



## Microbial stability evaluation of cement-based waste forms at different waste to cement ratio

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### Abstract

An evaluation of the effect of differences in chromium nitrate to cement ratio on the microbial stability of a chromium nitrate/cement waste form, as reflected in the leaching of chromium, calcium, magnesium and aluminum; was carried out in this study. An increase in the proportion of chromium in the waste form from 4.8 to 8.7% had no noticeable effect on microbial stability, with the total chromium leached essentially unchanged. Further increases in the proportion of chromium in the waste form from 8.7 to 10.7%, and from 10.7 to 15.9% resulted in a substantial decrease in microbial stability, with 3-fold and 1.3-fold increase in the total chromium leached, respectively, observed. For calcium, increases in the chromium proportion were accompanied with increases in the total calcium leached even though the increases were not in direct proportion to the increases in chromium proportion. For magnesium and aluminum, increases in the proportion of chromium within the range 4.8–10.7% were accompanied with increases in the total respective metals leached, with minor variation for each metal. On the whole, the maximum percentage chromium leached from the different waste forms was substantially lower than those of the other metals.

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### 1. Introduction

Stabilization and solidification technologies involving cementitious materials have been used for many decades, and remain viable options for the treatment and disposal of radioactive and chemically hazardous materials [1]. Major attractions of solidification/stabilization

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(S/S) that led to its being described as a best demonstrated available technology (BDAT) include low materials and operating costs, ease of use, and capacity to contain waste and prevent its migration in the natural environment [2–4]. The most commonly used binder for waste stabilization/solidification is the ordinary Portland cement (OPC) [5].

With cement S/S processes, water in the waste reacts chemically with OPC to form hydrated silicate and aluminate compounds, while the solids act as an aggregate to form a “concrete” [6]. Salts of several heavy metals including chromium have been implicated in the inhibition of the hydration process with resultant retardation in the setting and curing of the waste/cement mix, and also a reduction in its physical strength [1,7]. Thus, an optimum waste to cement ratio is required in order to produce a waste form with high physical stability [6]. In this study, an evaluation of the effect of waste to cement ratio on microbial stability was carried out using a simulated chromium waste (chromium nitrate) as an example. Microbial stability evaluation is now accepted as a major component of stability criteria for materials which suitability for use for waste containment is being considered. This is a direct consequence of the isolation of microorganisms from low-level radioactive waste (LLW) environments, and other locations where their growth was previously thought impossible [8,9]. Early evaluations of material suitability for waste containment only relied on physical and chemical stability. The selection of chromium for this simulation study is primarily because it is a very toxic metal of significant health importance. In the hexavalent form, chromium has been shown to be carcinogenic [10,11]. More so, waste immobilization in solid matrix has previously been put forward as a possible strategy to deal with the problem of chromium wastes accumulation and associated health hazards [12,13]. Given that no study currently exists that links the behaviors of metals in cement matrices with their oxidation states, it was decided to use the less toxic trivalent chromium specie in this simulation studies. In addition to determining the best working combination of chromium nitrate to cement, it is the aim of this study to investigate the effect of chromium presence and levels on the leaching profiles of calcium, magnesium, aluminum; which are major components of cement. This is especially important since the overall efficiency of the waste fixation process is directly related to how effectively the components of the binder are held in place.

## 2. Materials and methods

### 2.1. Microorganism

*Thiobacillus thiooxidans* (*T. thiooxidans*) was the microorganism used in this study, it was obtained from Idaho National Engineering and Environmental Laboratory (INEEL). The composition of the *T. thiooxidans* growth media is as follows (g/l):  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  (0.4),  $(\text{NH}_4)_2\text{SO}_4$  (0.5),  $\text{CaCl}_2$  (0.1),  $\text{FeSO}_4$  (0.01), potassium tetrathionate (3.0), potassium phosphate mono-basic (3.0). Appropriate amounts of all the media components, except the ferrous sulfate and potassium phosphate monobasic, were suspended in distilled water contained in a 10-l bottle and autoclaved at 121 °C for 25 min. To avoid precipitation, the potassium phosphate monobasic was prepared, autoclaved separately, and mixed with the rest of the components prior to use. The ferrous sulfate was added to the other components

after autoclaving using sterile disposable membrane filters to avoid oxidation to the ferric state during autoclaving.

