP and DWLP were applied using 3 g waste samples from each size fraction, because the volume of extract obtained would be sufficient to support all the analyses required. The use of sample sizes much smaller those required by the TCLP and DWLP leaching methods was adopted to assess the effectiveness of the S/S process in a much more conservative manner.

Toxicity characteristic leaching procedure (TCLP)

TCLP is used to prepare an extract from waste samples that are initially liquid, solid or multiphasic. To prepare the extract, a portion of a sample is combined with an extraction fluid and shaken. After shaking for about 17 h the sample is filtered. For filtration, glass filter devices and borosilicate fiber filters with an effective pore size of 0.8 μm and a diameter of 47 mm were used. The filtrate is the so-called TCLP extract. Following this procedure, the extract is then analyzed for the presence of inorganic analytes, which if present will demonstrate their mobility in a leaching environment. If the concentrations in the extract exceed the permitted levels, the initial sample is classified as hazardous.

There are two extraction fluids in the TCLP, and

the appropriate one is used, depending on the initial pH of the waste. To determine the appropriate extraction fluid, 5.0 g of solid phase of waste was transferred into a beaker. Distilled water with a volume of 96.5 ml was added to the same beaker and covered with a watch glass and stirred vigorously for 5.0 min. The pH of the solution was then measured. If the pH was less than 5.0, “extraction fluid # 1” would be used directly. Since the measured pH was greater than 5.0 for all cases, 3.5 ml of 1 N HCL was added, covered with glass and heated to 50 °C for 10 min. After allowing the solution to cool to room temperature, the pH of the solution was recorded. If the final pH had been greater than 5.0, “extraction fluid # 2” would have been used. However, the final measured pH was less than 5.0, so “extraction fluid # 1” was used.

Table 4. Results of total metal analyses for Portland cement.

Metal	Metal concentrations of Portland cement (mg/kg)
Cd	0
Cu	30
Cr	500
Pb	0
Zn	40
Fe	15,630
Al	29,070
Ca	276,310
Mg	8240

Table 5. Chemical composition of fine and coarse mining waste and cement mixtures.

Elements	Chemical Compositions of Mixtures (mg/kg)			
	10% cement + fine mining waste	10% cement + coarse mining waste	20% cement + fine mining waste	20% cement + coarse mining waste
Cd	1250	850	1000	750
Cu	3330	1690	2550	1250
Cr	3060	1920	2140	1770
Pb	3090	1420	2320	1210
Zn	1900	1350	1990	1050
Fe	13,500	10,470	13,310	8780
Al	26,130	11,170	24,360	8250
Ca	7830	15,540	17,720	19,400
Mg	1710	3100	2490	1560
K	21,550	9950	12,950	9000
Na	27,780	7150	20,000	21,000

To prepare 1 l of extraction fluid # 1, 5.7 ml glacial acetic acid was added to 500 ml of distilled water. Then 64.3 ml of 1 N sodium hydroxide was added and diluted to a volume of 1 l. The pH was around 4.93 ± 0.05 . Since the examined wastes were 100% solid, the amount of extraction fluid was 20 times that of the weight of the waste. Therefore, 40 and 60 ml of extraction fluid # 1 were added to the Erlenmeyer flasks with 2 and 3 g of the waste, respectively, for each case. The flasks were placed in a rotary extractor and allowed to rotate at 30 ± 2 rpm for 18 ± 2 h. After rotation, the samples were filtered and the filtrate was analyzed for various elements (Cr, Zn, Pb, Cd, Ni, Cu, Mg, Ca, Fe, Na and K) and some ions (Cl^- , SO_4^{2-} , CO_3^{2-} and PO_4^{3-}).

Distilled water leaching procedure (DWLP) of the Turkish Hazardous Waste Control Regulation (THWCR)

According to this procedure, waste samples crushed into sizes greater than 2 mm and between 1 and 2 mm were put into glass flasks and distilled water was added in an amount 10 times the dry weight of the waste. Then the flasks were shaken slowly by turning them upside down (i.e. rotating them 180 degrees) a number of (approximately 29) times per minute for 24 h. The samples were filtered in a manner similar to the TCLP filtration and analyzed for various elements (Cr, Zn, Pb, Cd, Ni, Cu, Mg, Ca, Fe, Na and K) and some ions (Cl^- , SO_4^{2-} , CO_3^{2-} and PO_4^{3-}).

