

CHROMIUM LEACHABILITY FROM STABILIZED/SOLIDIFIED SOILS UNDER MODIFIED SEMI-DYNAMIC LEACHING CONDITIONS

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Abstract : The effectiveness of fly ash-, quicklime-, and quicklime-fly ash-based stabilization/solidification (S/S) in chromium (Cr) contaminated soils was investigated using modified semi-dynamic leaching tests. Artificial soil samples composed of kaolinite or montmorillonite contaminated with chromium nitrate (4000 mg Cr³⁺ kg⁻¹ of solid) were prepared and then subjected to S/S treatment using quicklime, fly ash, or quicklime-fly ash. The effectiveness of the treatment was evaluated by assessing the cumulative fraction of leached Cr³⁺ as well as, by computing the effective diffusivity (D_e) and the leachability index (LX) of the treated samples. The reduction in Cr³⁺ release for the untreated samples was more pronounced in the presence of montmorillonite, which was attributed to sorption. Treatment with quicklime, fly ash, or quicklime-fly ash was significantly effective in reducing Cr³⁺ release most probably due to the formation of pozzolanic reaction products and Cr(OH)₃ precipitation. The most effective treatment was observed in montmorillonite-sand soil samples treated with quicklime-fly ash (99.8% removal). The mean D_e decreased significantly and the mean LX was greater than 9 for all treated samples, indicating that the treated soils were acceptable for "controlled utilization". The mechanism controlling Cr³⁺ leaching from all treated samples during the first 5 days appeared to be diffusion.

Key Words : chromium (Cr³⁺), leachability index (LX), quicklime, semi-dynamic leaching test, stabilization/solidification (S/S)

INTRODUCTION

Chromium (Cr) is an important natural resource used in many industrial and commercial activities, such as steel making, chromium electroplating, leather tanning, and chemical manufacturing.^{1,2)} At low levels, it is an essential nutrient for plant and animal metabolism.¹⁻³⁾ However, accumulation of high levels of Cr in humans can cause nausea, skin ulcerations, and lung cancer.¹⁾ Moreover, Cr can be lethal at accumulation levels close to 0.1 mg g⁻¹ of body

weight.³⁻⁵⁾ In nature, chromium occurs in a hexavalent (Cr⁶⁺) and a trivalent (Cr³⁺) form. Cr⁶⁺ is more mobile and toxic than Cr³⁺. However, reduction of Cr⁶⁺ to Cr³⁺ can be achieved with relative ease using metals (e.g., zinc, iron, brass, or aluminum) or salts of ferrous iron, sulphites, etc..⁶⁾ In the present study, Cr³⁺ was used as a chromium source for artificially contaminated soils to investigate the mechanism controlling Cr³⁺ release in fly ash-, quicklime-, and quicklime-fly ash-based stabilized/ solidified monolithic solids.

Stabilization/solidification (S/S) is one of the most effective treatment processes for the remediation of heavy metal-contaminated soils.⁷⁾ During the S/S process, contaminants present in

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waste forms can be physically and chemically "fixed", which significantly reduces their mobility.^{8,9)} Various stabilizing agents, such as cement, hydrated lime, and fly ash, have been used in S/S processes.⁷⁻¹⁶⁾

In soils treated with quicklime or fly ash or both, there are three possible mechanisms that may be responsible for the immobilization of Cr^{3+} : 1) Precipitation as a result of the formation of insoluble $\text{Cr}(\text{OH})_3$ ^{8,9)}; 2) Inclusion, either physical encapsulation or chemical inclusion. Physical encapsulation can be achieved by creating a solidified monolith. Chemical inclusion can be achieved through the incorporation of Cr in binder hydration products, such as calcium silicate hydrates (CSH), by isomorphic substitution^{8,9)}; 3) Sorption on clays and pozzolanic reaction products.^{8,9)}

In this study, quicklime (CaO), rather than cement or hydrated lime, was used as the main stabilizing agent. In some samples, fly ash was also used to try to immobilize Cr^{3+} . There is a clear economic advantage to using quicklime as the main S/S agent, as commercial quicklime is less expensive than either cement or hydrated lime. Furthermore, quicklime accelerates the rate of reaction because of its heat of hydration. Finally, there is only limited information available to date on quicklime-based stabilization for Cr^{3+} .

The effectiveness of fly ash-, quicklime-, and quicklime-fly ash-based S/S in immobilizing Cr^{3+} was assessed using the American Nuclear Society 16.1 test.¹⁷⁾ The ANS 16.1 test was selected over the Toxicity Characteristic Leaching Procedure (TCLP) test¹⁸⁾ and the Extraction Procedure Toxicity (EP Tox) test¹⁹⁾ because the ANS 16.1 test provides significantly more information regarding the "real time" rate at which metals are released from the solidified product. ANS 16.1 is a semi-dynamic leaching test that evaluates the release of metals in a diffusion-controlled environment. Specifically, the cumulative fraction of chromium leached over time can be obtained by applying this method. The release of contaminants from cement-based

waste is reported to be mostly controlled by diffusion.^{10,20,21)} In natural environments, diffusion is considered to be the main mechanism for contaminant transfer when a low permeability waste form lies below the groundwater table in a very low hydraulic gradient flow regime (aquitarde scenario). Preliminary column percolating tests were performed on specimens identical to those used in this study. The results obtained from these tests showed that the hydraulic conductivity of artificial soil monoliths was low (between 2×10^{-6} and 5×10^{-10} cm s^{-1}). Therefore, it was assumed that chromium release in quicklime-treated waste is also controlled by diffusion.

The objectives of this study were to 1) assess the effect of surface area and cation exchange capacity (CEC) on Cr^{3+} release, 2) determine the leaching behavior of Cr^{3+} in soils treated with quicklime or fly ash or both by performing semi-dynamic leaching tests, and 3) evaluate the effectiveness of treatment with quicklime and/or fly ash by measuring the leachability index (LX).

EXPERIMENTAL METHODOLOGY

Reagents and Materials

Analytical grade chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) obtained from Fisher Scientific (GA, USA) was used as the source of Cr^{3+} . Two types of clay minerals were used: kaolinite, an inert clay, and montmorillonite, a reactive clay with respect to sorption and chemical inclusion. These clays were chosen to represent the two extremes of physicochemical clay behavior based on their surface areas and cation exchange capacities (CEC). In addition, the amount of clay was varied to evaluate its relative contribution to Cr^{3+} release. Kaolinite was obtained from Dry Branch Kaolin (GA, USA) and montmorillonite from Kaopolite, Inc. (NJ, USA).

Chemical grade quicklime powder (95% CaO) was provided by the Bellefonte Lime Company (PA, USA). Class C Coal fly ash was obtained

from the American Fly Ash Company (IL, USA). The chemical and physical properties of the kaolinite, montmorillonite, quicklime, and fly ash are presented in Table 1.