## 2.2. Waste formulation

The waste formulations used in this study consist essentially of a locally purchased Portland cement type 1 (Tuskegee cement) and chromium(III) nitrate nonahydrate crystals (analytical grade, Fisher Scientific) in different proportions. Four different combinations of chromium nitrate:cement was used. The combinations and their composition are as follows (wt.%): 4.8% chromium nitrate (1 part chromium nitrate, 20 parts cement, 10 parts water); 8.7% chromium nitrate (1 part chromium nitrate, 10.5 parts cement, 6.25 parts water); 10.7% chromium nitrate (1 part chromium nitrate, 8.3 part cements, 5.83 parts water); and 15.9% chromium nitrate (1 part chromium nitrate, 5.3 parts cement, 4.5 parts water). To formulate the various combinations, appropriate amounts of the chromium nitrate, cement, and water were mixed and allowed to set in 5-ml plastic vials serving as moulds. All the waste forms were cylindrically shaped after setting and had the following dimensions: 2.0 cm height  $\times$  1.5 cm diameter. Waste forms used as both experimental and control samples are the same in terms of composition, they only differ in the type of solution to which they were exposed during the evaluation procedures. Experimental samples were exposed to *T. thiooxidans* during the first stage of evaluation while control samples were exposed to ordinary sterile medium for the growth of *T. thiooxidans* in which the pH was pre-adjusted to reflect the pH of the *T. thiooxidans* culture.

## 2.3. Waste form stability evaluation

Evaluations of waste form stability to microbially induced degradation (MID) were carried out using the refined biofilm formation method of Idachaba et al. [14]. The refined biofilm formation approach is a two-stage process. The first stage involves the pumping of sterile medium for *T. thiooxidans* (pH pre-adjusted to 1.9 using sulfuric acid) from a reservoir over the control samples contained in soxhlet tubes for a 24-h period. At the same time fermenter broth of *T. thiooxidans* (pH 1.9) was also pumped from a continuously operated bioreactor over experimental waste forms contained in soxhlet tubes. This stage of the process, which is meant for colonization of the experimental waste forms by *T. thiooxidans*, ends with the shutting off of supply of *T. thiooxidans* to the experimental waste forms, and the supply of sterile medium of pH 1.9 to the control waste forms. The second stage of the refined biofilm formation process begins and continues to termination, with the supply of a fresh normal medium for *T. thiooxidans* (pH about 4.00) to both control and experimental waste forms. The pumps in both stages 1 and 2 were set to deliver *T. thiooxidans* broth and sterile medium to the soxhlet tubes at a rate of about 100 ml per day. The approximate time for filling and draining of the soxhlet tubes was about 7 h. Effluents were collected in vessels and removed periodically for analysis. Formation of biofilm was confirmed from changes in pH and sulfate concentration. The pH value of 1.9 used in the first stage for both the control and experimental inflows reflect the approximate pH of a fully growing *T. thiooxidans* culture while the pH of 4.0 for the medium in the second stage is the normal pH of the growth medium for *T. thiooxidans*. The 24-h duration of the first stage is

the recommended duration by Idachaba et al. [14] whose method is being followed in this study.

#### 2.4. Analytical

Analyses of the metals in the media, fermenter broth, and the effluents were carried out using inductively coupled plasma (ICP) Optima 3300 DV (Perkin-Elmer) spectrophotometer. The sulfate concentration of the media and effluents was estimated by the Turbidimetric method based on the standard methods for the examination of water and wastewater [15]. This method involved adding a quantity of barium chloride crystals to a buffered amount of the sample and measuring the absorbance of the barium sulfate formed at 420 nm using the Hach 2010 DR Spectrophotometer. The sulfate concentration was calculated using a standard calibration curve. The pH of the media, fermenter broth and effluents was determined using a Corning pH meter 345.