Analyses of total metal concentration

The initial metal compositions of the mining waste and Portland cement were determined before the S/S process by the acid digestion method.

By conducting a flame atomic absorption spectrophotometric analysis, the metal concentrations of the samples were determined. In this study, a Unicam flame atomic absorption spectrophotometer was used.

In addition to the flame atomic absorption spectrophotometric analysis, a Jenway PFP-7 flame photometer was used for the sodium and potassium analyses.

Analyses of ions As ions, sulfate (SO_4^{2-}), carbonate (CO_3^{2-}), phosphate (PO_4^{3-}) and chloride (Cl^-) were measured. These analyses were performed based on standard methods (AWWA, APHA, 1989). Sulfate and phosphate were measured by spectrophotometer (Milton Roy Company Spec-

tronic 20D and Jasco Uvidec-4 digital spectrophotometers were used). Chloride and carbonate analyses were based on titrimetric methods.

In this study, sulfate was measured by the spectrophotometer at the 420 nm wavelength.

The phosphate concentrations of the samples were measured using a spectrophotometer and by the ascorbic acid method of standard methods (AWWA, APHA, 1989).

Carbonate ions were measured by the titrimetric method of acidity. In this method, first calcium carbonate concentration was obtained and then it was converted to a carbonate concentration.

The concentration of chloride ions was determined by the argentometric method of the standard methods (AWWA, APHA, 1989). This method was based on titration of the sample with silver nitrate titrant.

Results of Leaching Tests and Discussion

At the end of the 28-day cure period, TCLP and DWLP were applied and leachate obtained for each mining waste group (fine and coarse waste, 10% and 20% cement; crushed solidified sample size greater than 2 mm and between 1 and 2 mm) was analyzed for heavy metals and some ions. The results of these analyses are given in Table 6.

In general, the following observations can be made from Table 6. Metal concentrations in the TCLP leachate were significantly higher than the metal concentrations in the DWLP leachate. This is due to the pH difference between the applied extraction fluids and also between the final leachate pHs. The pH of the TCLP extraction fluid was around 4.93, but that of the DWLP was around 7.0. Therefore, the TCLP provided more acidic conditions for the waste samples than the DWLP. Moreover, after shaking, the final pH values of the TCLP leachates were within the range 6.05-6.8 and those of the DWLP in the range 8.1-9.5. The pH of the extraction fluids, as expected, affected the final pH of the leachates, and the alkalinity present in the cement also led to higher leachate pH values. Many metals are converted to insoluble precipitates in S/S processes and are subsequently trapped within the pores of the cement matrix (Webster and Loehr, 1996). At high pH levels, many heavy metals reach their lowest solubility and precipitate as their respective insoluble hydroxides, carbonates, phosphates, etc. (Lagrega

Table 6. The chemical compositions of leachates obtained from mine waste using TCLP and DWLP.