Preparation of Artificially Contaminated Soil

Soil samples were prepared by mixing clay with fine quartz sand. Clay-sand mixtures were used instead of pure clay to obtain specimens with a gradation more comparable to that of naturally occurring soils. Moreover, soils prepared with quartz sand could be more easily compacted than pure clays. The soil samples were spiked with chromium nitrate to reach a total Cr^{3+} content of 4000 mg per kg of the solid. This initial maximum Cr^{3+} concentration was used at the request of the sponsor (US Department of Energy). After the preparation of the dry Cr^{3+} -clay-sand mixtures, water was added to the samples to achieve the Modified Proctor optimum water content. Samples were then aged for 3 days to reach equilibrium. To investigate the effect of fly ash alone on Cr^{3+} immobilization, samples of fly ash mixed with fine quartz sand were also prepared and spiked with the same Cr^{3+} concentration as the other samples.

Treatment of Contaminated Soil

The contaminated soils were treated with quicklime or fly ash or both by mixing the solid additives with the soil in a dry state. The

quicklime content was 10% of the total solids weight and the fly ash content was 25% by weight (clay-sand-fly ash). The fly ash content for the sample containing only fly ash was 30% by weight (fly ash-sand). Samples were then compacted in accordance with the ASTM D1557-91 standard (Test Methods for Laboratory Compaction Characteristics of Soil Using Modified Effort.²²) Specifically, samples of 4.0 ± 0.4 cm in height and 4.70 ± 0.05 cm in diameter were prepared. The compacted samples were then cured at 20°C and 95% relative humidity (RH) in sealed sample bags for 28 days and subjected to the ANS 16.1 leaching test.

Sample Designation

A sample designation guide is presented in Figure 1. Letters in each specimen designation indicate mineralogical components, i.e., K: kaolinite, M: montmorillonite, C: Class C fly ash, and L: quicklime. The numbers following the letters indicate the weight percent of the given components. Sand was not included in the sample designation because the same type of fine quartz sand was added to all mixtures. Sand was added to the clay, fly ash, or clay and fly ash mixtures on a 100% dry weight basis (Figure 1).

ANS 16.1 Semi-Dynamic Leaching Test

The ANS 16.1 test was used to evaluate Cr^{3+}

Table 1. Summary of chemical and physical properties of kaolinite, montmorillonite, quicklime, and fly ash

	Kaolinite	Montmorillonite	Quicklime	Fly ash(Class C)
SiO_2 (dry wt %)	45.7	67.2	1.2	38.2
Al_2O_3 (dry wt %)	38.5	15.2	-	19.8
Iron Oxide (dry wt %)	0.4	1.87	-	5.11
CaO (dry wt %)	0.2	1.92	95.4	21.4
MgO (dry wt %)	0.1	3.2	0.85	3.86
SO_3 (dry wt %)	-	-	0.012 (as S)	2.2
Na_2O (dry wt %)	0.04	2.58	-	2.04
K_2O (dry wt %)	0.1	0.96	-	0.65
TiO_2 (dry wt %)	1.4	0.16	-	-
Surface area (m^2/g)	66	760	40.0-41.5	31
pH	4.0-6.5	7	12.9	12.3

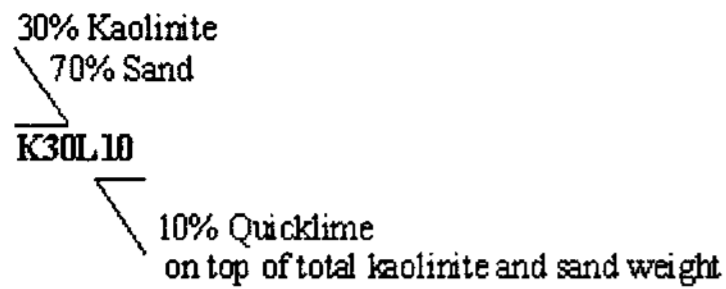
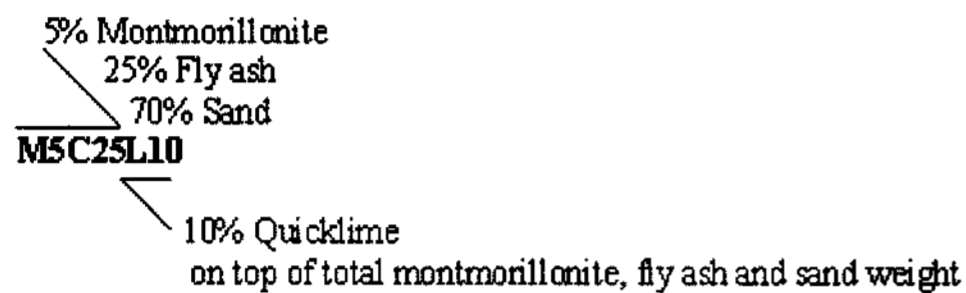
Example 1: K30L10**Example 2: M5C25L10**

Figure 1. A specimen designation guide.

leachability from samples treated with quicklime or fly ash or both. This leaching test is considered semi-dynamic because the leachant is replaced after intervals of static leaching. The ANS 16.1 method was modified by using a 0.014 N acetic acid solution (pH = 3.25) instead of distilled water to simulate the worst possible leaching conditions of an S/S waste being disposed of in a landfill environment. The ratio of leachant volume (V_L) to the specimen's external surface area (S) was maintained at 10 ± 0.2 cm, in accordance with the ANS 16.1 method, to minimize leachant composition changes as well as to provide an ample concentration of extracted species for analysis.¹⁷⁾ Prior to the ANS 16.1 leaching experiment, any loose particles from the specimen's surface were removed by immersion in distilled water for 30 s. Each specimen was then suspended near the centroid of the leachant in a polyethylene container with a nylon mesh harness. As specified by the ANS 16.1 method, the leachate was collected and entirely replaced at designated time intervals (2, 7, 24, 48, 72, 96, 120, 456, 1128, and 2160 hours).¹⁷⁾ A 0.4- μ m pore-size membrane filter was used to separate the sampled leachate.

Sample Analysis

The concentrations of dissolved Cr^{3+} were analyzed with an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES; Varian Vista-MPX, Palo Alto, CA, USA). A number of

blanks, replicates, and spiked samples were prepared with each batch of samples for quality control purposes.