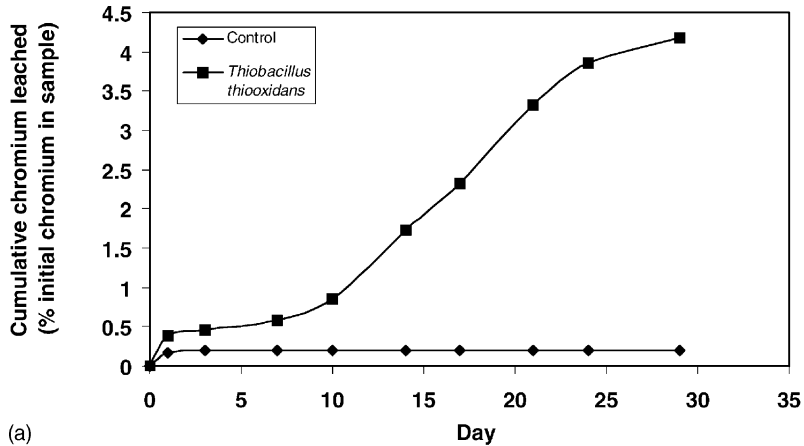
### 3. Results

A typical profile for the leaching of chromium from a cement-based waste form containing chromium, on exposure to *T. thiooxidans*, is presented in Fig. 1a. The figure is based on evaluations using the 4.8% chromium nitrate waste form, and it indicates that within the first 24 h about 0.4% of total chromium were leached from the experimental sample as against 0.2% from the control. While the total chromium leached from the experimental sample after 30 days of evaluation increased to 4.2%, the total chromium leached from the control was relatively constant at 0.2%.

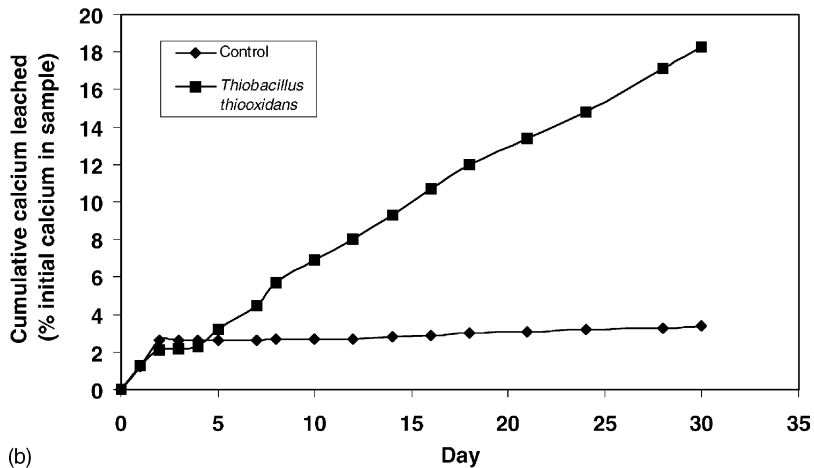
A typical profile for the leaching of metals from a cement form (containing no added chromium nitrate) is presented in Fig. 1b, and is based on the leaching of calcium. The figure shows that the calcium leached from both control and experimental samples within the first 24 h of evaluation were similar. About 1.2% of total calcium was leached from the control sample within this period while about 1.3% of total calcium was leached from the experimental sample. However, the total calcium leached from the experimental sample (about 19%) was significantly higher than the total calcium leached from the control (about 3.4%) within 30 days of evaluation.

The results of evaluation of the effect of variation in chromium nitrate to cement ratio on the leaching profiles of chromium are presented in Fig. 2. The results show that increase in the proportion of chromium in the waste form from 4.8 to 8.7% had negligible effect on the leaching profile of chromium, with similar total chromium (about 4%) leached from both waste forms within 30 days of evaluation. However, further increase in the proportion of chromium from 8.7 to 10.7% resulted in a substantial increase in the total chromium leached from 4 to 17%. The highest total chromium leached (24%) was obtained at the highest chromium proportion in waste form (15.9%).

The relationship between the proportion of chromium in the waste forms and the leaching of calcium was slightly different from what was obtained for chromium as can be seen from Fig. 3. For calcium, increases in the chromium proportion were accompanied with increases in the total amount of calcium leached even though the increases in leaching were not in



(a)



(b)

Fig. 1. Typical profiles for the leaching of metals from waste containing and non-waste containing waste forms on exposure to *Thiobacillus thiooxidans*. (a) The profiles of chromium from a chromium nitrate to cement (1:20) waste form. (b) The profiles of calcium from a non-waste containing (100%) cement form.

direct proportion to the increases in chromium proportion. While a minor increase in the total calcium leached was observed when the chromium proportion was increased from 4.8 to 8.7%, a substantial increase was observed when the chromium proportion was increased from 8.7 to 10.7%. The total percentage calcium leached from the different waste forms is as follows: 4.8% chromium nitrate (22%), 8.7% chromium nitrate (30%), 10.7% chromium nitrate (54%), and 15.9% chromium nitrate (57%).

