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Solidification/stabilization of Cr(VI) with cement
Leachability and XRD analyses

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Abstract

The leachability of Cr(VI) from solidified Cr(VI)–Portland cement mixtures cured for 28 days were investigated. Cr(VI) was solidified with Type I Portland cement at concentrations of 0.5%, 2%, and 5% (based on K_2CrO_4) by weight of the cement. The addition of Cr(VI) increased the initial and final setting times of cement. X-ray diffraction (XRD) study indicates that Cr(VI) inhibits cement hydration process by reacting with Ca^{2+} during the hydration of cement, which was also supported by increased setting times. Increasing the Cr(VI) content in the cement reduced the compressive strength of the solidified cement. The leachability of Cr(VI) during the toxicity characteristics leaching procedures (TCLP) test was dependent on the initial Cr(VI) concentration and the leaching time. The treatment efficiency of cement was independent of the initial Cr(VI) concentration. The reaction products and crystalline phases were identified using the XRD. One of the reaction products identified was $CaCrO_4$. An empirical relationship was developed to predict the leaching of Cr(VI). Based on this relationship, the treatable amount should be limited to K_2CrO_4/cement ratio of 0.2% to meet the TCLP limit of 5 mg/l. © 2000 Elsevier Science Inc. All rights reserved.

Keywords: Cement; Chromium; Waste management; Physical properties; X-ray diffraction

1. Introduction

The safe disposal of the chromium wastes generated from steel and other alloys' production, chrome plating, pigments and leather tanning industries to protect human health and environment is an issue of concern [1,2]. Chromium contamination up to 130,000 mg/kg have been reported [3,4]. Among the many forms of chromium, Cr(VI) is the most important one because of its toxicity, solubility, and mobility characteristics [2,4,5]. Most treatment methods have failed to reduce the leaching of chromium to meet the toxicity characteristics leaching procedures (TCLP) extraction limit of less than 5 mg/l because of the complexity of chromium chemistry [6,7].

Cement-based solidification/stabilization (S/S) has been effectively demonstrated as a treatment technique to isolate hazardous wastes from the environment [8]. However, wastes such as organics, salts, and heavy metals may not be amenable to this treatment [9]. Interfering effects in setting, chemical stability, and strength are often cited as evidences of cement-based S/S as not being adequate in treating some of these wastes [10,11]. X-ray diffraction (XRD) has been found to be a useful application to characterize the crystalline phases of the solidified wastes [7,11]. Information from such studies can be used successfully to obtain the immobilization mechanisms and reactions occurring in an S/S process [11,12].

At present, TCLP is used by the US EPA to evaluate whether a particular S/S process is effective in treating a given waste. Factors such as waste form, binder system, curing time and cement-to-waste ratio have been identified to affect the leachability of a waste after an S/S treatment [11,13,14,15]. The TCLP limit for chromium is 5 mg/l.

2. Experimental program

The effect of Cr(VI) on the cement matrix and its leachability was evaluated in this study. The testing

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protocol included (a) setting time, (b) compressive strength, (c) leachability of Cr(VI) using the TCLP test, and (d) identification of crystalline phases using XRD. The hexavalent chromium used was potassium chromate (K_2CrO_4), which had a solubility of 64,000 mg/l at 20°C [16]. Potassium chromate concentrations of 0.5%, 2%, and 5% (by weight of cement) were investigated in this study (1% of K_2CrO_4 used is equivalent to 2800 ppm of Cr(VI)). Chromium contaminated water was prepared by adding measured amounts of potassium chromate directly to the water and mixed well until all the potassium chromate was dissolved. A water-to-cement ratio of 0.5 (by weight) was used. Samples were cast in Teflon® moulds (38 mm in diameter and 80 mm in height). After extraction from the moulds, the samples were cured in air-tight bags in a temperature (72°F) controlled humid (>96%) room for 28 days. Triplicate samples were tested for each condition and average results are reported and analyzed.