EVALUATION OF LONG-TERM LEACHING BEHAVIOR**Diffusion Model**

The long-term leaching behavior of Cr^{3+} was evaluated using the ANS 16.1 model.¹⁷⁾ This model employs Fick's diffusion theory and provides diffusion rates that can be applied to give parameters that can be used to evaluate the effectiveness of the S/S treatment. Using this model the effective diffusion coefficients can be calculated as follows:

$$D_e = \pi \cdot \left[\frac{\left(\frac{a_n}{A_0} \right)}{(\Delta t)_n} \right]^2 \cdot \left[\frac{V}{S} \right]^2 \cdot T_n \quad (1)$$

where a_n = the contaminant loss (mg) during the particular leaching period with index n ; A_0 = the initial amount of contaminant present in the specimen (mg); $(\Delta t)_n = t_n - t_{n-1}$; V = the volume of the specimen (cm^3); S = the geometric surface area of the specimen as calculated from measured dimensions (cm^2); T_n = elapsed time (s) to the middle of the leaching period n ; and D_e = the effective diffusion coefficient ($\text{cm}^2 \text{sec}^{-1}$).

Because diffusion takes place in the interstitial liquid of a porous body, the D_e values from Equation 1 are termed "effective".

The diffusion of Cr^{3+} from the solid to the solution can be reduced by physical retardation (τ) or chemical retention (R) or both. The general equation for the effective diffusion coefficients as a function of the physical retardation and chemical retention can be expressed as follows²³⁾:

$$D_e = D_{o, Cr} \cdot \left(\frac{1}{R \cdot \tau} \right) \quad (2)$$

where $D_{o,Cr}$ = the diffusion coefficient of Cr^{3+} in water ($5.95E-6 \text{ cm}^2 \text{ s}^{-1}$)²⁴); R = the chemical retention factor of Cr^{3+} in the solid; and τ = the physical retardation in the solid.

Once the D_e values were determined using Equation 1, the leachability index (LX) could be defined as the negative logarithm of the effective diffusivity. The value of LX is given by:

$$LX = \frac{1}{m} \cdot \sum_{n=1}^m [-\log(D_e)]_n \quad (3)$$

where n = the number of the particular leaching period; and m = the total number of individual leaching periods.

In accordance with Waste Technology Centre²⁵), the LX values can be considered as performance criteria for the utilization and disposal of S/S treated wastes. For LX values above 9, a treatment process may be considered effective and S/S treated wastes would be appropriate for "controlled utilization," i.e., quarry rehabilitation, lagoon closure, road bases, etc. For LX values between 8 and 9, S/S treated wastes may be disposed of in segregated or sanitary landfills. S/S waste with an LX value below 8 is not considered appropriate for disposal.

Determination of The Controlling Leaching Mechanism

The mechanism controlling Cr^{3+} leaching was determined using a diffusion theory model developed by de Groot & van der Sloot.²³) In this model, the cumulative maximum release of the component (in mg m^{-2}) is expressed as:

$$\log(B_t) = \frac{1}{2} \cdot \log(t) + \log \left[U_{\max} \cdot d \cdot \sqrt{\left(\frac{D_e}{\pi}\right)} \right] \quad (4)$$

where D_e = the effective diffusion coefficient in $\text{cm}^2 \text{ s}^{-1}$ for component x (Cr^{3+} in this study); t = the contact time in seconds; U_{\max} = the maximum leachable quantity expressed in mg

kg^{-1} ; and d = the bulk density of the product in kg m^{-3} .

Three potential controlling mechanisms for Cr^{3+} release, wash-off, diffusion, and dissolution, can be distinguished by evaluating the slope of the curve in Equation 4. Slope values close to 0.5 indicate that the release of Cr^{3+} is slow and controlled by diffusion. Slope values close to 1 indicate that dissolution is the controlling mechanism; Cr^{3+} release controlled by dissolution from the surface would proceed much faster than by diffusion through the pore space of the solid matrix. Slope values close to 0 would suggest that Cr^{3+} release is controlled by wash-off, occurring when a soluble layer exists on the surface of the material. During the initial phase of the leaching process, this soluble material would be dissolved and result in the release of highly soluble materials. Unlike dissolution-controlled Cr^{3+} release, wash-off would deplete this soluble material after the initial leaching phase.

RESULTS AND DISCUSSION

Cumulative Fraction of Cr^{3+} Leached before and following S/S Treatment

The cumulative fraction of Cr^{3+} leached from untreated and fly ash-treated samples is plotted in Figure 2 and that from quicklime- and quicklime-fly ash-treated samples is plotted in Figure 3. In both figures, the cumulative fraction of Cr^{3+} leached is plotted using a semi-log graph as a function of time. The cumulative fractions of Cr^{3+} leached from all samples upon test completion are summarized and presented in Table 2. Only two data points were obtained from sample K15L0, because it disintegrated after 7 hours of testing.

There was no significant immobilization of Cr^{3+} in untreated samples containing kaolinite. In contrast, the cumulative fraction of Cr^{3+} release from untreated samples that contained montmorillonite was significantly lower (Figure 2 and Table 2). Moreover, increasing the amount of montmorillonite from 15 to 30% led to a reduc-

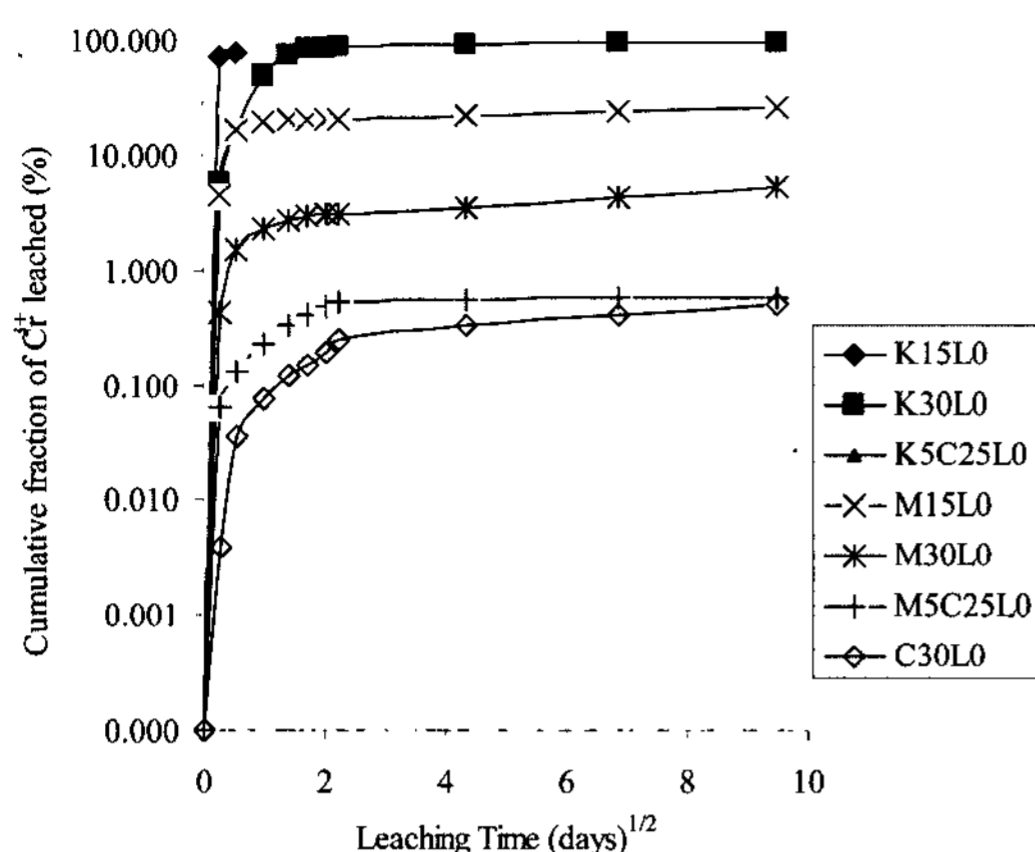


Figure 2. The cumulative fraction (%) of Cr^{3+} leached from untreated and fly ash-treated samples as a function of the square root of time.