Elements/ Ions	Chemical compositions of leachates (mg/l)																							
	10% cement + fine mining waste						20% cement + fine mining waste						10% cement + coarse mining waste						20% cement + coarse mining waste					
	1-2 mm			> 2 mm			1-2 mm			> 2 mm			1-2 mm			> 2 mm			1-2 mm			> 2 mm		
	TCLP	DWLP		TCLP	DWLP		TCLP	DWLP		TCLP	DWLP		TCLP	DWLP		TCLP	DWLP		TCLP	DWLP		TCLP	DWLP	
Cd	1.85 ± 0.27	0.23 ± 0.02	ND	3.89 ± 0.56	0.47 ± 0.08	0.12 ± 0.02	0.58 ± 0.08	0.08 ± 0.01	2	0.29 ± 0.04	0.13 ± 0.04	2.41 ± 0.42	0.73 ± 0.08	0.16 ± 0.04	0.19 ± 0.06	0.12 ± 0.03								
Cu	0.31 ± 0.04	ND	ND	0.44 ± 0.07	0.41 ± 0.04	0.12 ± 0.02	0.38 ± 0.06	0.07 ± 0.02	0.92 ± 0.14	0.51 ± 0.05	0.27 ± 0.06	0.68 ± 0.08	0.91 ± 0.13	0.51 ± 0.09	0.29 ± 0.05									
Cr	0.37 ± 0.06	ND	ND	ND	0.59 ± 0.09	0.55 ± 0.06	0.58 ± 0.06	0.59 ± 0.08	1.71 ± 0.32	0.6 ± 0.07	0.19 ± 0.06	0.76 ± 0.07	2.22 ± 0.27	1.03 ± 0.07	0.68 ± 0.07									
Pb	0.39 ± 0.03	ND	ND	0.23 ± 0.03	0.58 ± 0.07	0.45 ± 0.08	0.48 ± 0.07	0.39 ± 0.05	1.12 ± 0.26	0.51 ± 0.06	0.35 ± 0.05	0.76 ± 0.08	1.38 ± 0.17	0.55 ± 0.07	0.13 ± 0.06									
Zn	0.71 ± 0.08	0.24 ± 0.05	0.31 ± 0.06	1.85 ± 0.09	0.5 ± 0.08	0.07 ± 0.01	0.35 ± 0.03	0.02 ± 0	0.96 ± 0.18	0.33 ± 0.04	1.04 ± 0.13	1.04 ± 0.19	0.77 ± 0.08	0.24 ± 0.05	0.05 ± 0									
Fe	ND	ND	ND	ND	1.94 ± 0.21	0.84 ± 0.09	1.09 ± 0.11	0.51 ± 0.06	3.69 ± 0.71	3.08 ± 0.55	0.7 ± 0.19	2.2 ± 0.08	2.35 ± 0.22	2.18 ± 0.08	0.62 ± 0.07									
Al	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND									
Ca	94.6 ± 1.76	83.39 ± 1.24	80.83 ± 1.1	93.5 ± 1.96	172.1 ± 16.2	114.5 ± 9.74	161.3 ± 6.71	117.5 ± 8.54	288 ± 19.2	162.1 ± 13.7	170.4 ± 13.4	286.6 ± 15.4	218.4 ± 14.8	144.2 ± 12.4	136.7 ± 9.87									
Mg	17 ± 1.42	6.31 ± 0.83	4.95 ± 0.76	18.31 ± 1.54	21.98 ± 1.78	4.25 ± 0.92	23.63 ± 1.49	6.35 ± 0.76	30.7 ± 2.67	8.31 ± 0.91	8.76 ± 0.84	29.25 ± 2.01	3.16 ± 0.61	0.23 ± 0.06	0.36 ± 0.09									
K	58 ± 2.32	19 ± 1.41	19 ± 1.06	30.5 ± 2.51	45.5 ± 3.52	19 ± 1.53	43 ± 2.76	19 ± 1.28	21.5 ± 1.17	20 ± 1.33	20 ± 1.22	21.5 ± 1.22	20 ± 1.97	11.5 ± 1.31	12.5 ± 0.92									
Na	152.2 ± 27.7	36 ± 3.57	28 ± 2.49	385 ± 31.6	760.7 ± 42.8	7.7 ± 1.04	773.7 ± 38.7	6.45 ± 0.47	266 ± 19.3	10.35 ± 0.81	8.4 ± 0.71	260 ± 20.3	995 ± 48.7	19.3 ± 2.07	25.6 ± 1.65									
SO ₄ ²⁻	149.9 ± 16.8	76.5 ± 6.4	78.1 ± 7.3	143.8 ± 12.9	36.7 ± 2.26	4.47 ± 1.1	26.96 ± 1.31	16.3 ± 1.58	53.58 ± 6.53	8.77 ± 0.88	0	66.29 ± 5.8	17.12 ± 0.98	4.6 ± 0.99	2.3 ± 0.16									
PO ₄ ³⁻	0.31 ± 0.09	25.02 ± 2.6	8.94 ± 1.1	0.58 ± 0.04	0.88 ± 0.09	0	1.12 ± 0.17	0	1.44 ± 0.33	0	0	0	2.14 ± 0.14	2.2 ± 0.23	4.57 ± 1.02									
Cl ⁻	150 ± 13.5	274.9 ± 18.1	208.3 ± 16.9	208.3 ± 16.2	495.3 ± 32.8	574.8 ± 42.6	482.9 ± 28.7	524.8 ± 35.1	386.4 ± 18.9	418.9 ± 15.1	468.9 ± 17.4	623.8 ± 47.2	605.3 ± 37.6	320.9 ± 21.9	220.9 ± 13.9									
CO ₃ ²⁻	185.4 ± 58.9	4320 ± 102.7	1440 ± 57.6	1320 ± 49.7	1110 ± 41.4	2370 ± 89.4	300 ± 19.4	4020 ± 101.2	2940 ± 79.2	1350 ± 52.7	630 ± 32.3	1500 ± 38.6	495 ± 22.1	780 ± 32.4	150 ± 34.6									