The initial and final setting times of cementious paste with and without Cr(VI) were determined according to ASTM C191 using a Vicat needle. The unconfined compressive strengths (UCS) of solidified samples were determined according to ASTM 2166. The S/S samples were also subjected to the standard protocol of TCLP test [17] except that the leaching was continued for 96 h. The leaching solution was prepared by adding 5.7 ml of acetic acid (99.7%) and 64.3 ml of 1.0 N NaOH, and diluting with deionized water to a volume of 1 l. The pH of this solution was 4.93 ± 0.05. During the TCLP test, samples were collected and centrifuged at a speed of 10,000 rpm for 10 min. The supernatant was then analyzed for Cr(VI) and total chromium (Total Cr) according to the Standard Method 312B [18]. In determining Cr(VI), the sample was reacted with diphenylcarbizide in acid solution to produce a pink color. The absorbance of the solution was then measured at a wavelength of 540 nm by a spectrophotometer. For Total Cr measurement, the sample was oxidized to Cr(VI) by $KMnO_4$ then followed the aforementioned procedures. The detection limit was estimated to be 100 μg/l. XRD analysis was performed using a Siemen's D5000 Diffractometer with a copper tube operated at 40 kV and 30 mA. Samples were ground to fine powders and investigated for the reflection angle (2θ) in the range 10° to 50° [7]. The joint Committee on Powder Diffraction Standards (JCPDS) was used to identify various crystalline phases.

3. Test results and discussion

The effects of various Cr(VI) concentrations on the setting, degree of immobilization, and mechanical properties of cement were investigated. The test results are reported and discussed in the following sections.

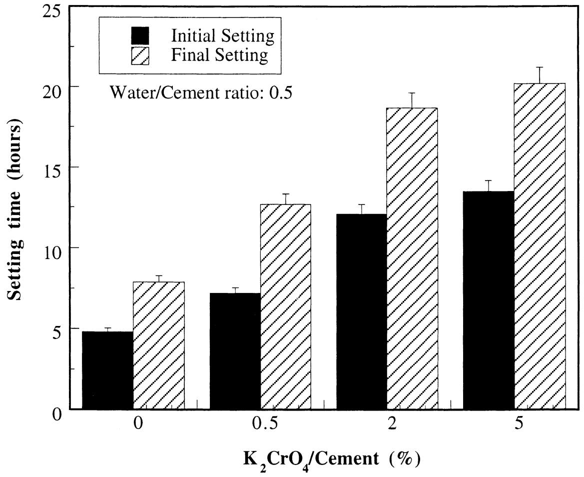

Fig. 1. Effect of Cr(VI) on the cement's setting time determined using the Vicat needle.

3.1. Setting time

The initial and final setting times of Portland cement with and without Cr(VI) were measured. Concentrations of Cr(VI) between 0% and 5% (as K_2CrO_4) were studied. The results are shown in Fig. 1. It is apparent that Cr(VI) retards the setting process of cement. The change in initial and final setting times are very much dependent on the initial Cr(VI) concentration. The control cement reached initial set in 5 h and final set in 8 h. In the presence of 0.5% K_2CrO_4, the initial and final setting times were 7 and 13 h, respectively. For the 5% K_2CrO_4 samples, the time for initial set was 14 h and the time to final set was 20 h.

3.2. Mechanical properties

Cylindrical samples cured for 28 days, with and without Cr(VI) (up to 5%) were tested for UCS according to ASTM 2166. The results of the UCS tests are shown in Fig. 2 The UCS was dependent on the amount of Cr(VI) added in the binder system. The highest strength of 41 MPa was observed for the control sample. Meanwhile, the average UCS values obtained with 0.5%, 2% and 5% K_2CrO_4 samples were 32, 26, and 23 MPa. Increasing the K_2CrO_4 content in the cement reduced the UCS. A maximum reduction of 44% in UCS value was observed from the 5% K_2CrO_4 containing sample. All the UCS were greater than the EPA compressive strength requirement for S/S treated waste of 0.3 MPa.