Table 2. The cumulative fraction (%) of Cr^{3+} leached from samples following test completion.

Sample	Cumulative fraction of Cr^{3+} leached (%)
K15L0	77.1*
K30L0	96.3
K5C25L0	0.64
M15L0	26.1
M30L0	5.26
M5C25L0	0.58
C30L0	0.49
K15L10	0.55
K30L10	0.33
K5C25L10	0.24
M15L10	0.24
M30L10	0.20
M5C25L10	0.12

*Note: K15L0 sample disintegrate after 7 hours of testing

tion in leached Cr^{3+} of more than 20%, most probably as a result of the large surface area and high CEC of montmorillonite.

Upon addition of fly ash to the clays, Cr^{3+} release was reduced by as much as 99% (Figure 2 and Table 2). Fly ash contains 21.4% CaO by weight (Table 1); thus, the addition of fly ash can be an indirect way of adding lime to the soils. The significant immobilization of Cr^{3+} may be attributed to the inherent alkalinity of fly ash, suggesting that the release of Cr^{3+} is mainly

controlled by the solubility of $\text{Cr}(\text{OH})_3$ at high pH, as induced by quicklime. Cr^{3+} release has been reported to be primarily caused by the precipitation of insoluble hydroxides under alkaline conditions induced in quicklime and quicklime-fly ash-treated media.^{8,9,26)} Given that no significant differences were observed between samples K5C25L0 and M5C25L0, the pozzolanic reaction of the clay does not appear to play an important role in Cr^{3+} immobilization. This implies that the addition of fly ash does not create pH levels high enough to activate the release of silica from the clay.

In the sample containing fly ash without clay (C30L0), Cr^{3+} immobilization was more effective than in samples K5C25L0 and M5C25L0, indicating that Cr^{3+} release could be significantly reduced by increasing the fly ash content.

In all quicklime-treated samples, a significant immobilization of Cr^{3+} was achieved, i.e., the cumulative fraction of leached Cr^{3+} was reduced by more than 94% (Figure 3 and Table 2). This indicates that neither the amount nor the type of clay had an effect on Cr^{3+} release upon treatment. The role of surface adsorption, once evident in sample M30L0, was no longer dominant following treatment. Therefore, the immobilization of Cr^{3+} was mainly controlled by the solubility of $\text{Cr}(\text{OH})_3$. Moreover, upon treatment with quicklime, the formation of pozzolanic reaction products such as CSH seemed to play a role in the immobilization of Cr^{3+} . This conclusion was based on the observation of a more pronounced reduction of more than 39% in the cumulative fraction of Cr^{3+} leached in samples containing montmorillonite than in samples containing kaolinite. Montmorillonite samples treated with quicklime should have a much higher silica content than quicklime-treated kaolinite samples. Therefore, these samples should create pozzolanic reaction products in greater quantities and at a higher rate. The studies of Ricou-Hoeffler et al.²⁷⁾ have also shown that the formation of CSH in alkaline conditions plays a role in the removal and stabilization of metallic cations.

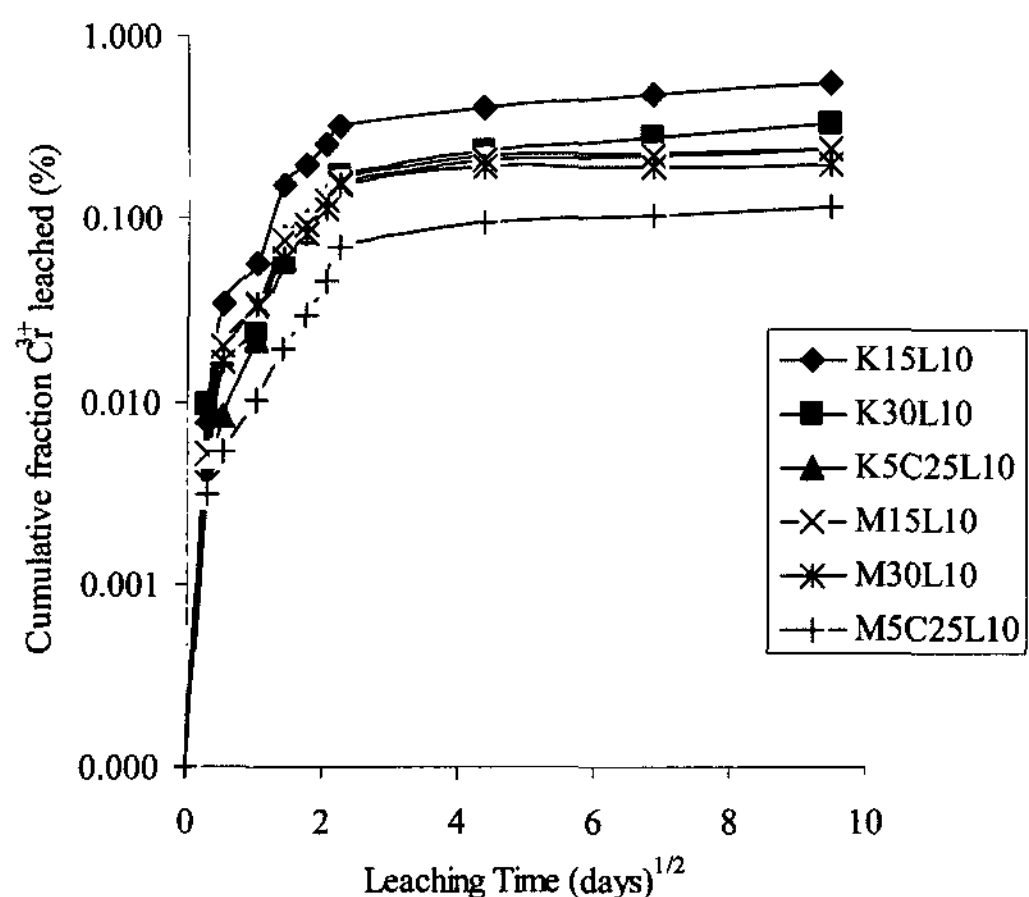


Figure 3. The cumulative fraction (%) of Cr³⁺ leached from quicklime- and quicklime-fly ash-treated samples as a function of the square root of time.