ND: Concentration is below the detection limit (for Cd 0.05 mg/l; Cu 0.05 mg/l; Cr 0.1 mg/l; Pb 0.1 mg/l; Fe 0.5 mg/l; and Al 5mg/l)

et al., 1994). Moreover, the major aqueous components of cement are sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺), hydroxide (OH⁻) and sulfate (SO₄²⁻) ions. These ions are potentially available to react with wastes (Glasser, 1997) and make insoluble precipitates of heavy metals. Therefore, the higher concentrations of metals in TCLP leachates compared to those in DWLP leachates were due to the lower pH of the TCLP leachate. Table 7 shows the pH range for the precipitation of some heavy metals (Porteus, 1985).

Table 7. pH range for the quantitative precipitation of heavy metals.

Metals	pH Range
Cd	6.8-12
Cr	5.4-10
Pb	6.0-9.0
Cu	5.4-12
Fe	2.3-12
Zn	5.3-9.0

The EPA toxicity characteristic limits in Table 8 mean that wastes that contain extract constituents on the list at concentrations that equal or exceed the listed concentrations are considered to be characteristically hazardous and are said to have a toxicity characteristic. The procedure recommended by the EPA for this purpose is TCLP. When the results of the TCLP in Table 6 were compared with the EPA toxicity characteristic limits, given in Table 8, it was observed that only Cd concentrations in the leachate from waste samples of the 10% cement ratio exceeded the permitted level. The rest of the metal concentrations in the leachate did not exceed the permitted levels and were much lower than these regulated levels. This higher Cd concentration in the 10% cement-waste samples of the TCLP leachate may be due to the lower leachate pH value of 10% cement-waste samples, which is around 6. These slightly acidic conditions most probably prevent the precipitation of Cd within the cement matrix. In the study by Cioffi *et al.* (1998) it is stated that cadmium is retained within the matrix provided that the pH does not drop to the acid range. Moreover, cadmium release to the leachate coincided exactly with the sudden decrease of the final leachant pH from 11 to about 5.

Table 8 also shows the metal concentration range of hazardous wastes in the THWCR. According to

this table, wastes that have leachate metal concentrations within the specified range are considered to be hazardous, although they do not require any pre-treatment before landfilling. In brief, these wastes can be disposed of in a hazardous waste landfill. However, if one of the metal concentrations exceeds its corresponding limit range, that waste should be treated before landfilling.

Table 8. EPA and THWCR toxicity characteristic limits.