3.3. Leachability

The leaching of Cr(VI) was evaluated on cured (28 days) samples using the TCLP test. Although the EPA requirement is only for 18 h of leaching, the test here was continued for 96 h to evaluate the effect of leaching duration. The results showed that there was close agreement between the Cr(VI) and Total Cr analyses, confirming that

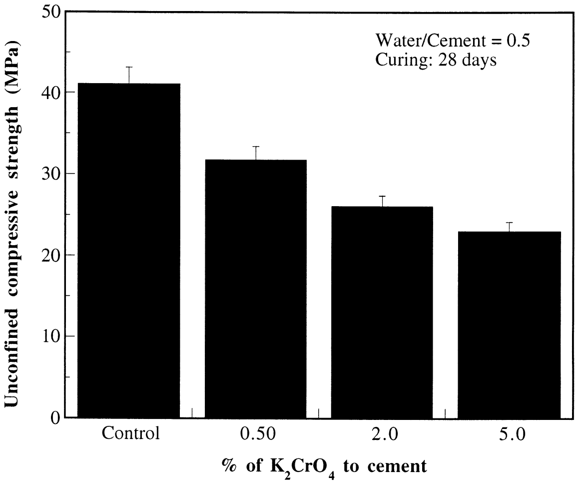

Fig. 2. Effect of Cr(VI) on the cement paste unconfined compressive strength.

most of the chromium in the leachate was in the form of Cr(VI). Thus, only the results of Cr(VI) concentration is reported in Fig. 3. The leaching of Cr(VI) occurred as a two-stage process. Initially, the loosely bonded Cr(VI) was washed out into the leaching solution during the first few hours. After that, the concentration gradient between the liquid and solid phase decreased and resulted in a small increase of Cr(VI) in the leachate with time.

After 18 h of leaching (TCLP requirement), the amounts of Cr(VI) detected from 0.5%, 2%, and 5% K_2CrO_4 samples were 38, 340, and 365 mg/l, respectively. The recoveries of Cr(VI) after 96 h of leaching from 0.5%, 2%, and 5% K_2CrO_4 samples were 43, 400, and 440 mg/l, respectively. Hence, the leaching of Cr(VI) is a function of the initial Cr(VI) concentration (as K_2CrO_4) and the leaching time. Theoretically, the maximum amount of Cr(VI) which could be recovered from 0.5%, 2%, and 5% K_2CrO_4 samples were 250, 1000, and 2500 mg/l, respectively. The treatment efficiency was in the range of 82% to 85% and was independent of the initial Cr(VI) concentration.

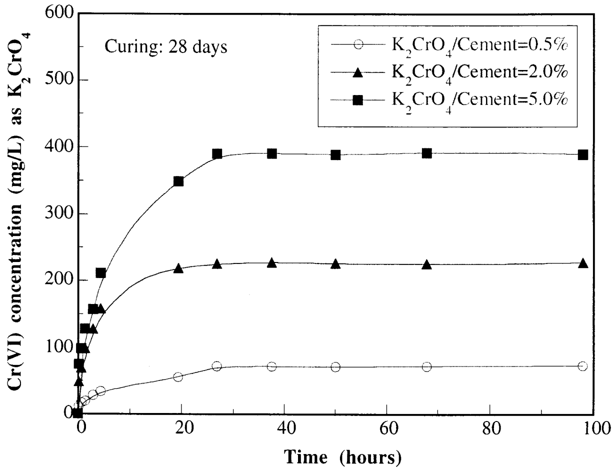

Fig. 3. Leaching of Cr(VI) from S/S samples during the TCLP test.

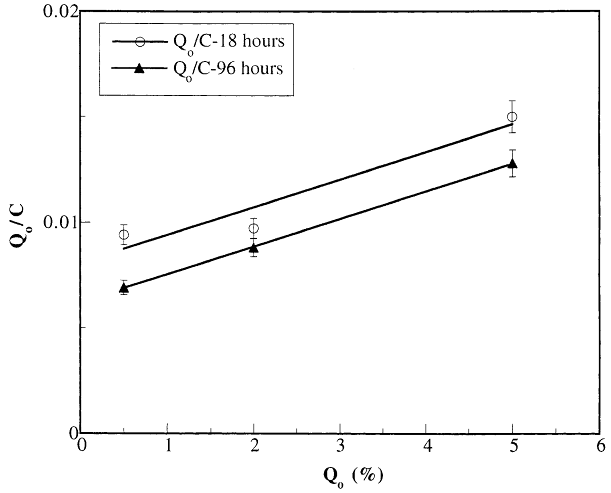

Fig. 4. Relationship between Q_0/C and Q_0 for various Cr(VI)/cement systems.