Treatment with quicklime-fly ash further improved the immobilization of Cr³⁺. Fly ash provides a greater source of silicates and may cause an increase in the production of pozzolanic reaction products under quicklime-induced conditions of high pH. The treatment was most effective in the presence of montmorillonite (Figure 3 & Table 2).

The Effect of Leachant pH on Cr³⁺ Leachability

The leachant pH was monitored at time intervals as designated by the ANS 16.1 protocol. The leachant pH values of untreated and fly ash-treated samples over time are presented in Figure 4, and those of the quicklime-treated and quicklime-fly ash-treated samples over time are presented in Figure 5. The leachant pH was lower than 4 for all untreated samples. However, the leachant pH of fly ash-treated samples increased significantly after 5 days, and at the completion of the test (after 90 days) the pH was higher than 5.5. This indicates that after 5 days of testing the CaO present in the fly ash possibly consumed the buffering capacity of the liquid. As the monolithic solid remained in contact with the liquid for a longer period, the pH of the leachate was expected to continue to rise.

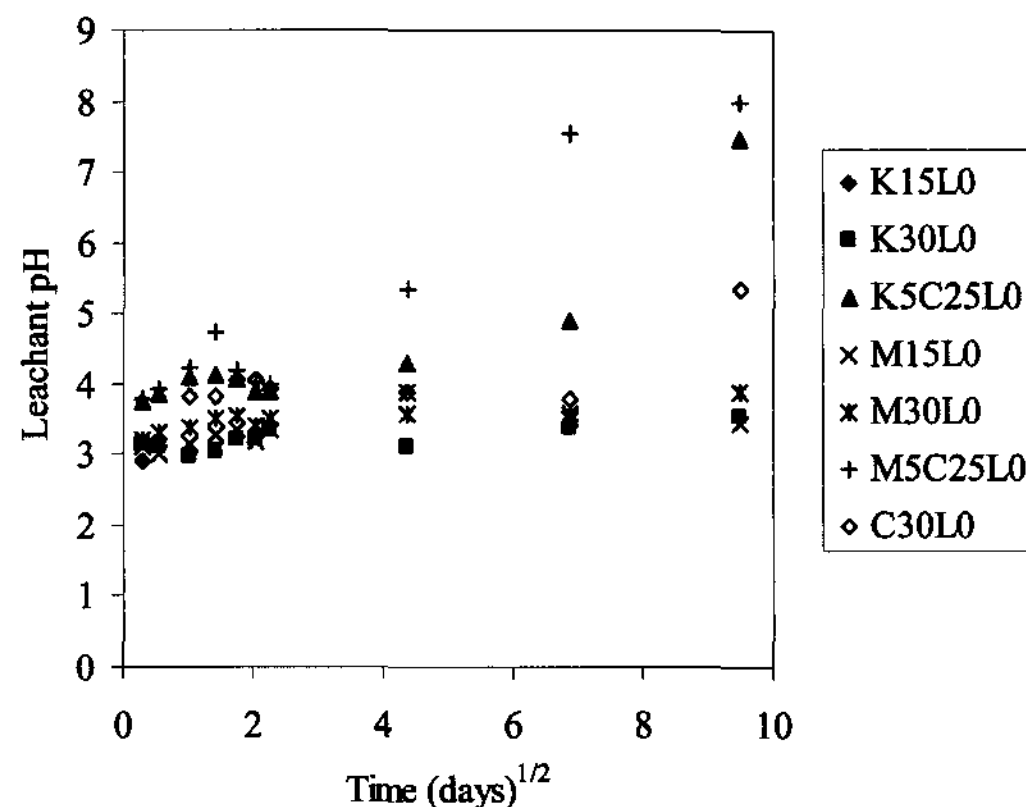


Figure 4. The leachant pH for untreated and fly ash-treated samples.

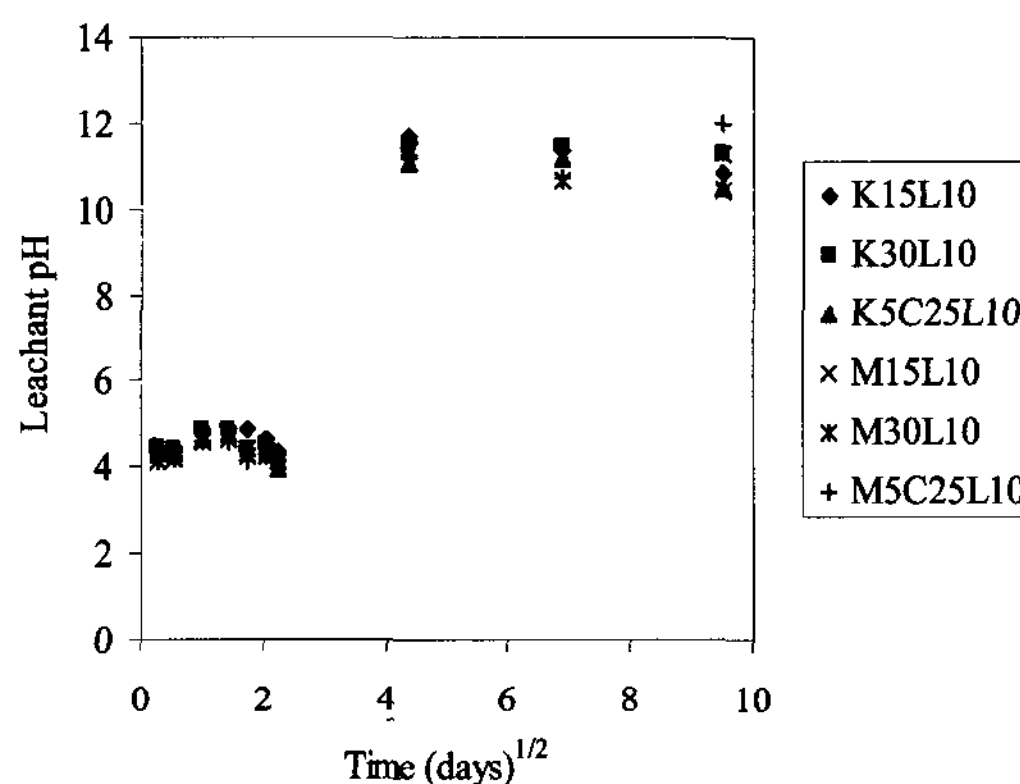


Figure 5. The leachant pH for quicklime- and quicklime-fly ash-treated samples.