Metals	Toxicity characteristic limits	
	EPA regulatory level (mg/l)	THWCR limits (mg/l)
Cd	1	0.1-0.5
Cr	5	0.1-0.5*
Pb	5	0.4-2.0
Cu	130	2-10
Fe	30	-**
Zn	500	2-10

* specified for Cr (VI)

** not specified

When the results in Table 6 were compared with the ranges of the THWCR in Table 8, it was seen that the leachate concentrations of cadmium and lead were within this specified range. Zinc and copper concentrations in the leachate were lower than their corresponding ranges. In this study, chromium determination was performed with a spectrophotometer, and total chromium values were calculated, so a comparison of chromium (VI) criteria could not be made with the total chromium results. However, Haskök (1998) performed both total chromium and chromium (VI) analyses in the leachates, and the ratio of chromium (VI) to total chromium was around 0.5 in TCLP leachates. When this ratio was also used in this study, chromium (VI) concentrations in the leachates could be within the acceptable range of the THWCR. Therefore, the application of the S/S process as a pretreatment method gave consistent results with the criteria of the THWCR and wastes with metal concentration levels similar to the mining waste considered in this study can be disposed of in landfills.

With regard to the crushing effect on metal concentrations in the leachate, the results in Table 6

show that solidified samples crushed to form particle sizes greater than 2 mm produced lower metal concentrations in the DWLP leachate than the solidified samples crushed to form particle sizes between 1 and 2 mm. In our study, in the case of the TCLP leachate, crushing the solidified samples into different particle sizes did not affect the metal concentrations in the leachate. An increase in the leachate concentration with a decrease in the sample size was observed only for coarse waste samples with a 20% cement ratio.

In general, at the same cement ratio, fine waste samples produced a leachate with lower metal concentrations than coarse waste samples. Therefore, when initial waste characterization is taken into consideration, waste samples with finer textures will result in a better S/S process. Despite a slight difference between the initial metal compositions of 10% and 20% cement-waste mixtures, increasing the cement ratio did not have any significant effect on metal concentrations in the leachate.

The ratio of Ca/Si for typical Portland cement is around 3. At high Ca/Si ratios, the hydration product of Portland cement, calcium silicate hydrogel known as C-S-H, has a positive surface charge and thus sorbs mainly anionic species. Since anions are abundant in the cement (i.e. OH^- and SO_4^{2-}), the performance of cement for anions is generally poor. That is, these anions have to compete with more abundant OH^- etc. for anionic sites (Glasser, 1997). Therefore, this situation explains the reason for the high concentration of ions other than metals in this study (Table 6).

The percentages of retained metal concentrations after S/S were calculated for both extraction procedures. These calculations demonstrate what percentage of the metal, which was initially in the solidified waste, was still in the waste after leaching. For example, 90% retention means that 10% of the metal existing in the waste leached into the water and 90% of the metal remained in the solidified waste. The following formula was used to calculate percent retained (% RT):

$$\%RT = \frac{M_T - (V_L)(C_L)}{M_T} \quad (1)$$

where M_T : Total initial mass of contaminant, mg

V_L : Leachate volume, l

C_L : Leachate concentration of contaminant, mg/l.

The aim of percent-retained calculations was to understand whether S/S application was achieved with high efficiency or not. The percent-retained metal concentrations after TCLP and DWLP are given in Table 9 and Table 10, respectively. According to these tables, the application of S/S in both extraction procedures resulted in high efficiency. Although the metal concentrations of fine waste samples with 10% cement were initially higher than the others, the efficiency of S/S was better for this case. One of the most important technical criteria for the effectiveness of the S/S process is the assessment of the quality of the leachate. Therefore, all four cases (fine and coarse size waste with 10% and 20% cement) yielded very good results in terms of leachate quality.

In this study, unconfined compressive strength tests were also performed on duplicate cylindrical solidified samples of each treatment at the end of the 28-day cure period. The unconfined compressive strength values of 10% cement-fine mining waste, 20% cement-fine mining waste, 10% cement-coarse mining waste and 20% cement-coarse mining waste samples are 1154 kPa, 2520 kPa, 1019 kPa and 3250 kPa, respectively. The results for both fine and coarse mining wastes showed that as the cement ratio in the mining waste increases unconfined compressive strength also rises. As expected, this strength development was due to the increased cement addition to the mining waste samples. According to the U.S. EPA standards, the minimum value of unconfined compressive strength is 350 kPa for the disposal of solidified hazardous wastes in landfills. Unconfined compressive strength values measured for all treatments considered in this study are well above this limiting value. Therefore, these solidified mining waste samples can easily be disposed of in landfills.