3.4. Leaching model

The leaching of Cr(VI) from solidified cement paste during the extended TCLP test depended on the amount of initial Cr(VI) concentration (Q_0) and the leaching time. A hyperbolic relationship is proposed to express the Cr(VI) concentration after 18 or 96 h of leaching:

$$C(t) = \frac{Q_0}{A(t) + B(t)Q_0} \tag{1}$$

where $C(t)$ = contaminant concentration after 18 or 96 h of leaching, mg/l, Q_0 = the initial Cr(VI) added, %, and $A(t)$, $B(t)$ = leaching parameters, mg/l. Eq. (1) can be rearranged as Eq. (2):

$$\frac{Q_0}{C(t)} = A(t) + B(t) \times Q_0. \tag{2}$$

The relationship between Q_0/C and Q_0 was linear and the correlation coefficients (R) were all greater than 0.96 (Fig. 4). The parameters 'A' and 'B' are summarized in Table 1. The prediction made using Eq. (1) was in good agreement with the experimental data (Fig. 5). Thus, Eq. (1) could be used to predict the leaching of Cr(VI) from S/S treated samples. In order to treat Cr(VI) successfully to meet the

Table 1
Summary of parameters 'A' and 'B' for solidified Cr(VI)/cement systems

S/S system	Cr(VI)/cement	
Leaching time (h)	18	96
$A(t)$	0.006	0.008
$B(t)$	0.001	0.001
Coefficient of correlation	0.96	0.99

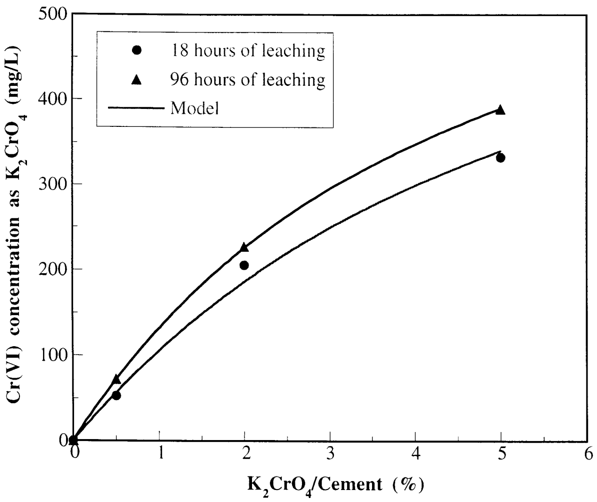

Fig. 5. Model prediction of Cr(VI) leaching after 18 and 96 h.

TCLP limit of 5 mg/l (18 h of leaching) by cement-based S/S, K_2CrO_4/cement ratio should be less than 0.2% based on the calculation using Eq. (1) (Fig. 5).

3.5. XRD studies

XRD was used to study changes in the crystalline phases of the cement with and without Cr(VI) after 28 days of curing. Type I Portland cement, before and after hydration, was used as a control sample. The most prominent peaks in the unhydrated cement (Fig. 6a) were those of tricalcium silicate (C_3S) at 2θ of 29.5°, 32.6°, 34.5° and dicalcium silicate (C_2S) at 2θ of 32.3°. Calcium aluminum oxide ($CaO \cdot Al_2O_3$), an impurity in cement, was identified at 2θ of 30.2°. For hydrated cement (Fig. 6b), the peaks of C_3S (32.6°) and C_2S decreased. Calcium hydroxide, $Ca(OH)_2$, one of the cement hydration products, was identified at 2θ of 18° and 47.3°.

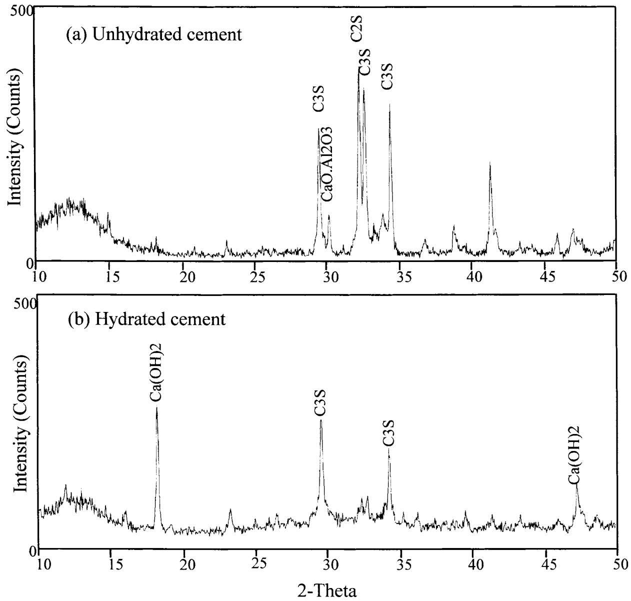

Fig. 6. XRD pattern of Type I Portland cement before and after hydration.