Similarly, the leachant pH of the quicklime and quicklime-fly ash samples was lower than 5 up to the 5-day testing point. However, the pH increased drastically at all points beyond 5 days and ranged from 10.5 to 12, suggesting that the fast consumption of the buffering capacity was a result of the high calcium content in the samples. Moreover, this indicates that following 5 days of testing, Cr³⁺ release was affected by the change in pH.

The Controlling Leaching Mechanism and The Effectiveness of Quicklime, Fly ash, and Quicklime-Fly ash Treatment

The mechanism controlling Cr³⁺ leaching from fly ash-, quicklime-, and quicklime-fly ash-treated samples was evaluated using the diffusion model developed by de Groot & van der Sloot.²³⁾ As

the cumulative release of Cr^{3+} stabilized in the first 5 days of testing, the diffusion model was applied only to the first 5 days of the leaching period. The cumulative release of Cr^{3+} from the fly ash-treated samples (K5C25L0 and M5C25L0), the quicklime-treated sample (K30L10), and the quicklime-fly ash-treated sample containing montmorillonite (M5C25L10) was plotted as a function of time (Figure 6), as an example. The cumulative release of Cr^{3+} for the other samples was also plotted (not presented) and the slope and R^2 values obtained are summarized in Table 3.

Table 3. Regression analysis of Cr^{3+} release over the first 5 days.

Sample	Slope	R^2
K15L0	0.05*	-
K30L0	0.19	0.91
K5C25L0	0.61	0.99
M15L0	0.07	0.86
M30L0	0.26	0.96
M5C25L0	0.51	0.99
C30L0	0.65	0.99
K15L10	0.77	0.95
K30L10	0.68	0.93
K5C25L10	0.71	0.94
M15L10	0.72	0.96
M30L10	0.77	0.96
M5C25L10	0.73	0.95

*Note: K15L0 sample disintegrate after 7 hours of testing

In untreated samples, the slope ranged from 0.05 to 0.26 (Table 3). Based on these slope values, surface wash-off appeared to be the main controlling mechanism. For samples treated with fly ash with and without clays, the slope increased to as high as 0.65 (Table 3), indicating that Cr^{3+} release from fly ash-treated samples (K5C25L0 and M5C25L0) was mainly controlled by diffusion. Quicklime and quicklime-fly ash treatment produced slopes ranging from 0.68 to 0.77 (Table 3). These slope values indicate that Cr^{3+} release in all treated samples is most likely to be controlled by diffusion. Dissolution could have contributed to the release of Cr^{3+} from samples K15L10 and K30L10, as their slope values were somewhat higher.

The regression results for the first 5 days of testing indicate that Cr^{3+} release in quicklime-, fly ash-, and quicklime-fly ash-treated samples appears to be controlled by diffusion (Figure 6). This agrees with previous research, which found that Cr^{3+} release from soils containing montmorillonite treated with lime was controlled by diffusion.²⁶⁾ Moreover, it has been reported that the leaching process in most pozzolanic-based materials should be diffusion controlled.²³⁾ In a study on Cr^{3+} release from cement-fly ash-treated samples, Côté and Constable²⁸⁾ also found that the rate of Cr^{3+} release was controlled by diffusion.

The treatment effectiveness was evaluated based on the mean D_e , $R \cdot \tau$, and LX values. Because a linear relationship between the logarithm of the cumulative release of Cr^{3+} and the logarithm of time was obtained for up to 5 days (Figure 6), the mean D_e values were obtained for the same period. As mentioned above in the ANS 16.1 model section, the mean LX values were obtained by taking a negative logarithm of the mean D_e values. The mean D_e , $R \cdot \tau$, and LX values for all samples were computed, and are listed in Table 4. The D_e values for untreated samples were also included, even though Cr^{3+} release from untreated samples was not controlled by diffusion, so that the

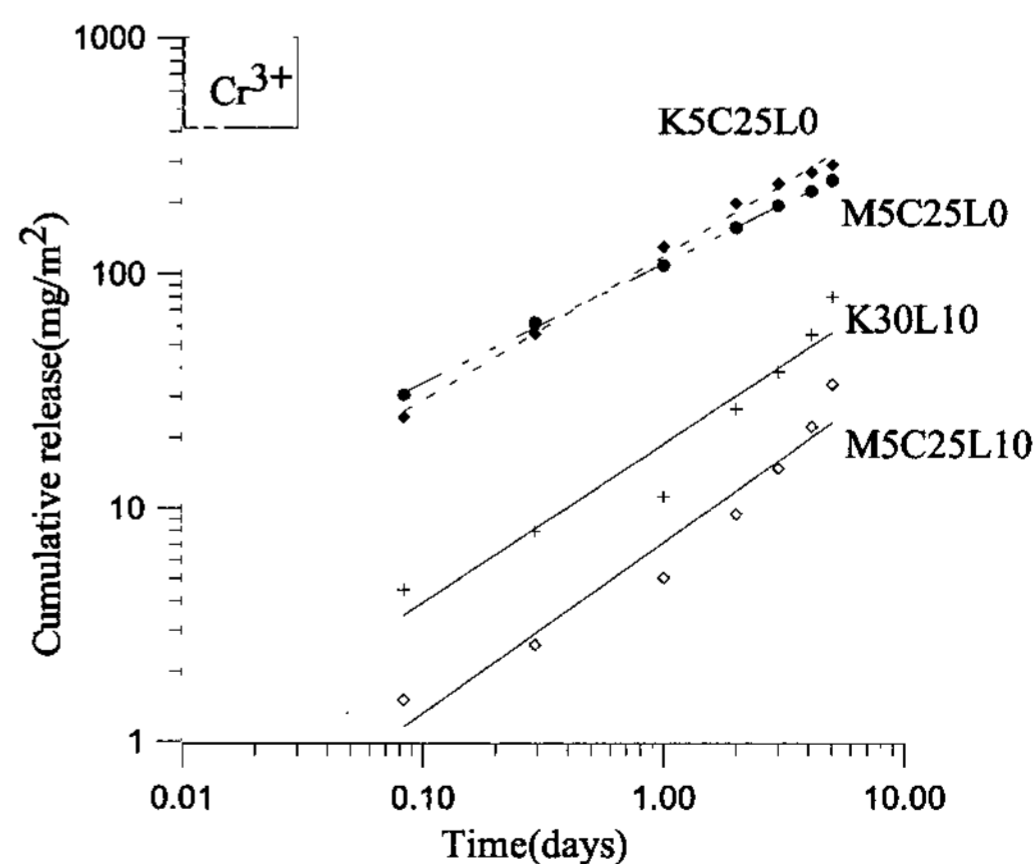


Figure 6. Logarithm of the cumulative release of Cr^{3+} versus the logarithm of time for samples K5C25L0, M5C25L0, K30L10 and M5C25L10.