Similar leaching profiles were obtained for magnesium (Fig. 4) and aluminum (Fig. 5). In both cases, increases in the total percentage of respective metals leached accompanied increases in the proportion of chromium within the range 4.8 and 10.7% chromium nitrate. Further increase in the proportion of chromium nitrate from 10.7 to 15.9% resulted in

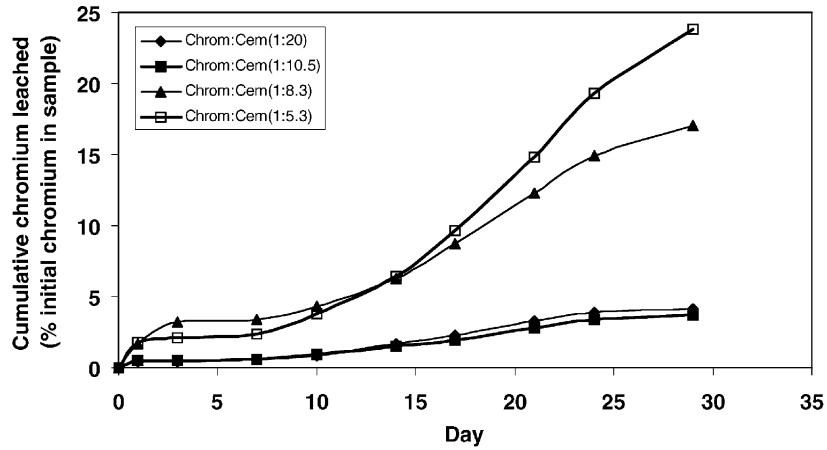


Fig. 2. The effects of chromium nitrate to cement ratio on the leaching profiles of chromium.

substantial decrease in the total percentage of the respective metals leached. Major differences in the general trend for specific metals were, however, observed. While proportionate increases in the total percentage of magnesium leached occurred with increases in the proportion of chromium nitrate within the range 4.8 to 10.7%, increases in the total percentage of aluminum leached was not proportional to increases in the proportion of chromium nitrate. For instance, a 1.8-fold increase in the proportion of chromium from 4.8 to 8.7% resulted in a 1.8-fold increase in the total percentage of magnesium leached (i.e. from 17 to 31%). Only a marginal increase in the total percentage of aluminum leached (i.e. from 11 to 14%) was observed. Similarly, a 1.3-fold increase in the proportion of chromium from 8.7 to 10.7% resulted in 1.4-fold increase in the total percentage of magnesium leached (i.e. from 31 to 46%), but 2.9-fold increase in the total aluminum leached.

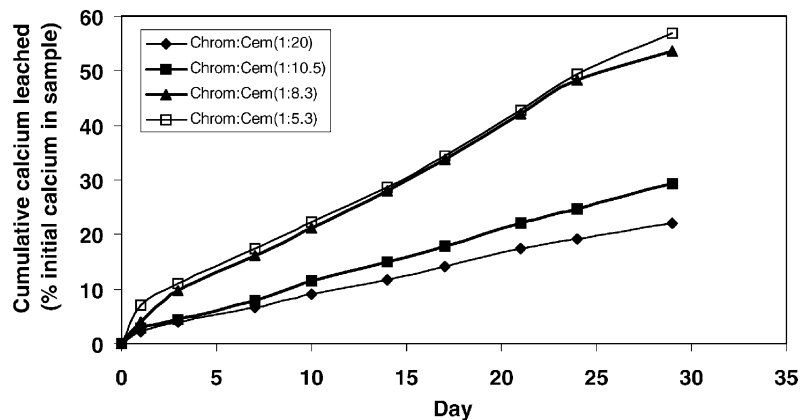


Fig. 3. The effects of chromium nitrate to cement ratio on the leaching profiles of calcium.