The XRD patterns for cement with different concentrations of Cr(VI) are shown in Fig. 7. The peak of the cement hydration product $Ca(OH)_2$ decreased with the increase in the amount of Cr(VI) in the cement. Calcium chromate, $CaCrO_4$, was identified at 2θ of 32.3° and 35.2° for solidified Cr(VI)/cement samples. This formation product was also observed by Lin et al. [15]. It should be noted that there was untreated K_2CrO_4 in all the K_2CrO_4/cement systems investigated here. The most prominent species of Cr(VI) in the S/S system was CrO_4^{2-} because the pH of cement was greater than 12 in the cement hydration condition [4]. The possible reaction between Cr(VI) and cement can be reported as Eq. (3):

$$Ca^{2+} + CrO_4^{-2} \xrightarrow{\text{high}} {}^{\text{pH}} CaCrO_4. \qquad (3)$$

The solubility product (k_{sp}) for $CaCrO_4$ is 5.1×10^{-6} [16]. The immobilization of Cr(VI) by cement-based S/S was achieved due to the formation of this low solubility complex. The intensity of $Ca(OH)_2$ decreased in the Cr(VI) containing sample because part of Ca^{2+} was reacted with

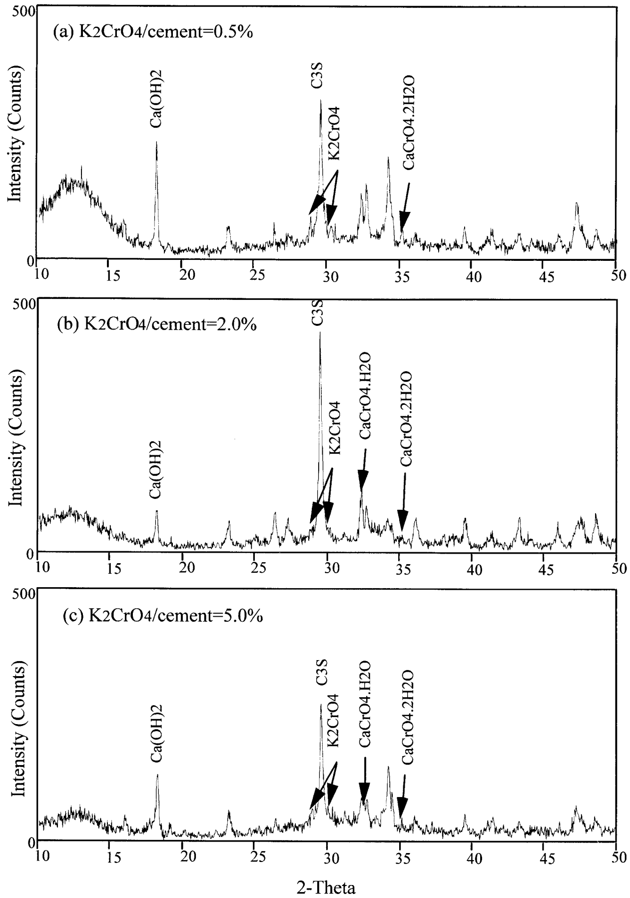

Fig. 7. XRD pattern of K_2CrO_4/cement system.

CrO_4^{2-}. This reaction between Ca^{2+} and Cr(VI) retarded the setting of cement. Besides the untreated K_2CrO_4 leached out during the TCLP test, $CaCrO_4$ dissociated and reacted with the hydrogen ion according to the following reaction:

$$CrO_4^{2-} + H^+ \rightarrow HCrO_4^- . \qquad (4)$$

This reaction [Eq. (4)] explained the recovery of Cr(VI) during the TCLP test.