Table 4. Mean diffusion coefficients (D_e), physical retardation and chemical retention ($R \cdot \tau$), and the leachability indices (LX) from the first 5 days.

Sample	Mean D_e (cm ² /s)	$R \cdot \tau$	Mean LX
K15L0	7.33E-06	8.12E-01	5.1*
K30L0	6.78E-07	8.78E+00	6.2
K5C25L0	2.11E-11	2.82E-05	10.7
M15L0	1.05E-07	5.67E+01	7.0
M30L0	1.43E-09	4.16E+03	8.8
M5C25L0	2.21E-11	2.69E+05	10.7
C30L0	4.66E-12	1.28E+06	11.3
K15L10	1.56E-11	3.81E+05	10.8
K30L10	5.90E-12	1.01E+06	11.2
K5C25L10	4.47E-12	1.33E+06	11.3
M15L10	4.07E-12	1.46E+06	11.4
M30L10	4.39E-12	1.36E+06	11.4
M5C25L10	1.30E-12	4.58E+06	11.9

*Note: K15L0 sample disintegrate after 7 hours of testing

changes in mean D_s , $R \cdot \tau$, and LX could be compared with those following treatment.

The mean D_e of untreated samples ranged from 7.33×10^{-6} to 1.43×10^{-9} cm² s⁻¹ (Table 4). The clay-fly ash samples, K5C25L0 and M5C25L0, had mean D_e values of 2.11×10^{-11} and 2.21×10^{-11} cm² s⁻¹, respectively (Table 4). The mean D_e value of sample C30L0 was 4.66×10^{-12} cm² s⁻¹ (Table 4). After quicklime treatment, the mean D_e values ranged from 1.56×10^{-11} to 4.07×10^{-12} cm² s⁻¹ (Table 4). Quicklime-fly ash treatment of samples K5C25L10 and M5C25L10 produced mean D_e values of 4.47×10^{-12} and 1.30×10^{-12} cm² s⁻¹, respectively (Table 4).

D_e values generally range from 10^{-5} (very mobile) to 10^{-15} cm² s⁻¹ (immobile), according to Nathwani & Phillips²⁹⁾ Therefore, the mobility of Cr³⁺ in this study was reduced by quicklime, fly ash, and quicklime-fly ash treatment. Specifically, the mean D_e of samples K30L10 and K15L10 was five orders of magnitude lower than that of their untreated counterparts (Table 4). Similarly, the mean D_e of samples M30L10 and M15L10 was five and three orders of magnitude lower, respectively, than that of their untreated counterparts (Table 4). The D_e of

sample C30L0 was one order of magnitude lower than that of samples K5C25L0 and M5C25L0 (Table 4). Quicklime-fly ash treatment resulted in a mean D_e one order of magnitude lower for samples M5C25L10 and K5C25L10 than that for samples M5C25L0 and K5C25L0 (Table 4). Overall, the lowest mean D_e value, i.e., the lowest Cr³⁺ mobility, was observed in sample M5C25L10 (Table 4); the cumulative fraction of leached Cr³⁺ was 0.12% (Table 2).

Physical retardation (τ) and chemical retention (R) were much higher in the treated samples than in the untreated samples. In sample K15L0, $R \cdot \tau$ was close to 1, indicating that the release rate of Cr³⁺ in K15L0 was similar to the diffusion rate of Cr³⁺ in water. This was caused by the disintegration of the sample after 7 hours of leaching tests. Treatment with quicklime or fly ash or both resulted in increases in $R \cdot \tau$ of more than five orders of magnitude in the kaolinite series samples and three orders of magnitude in the montmorillonite series samples. $R \cdot \tau$ in sample C30L0 was one order of magnitude higher than that from samples K5C25L0 and M5C25L0. Overall, treatment with quicklime or fly ash or both was effective in reducing the mobility of Cr³⁺ so that only trace levels were released.

The mean LX for untreated samples ranged from 5.1 to 8.8 (Table 4). These values increased with the addition of fly ash. The mean LX for samples K5C25L0 and M5C25L0 was about 10.7, while the mean LX for sample C30L0 was 11.3 (Table 4). Quicklime and quicklime-fly ash treatment resulted in a mean LX of about 11 to 12 (Table 4). Such high mean LX values suggest that Cr³⁺ retention was significantly improved with these treatments. Based on the protocol proposed by Environment Canada's Wastewater Technology Centre, all treated samples were acceptable for "controlled utilization". Ibáñez et al.³⁰⁾ concluded that, based on the same protocol, S/S treated wastes with LX values above 10 were acceptable for disposal in segregated or sanitary landfills or even for controlled utilization. Therefore, the S/S

treatment of Cr^{3+} contaminated soils in this study using quicklime and/or fly ash was effective in immobilizing Cr^{3+} .

CONCLUSIONS

In this study, the release of Cr^{3+} from quicklime-based S/S-treated samples was evaluated with semi-dynamic leaching tests. The mechanism controlling Cr^{3+} release was identified and the effectiveness of S/S treatment was evaluated. Overall, the treatment was effective in significantly reducing Cr^{3+} release, and the controlling mechanism of Cr^{3+} release appeared to be diffusion. The specific conclusions of this study are summarized as follows:

1. In untreated samples, the type of clay was an important factor influencing the reduction of Cr^{3+} release. Cr^{3+} release was significantly lower in the presence of montmorillonite, suggesting that sorption was the prevailing immobilization mechanism.
2. The amount of montmorillonite present in the soil was a significant factor affecting Cr^{3+} release, while the amount of kaolinite did not affect Cr^{3+} release. The reduced leaching of Cr^{3+} from samples containing montmorillonite was attributed to the large surface area and high CEC of this clay mineral.
3. The sole addition of fly ash to the clays in samples K5C25L0 and M5C25L0 reduced Cr^{3+} release by more than 99%. This may have been the result of $\text{Cr}(\text{OH})_3$ formation.
4. The sole addition of fly ash without clay in sample C30L0 reduced Cr^{3+} release by approximately 99.5%. This reduction was more pronounced than those in samples K5C25L0 and M5C25L0, suggesting that Cr^{3+} immobilization can be effectively achieved by increasing fly ash content.
5. Following quicklime-fly ash treatment (K5C25L10 and M5C25L10), Cr^{3+} release values were lowest in the presence of montmorillonite. This suggests that the release of Cr^{3+} was mainly controlled by the solubility of $\text{Cr}(\text{OH})_3$ and pozzolanic reaction

products under alkaline conditions.