Conclusions

In this study, two different leaching tests (the TCLP and DWLP of the Turkish Hazardous Wastes Control Regulation) were compared to assess the effectiveness of cement-based S/S. Based on the experimental findings of this research the following conclusions can be drawn:

Metal concentrations in the TCLP leachate were significantly higher than the metal concentrations in the DWLP leachate.

Table 9. Percent retained metal concentrations after TCLP.

Metals	10% cement + fine mining waste						20% cement + fine mining waste						10% cement + coarse mining waste						20% cement + coarse mining waste					
	1-2 mm			> 2 mm			1-2 mm			> 2 mm			1-2 mm			> 2 mm			1-2 mm			> 2 mm		
	C _i (mg/l)	RT (%)	C _i (mg/l)	RT (%)	C _i (mg/kg)	RT (%)	C _i (mg/l)	RT (%)	C _i (mg/l)	RT (%)	C _i (mg/kg)	RT (%)	C _i (mg/l)	RT (%)	C _i (mg/l)	RT (%)	C _i (mg/kg)	RT (%)	C _i (mg/l)	RT (%)	C _i (mg/l)	RT (%)	C _i (mg/l)	RT (%)
Cd	1250	97.0	1.85	97.0	3.89	93.8	1000	99.1	0.47	98.8	850	95.3	2	94.3	750	98.1	0.73	98.5	0.73	98.1	0.19	99.5	0.19	99.5
Cu	3330	99.8	0.31	99.8	0.44	99.7	2550	99.7	0.41	99.7	1690	98.9	0.92	99.2	1250	98.5	0.91	98.5	0.91	98.5	0.29	99.5	0.29	99.5
Cr	3060	99.8	0.37	99.8	ND	99.9	2140	99.4	0.59	99.5	1920	98.2	1.71	99.2	1770	97.5	2.22	97.5	2.22	97.5	0.95	98.9	0.95	98.9
Pb	3090	99.7	0.39	99.7	0.23	99.9	2320	99.5	0.58	99.6	1420	98.4	1.12	98.9	1210	97.7	1.38	97.7	1.38	97.7	0.22	99.6	0.22	99.6
Zn	1900	99.3	0.71	99.3	1.85	98.1	1990	99.5	0.5	99.6	1350	98.6	0.96	98.5	1050	98.5	0.77	98.5	0.77	98.5	0.17	99.7	0.17	99.7
Fe	13,500	99.9	0.50	99.9	0.50	99.9	13,310	99.7	1.94	99.8	10,470	99.3	3.69	99.6	8780	99.5	2.35	99.5	2.35	99.5	0.78	99.8	0.78	99.8
Al	26,130	99.6	5.0	99.6	5.0	99.6	24,360	99.6	5.0	99.6	11,170	99.1	5.0	99.1	8250	98.8	5.0	98.8	5.0	98.8	5.0	98.8	5.0	98.8
Ca	7830	94.6	94.6	75.8	93.5	76.1	17,720	80.6	172.1	161.3	15,540	62.9	288	286.6	19,400	77.5	218.4	77.5	218.4	215.4	77.8	215.4	77.8	
Mg	1710	80.1	17	80.1	18.31	78.6	2490	82.3	21.98	23.63	3100	80.2	30.7	29.25	1560	95.9	3.16	95.9	3.16	95.9	5.73	92.7	5.73	92.7

C_i: initial metal concentration in the waste (mg/kg)

C_f: leachate concentration of metal (mg/l)

RT: percent retained metal concentration

Table 10. Percent retained metal concentrations after DWLP.