4. Conclusions

The S/S of Cr(VI) by cement up to a concentration of 5% (based on K_2CrO_4) was investigated. The following conclusions can be advanced based on this experimental study.

(1) Cr(VI) retarded the initial and final setting times of cement by interfering with the normal hydration process. The presence of 5% K_2CrO_4 (equivalent to 14,000 ppm of Cr(VI)) increased the final setting time of cement by 14 h. Cr(VI) also reduced the UCS of cement.

(2) The XRD analyses showed that there was untreated Cr(VI) in the solidified cement system as evidenced by the presence of K_2CrO_4 peaks at the concentration investigated. The treatment efficiency was over 80% and was independent of the initial Cr(VI) concentration. To meet the TCLP limit of 5 mg/l, the K_2CrO_4/cement ratio should be less than 0.2% (560 ppm of Cr(VI)).

(3) The reaction products and crystalline phases were identified for Cr(VI)/cement systems using the XRD. The immobilization of Cr(VI) by cement-based S/S was achieved due to the formation of a complex calcium chromate ($CaCrO_4$) with low solubility. The cement hydration process was affected in the presence of Cr(VI) because part of the Ca^{2+} in the cement reacted with CrO_4^{2-}.

Acknowledgments

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References

[1] EPA, Natural Attenuation of Hexavalent Chromium in Groundwater and Soils, EPA, Washington, DC, 1994.
[2] B.R. James, The challenge of remediating chromium-contaminated soil, Environ Sci Technol 30 (1996) 248A–251A.
[3] B.A. Bolto, M. Kotowski, L. Pawlowski, Recovery of chromium from plating wastes, Proceedings of Hazardous and Industrial Waste Management and Testing, 1984, pp. 278–288.
[4] S.A. Katz, H. Salem, The Biological and Environmental Chemistry of Chromium, VCH Publications, New York, 1994.
[5] R.J.J. Bartlett, Chromium cycling in soils and water: Links, gaps, and methods, Environ Health Prospect 92 (1991) 17–24.
[6] J.H. Jacobs, Treatment and stabilization of a hexavalent chromium containing waste material, J Environ Prog 11 (1992) 123–126.
[7] C. Vipulanandan, S. Wang, Remediation of hexavalent chromium contaminated soil, Proceedings of in-situ Remediation of the Geoenvironment, ASCE, New York, 1997, pp. 363–373.
[8] EPA, The Superfund Innovative Technology Evaluation Program: Technology Profiles, 4th edn. EPA, Washington, DC, 1991.
[9] EPA, Stabilization/Solidification of CERCLA and RCRA Wastes, EPA, Washington, DC, 1989.
[10] D. Chalasani, F.K. Cartledge, H.C. Eaton, M.E. Tillebaum, M.B. Walsh, The effect of ethylene glycol on a cement-based solidification process, Hazard Wastes Hazard Mater 3 (1986) 167–173.
[11] C. Vipulanandan, S. Krishnan, Leachability and biodegradation of high concentrations of phenol and *o*-chlorophenol, Hazard Wastes Hazard Mater 10 (1993) 27–47.
[12] A. Roy, H.C. Eaton, F.K. Catledge, M.E. Tillebaum, Solidification/stabilization of a heavy metal sludge by a Portland cement/fly ash binding mixture, Hazard Wastes Hazard Mater 8 (1991) 33–41.
[13] P.L. Bishop, Emerging Technologies in Hazardous Wastes Management II, ACS, Washington, DC, 1991, pp. 302–315.
[14] S. Wang, C. Vipulanandan, Leachability of lead from solidified cement–fly ash binders, Cem Concr Res 26 (1996) 895–905.
[15] C. Lin, J. Chen, C. Lin, An NMR and XRD study of solidification/stabilization of chromium with Portland cement and β-C_2S, J Hazard Mater 48 (1996) 137–147.
[16] CRC, CRC Handbook of Chemistry and Physics, CRC Press, Cleveland, 1996.
[17] CFR, Code of Federal Regulations 40, Part 268, Appendix I, Toxicity Characteristic Leaching Procedure (TCLP), CFR, Washington, DC, 1997.
[18] AWWA, Testing Method for Water and Wastewater, AWWA, New York, 1997.