6. Treatment with quicklime or fly ash or both consumed the buffering capacity of the liquid, and alkaline conditions prevailed after 5 days. This implies that a possible limitation to the ANS 16.1 method might develop after 5 days.
7. The mechanism controlling Cr^{3+} release from all treated samples in the first 5 days appeared to be diffusion. Wash-off was the controlling release mechanism for untreated samples.
8. Quicklime-based S/S treatment was very effective in reducing Cr^{3+} leaching. All S/S treated samples were acceptable for "controlled utilization" based on the protocol proposed by Environment Canada's Wastewater Technology Centre.

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REFERENCES

1. Richard, F. C. and Bourg, A. C. M., "Aqueous geochemistry of chromium: a review," *Wat. Res.*, **25**(7), 807-816 (1991).
2. Rinehart, T. L., Schulze, D. G., Bricka, R. M., Bajt, S., and Blatchley, E. R., "Chromium leaching vs. oxidation state for a contaminated solidified/stabilized soil," *J. Hazard. Mater.*, **52**, 213-221 (1997).
3. Palomo, A. and Palacios, M., "Alkali-activated cementitious materials: alternative matrices for the immobilization of hazardous wastes part II: stabilization of chromium and lead," *Cement and Concrete Res.*, **33**, 289-295 (2003).
4. Mertz, W., "Chromium as a dietary essential for man," *In Trace Elements Metabolism*, W. G. Hoekstra, J. W. Suttie, K. E. Ganther, W. Mertz, eds., University Park Press, Baltimore, 185-198 (1974).
5. Ajmal, M., Nomani, A. A. and Ahmad, A.,

- "Acute toxicity of chrome electroplating wastes to microorganisms: adsorption of chromate and chromium (VI) on a mixture of clay and sand," *Wat. Air Soil. Pollut.*, **23**, 119-127 (1984).
6. Kindness, A., Macias, A. and Glasser, F. P., "Immobilization of chromium in cement matrices," *Waste Manage.*, **14**(1), 3-11 (1994).
 7. Yukselen, M. A. and Alpaslan, B. J., "Leaching of metals from soil contaminated by mining activities," *J. Hazard. Mater.*, **B87**, 289-300 (2001).
 8. Dermatas, D. and Meng, X., "Utilization of fly ash for stabilization/solidification (S/S) of heavy metal contaminated soils," *Eng. Geol.*, **70**, 377-394 (2003).
 9. Dermatas, D. and Moon, D. H., "Chromium leaching and immobilization in treated soils," *Environ. Eng. Sci.*, **23**(1), 77-87 (2006).
 10. Dutré, V., Kestens, C. and Schaep, J., Vandecasteele, C., "Study of the remediation of a site contaminated with arsenic," *Sci. of the Total Environ.*, **220**, 185-194 (1998).
 11. Moon, D. H., Dermatas, D., and Menounou, N., "Arsenic immobilization by calcium-arsenic precipitates in lime treated soils," *Sci. of the Total Environ.*, **330**, 171-185 (2004).
 12. Dermatas, D., Moon, D. H., Menounou, N., Meng, X., and Hires, R., "An evaluation of arsenic release from monolithic solids using a modified semi-dynamic leaching test," *J. Hazard. Mater.*, **B116**, 25-38 (2004).
 13. Lee, D. J., "Leachability of Pb-doped solidified waste forms using Portland cement and calcite: II. Investigation of SEM/EDS," *Environ. Eng. Res.*, **9**(2), 66-74 (2004).
 14. Lee, D. J., "Leachability of Pb-doped solidified waste forms using Portland cement and calcite: I. Investigation of X-ray diffraction," *Environ. Eng. Res.*, **9**(3), 103-112 (2004).
 15. Lee, D. J., "Leachability of Pb-doped solidified waste forms using Portland cement and calcite: III. Insight of leaching mechanism," *Environ. Eng. Res.*, **9**(4), 175-183 (2004).
 16. Moon, D. H., "Lead leachability from quicklime treated soils in a diffusion controlled environment," *Environ. Eng. Res.*, **10**(3), 112-121 (2005).
 17. ANS, "American national standard measurements of the leachability of solidified low-level radioactive wastes by a short-term test procedure," ANSI/ANS, 16.1, American Nuclear Society, ed., La Grange Park, Illinois, (1986).
 18. USEPA, "Solid waste leaching procedure manual," SW-924, USEPA, Cincinnati, OH, (1985).
 19. USEPA, "Test methods for evaluation solid wastes-physical/chemical methods," SW-846, USEPA, Cincinnati, OH, (1984).
 20. Dutré, V. and Vandecasteele, C., "Solidification/stabilization of arsenic-containing waste: leach tests and behavior of arsenic in the leachate," *Waste Manage.*, **15**(1), 55-62 (1995).
 21. Dutré, V. and Vandecasteele, C., "An evaluation of the solidification/stabilization of industrial arsenic containing waste using extraction and semi-dynamic leach tests," *Waste Manage.*, **16**(7), 625-631 (1996).
 22. ASTM, "The test method for laboratory compaction characteristics of soil using modified effort," Annual book of ASTM standards: ASTM D1557-91, Vol. 4.08, Philadelphia, PA, 227-234 (1993).
 23. de Groot, G. J. and van der Sloot, H. A., "Determination of leaching characteristics of waste materials leading to environmental product certification," *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes*, Vol. 2, ASTM STP 1123, T. M. Gilliam, C. C. Wiles, eds., American Society for Testing Materials, Philadelphia, PA, 149-170 (1992).
 24. Handbook of Chemistry and Physics, 74th ed., CRC Press, (1993-1994).
 25. Wastewater Technology Centre, "Proposed evaluation protocol for cement-based solidified wastes," Environment Canada Report EPS 3/HA/9, Ottawa, Ontario, Canada,

- (1991).
26. Dermatas, D. and Meng, X., "Leachability study of Cr contaminated soils to assess the long-term effectiveness of remediation technologies," *Geoenvironment*, No. 46, ASCE, New York, NY, 449-462 (1995).
 27. Ricou-Hoeffler, P., Lecuyer, I., and le Cloirec, P., "Experimental design methodology applied to adsorption of metallic ions onto fly ash," *Wat. Res.*, **35**(4), 965-976 (2001).
 28. Côté, P. L., Constable, T. W., and Moreira, A., "An evaluation of cement-based waste forms using the results of approximately two years of dynamic leaching," *Nucl. Chem. Waste Manag.*, **17**, 129-139 (1987).
 29. Nathwani, J. S. and Phillips, C. R., "Leachability of Ra-226 from uranium mill tailings consolidated with naturally occurring materials and/or cement: Analysis based on mass transport equation," *Water Air Soil Pollution.*, **14**, 389-402 (1980).
 30. Ibáñez, R., Andrés, A., Trabien, J. A., and Ortiz, I., "Fly ash binders in stabilization of FGD wastes," *J. Environ. Eng.*, **124**(1), 43-50 (1998).