Metals	10% cement + fine mining waste						20% cement + fine mining waste						10% cement + coarse mining waste						20% cement + coarse mining waste					
	1-2 mm			> 2 mm			1-2 mm			> 2 mm			1-2 mm			> 2 mm			1-2 mm			> 2 mm		
	C _i (mg/kg)	C _i (mg/l)	RT (%)	C _i (mg/l)	C _i (mg/l)	RT (%)	C _i (mg/kg)	C _i (mg/l)	RT (%)	C _i (mg/l)	C _i (mg/l)	RT (%)	C _i (mg/kg)	C _i (mg/l)	RT (%)	C _i (mg/l)	C _i (mg/l)	RT (%)	C _i (mg/kg)	C _i (mg/l)	RT (%)	C _i (mg/l)	C _i (mg/l)	RT (%)
Cd	1250	0.23	99.8	0.05	99.96	1000	0.12	99.9	0.08	99.9	850	0.29	99.7	0.13	99.8	750	0.16	99.8	0.12	99.8	0.16	99.8	0.12	99.8
Cu	3330	0.05	99.98	0.05	99.98	2550	0.12	99.95	0.07	99.97	1690	0.51	99.7	0.27	99.8	1250	0.51	99.6	0.22	99.8	0.51	99.6	0.22	99.8
Cr	3060	0.1	99.97	0.1	99.97	2140	0.55	99.7	0.59	99.7	1920	0.6	99.7	0.19	99.9	1770	1.03	98.4	0.68	99.6	1.03	98.4	0.68	99.6
Pb	3090	0.1	99.97	0.1	99.97	2320	0.45	99.8	0.39	99.8	1420	0.51	99.6	0.35	99.8	1210	0.55	99.5	0.13	99.9	0.55	99.5	0.13	99.9
Zn	1900	0.24	99.9	0.31	99.8	1990	0.07	99.96	0.02	99.99	1350	0.33	99.8	0.15	99.9	1050	0.24	99.8	0.05	99.95	0.24	99.8	0.05	99.95
Fe	13,500	0.5	99.96	0.5	99.96	13,310	0.84	99.94	0.51	99.96	10,470	3.08	99.7	0.7	99.9	8780	2.18	99.8	0.62	99.9	2.18	99.8	0.62	99.9
Al	26,130	5	99.96	5	99.8	24,360	5	99.8	5	99.8	11,170	5	99.6	5	99.6	8250	5	99.4	5	99.4	5	99.4	5	99.4
Ca	7830	83.39	89.4	80.83	89.7	17,720	114.5	93.5	117.5	93.4	15,540	162.1	89.6	170.4	89.0	19,400	144.2	92.6	136.7	93.0	144.2	92.6	136.7	93.0
Mg	1710	6.31	96.3	4.95	97.1	2490	4.25	98.3	6.35	74.5	3100	8.31	97.3	8.76	97.2	1560	0.227	99.9	0.36	99.8	0.227	99.9	0.36	99.8

C_i: initial metal concentration in the waste

C_j: leachate concentration of metal

RT: percent retained metal concentration

For all cases, leaching test results showed that the S/S produced efficiencies greater than 90% for the retention of metals in the solidified mass.

The application of the S/S process as a pretreatment method gave results consistent with the criteria of the THWCR, and wastes with metal concentration levels similar to the mining waste considered in this study can be disposed of in landfills. However, for 10% cement + mining waste, the application of S/S for cadmium was not successful because the leachate concentrations of cadmium exceeded the permitted limits of the EPA. Therefore, in order to make S/S applicable to mining wastes containing high concentration of cadmium (> 1000 mg/kg), the cement addition should be greater than 10%.

Nomenclature

C_L	leachate concentration of contaminant, (mg/l)
C_i	initial metal concentration in the waste, (mg/kg)
C_l	leachate concentration of metal, (mg/l)
C-S-H	calcium silicate hydrogel
DWLP	distilled water leaching procedure
M_T	total initial mass of contaminant, (mg)
% RT	percent retained metal concentration, (%)
S/S	solidification/stabilization
TCLP	toxicity characteristic leaching procedure
THWCR	Turkish Hazardous Waste Control Regulation
U.S.-EPA	Environmental Protection Agency (USA)
V_L	leachate volume, (l)

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