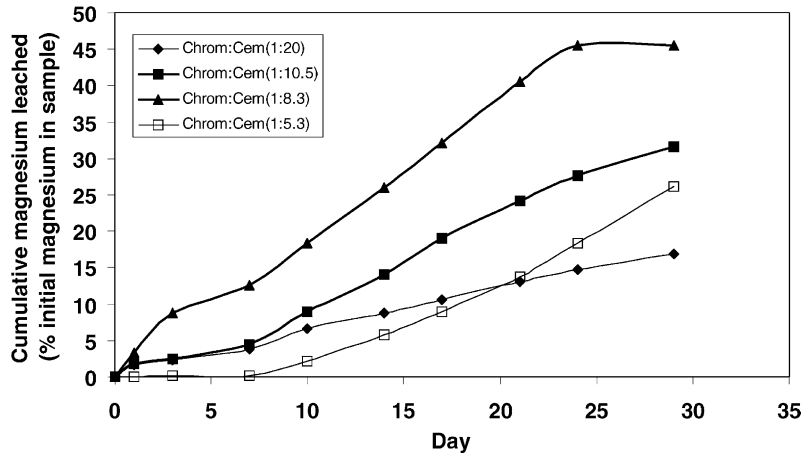


Fig. 4. The effects of chromium nitrate to cement ratio on the leaching profiles of magnesium.

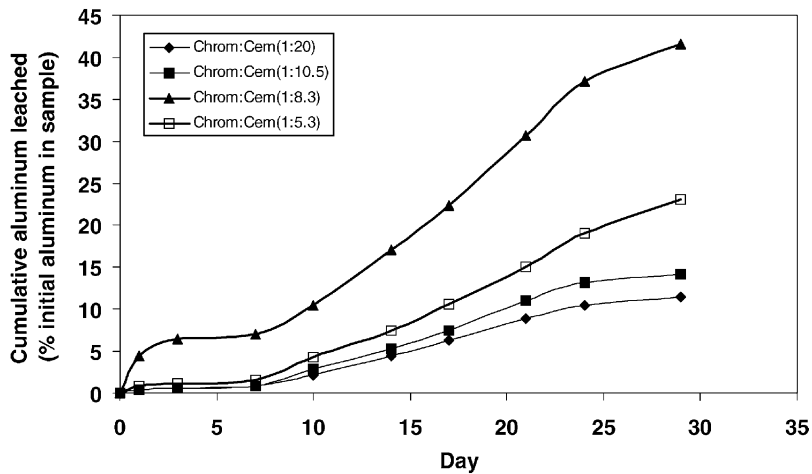


Fig. 5. The effects of chromium nitrate to cement ratio on the leaching profiles of aluminum.

On the whole, the total amount of chromium leached from the different waste forms was substantially lower in comparison to those of calcium, magnesium, and aluminum (metals contained in cement). For instance, the total chromium leached from the 10.7% chromium nitrate waste form was only 17% as compared to 54% for calcium, 46% for magnesium and 41% for aluminum.

#### 4. Discussion

The similarity in total chromium leached from the 4.8 and 8.7% chromium nitrate waste forms indicates that within this range, the addition of chromium will not result in any

substantial reduction in waste form stability, especially as it relates to chromium. The similarity also suggests that when the integrity of cement matrix is not compromised the amount of chromium leached is independent of its level in the waste form, especially as chromium is incorporated mainly within the calcium silicate matrix [16]. A similar observation has been reported by Cioffi et al. [17] in their work with cadmium, nickel and chromium in which they concluded that metal release is not limited by metal solubility in the liquid phase, but by the intrinsic stabilizing properties of the matrix. The 3-fold increase in total chromium leached with just a 1.3-fold increase in the proportion of chromium nitrate (i.e. from 8.7 to 10.7%) suggests that the level of chromium nitrate in the 8.7% chromium nitrate waste form is close to the upper limit for optimum stability.

The observed increase in the total percentage calcium leached with increase in the chromium proportion gives a strong indication that increasing levels of chromium nitrate resulted in reduced stability of the waste form. Calcium is the largest component element in cement, a large proportion of it is deposited on the outside of the waste forms as calcium hydroxide after setting, and the rest in the calcium silicate hydrate matrix [6]. With calcium found both within and outside silicate matrix of the waste form, its leaching profile could give a general picture of the overall structural stability of the waste form. The fact that a 2-fold increase in the proportion of chromium resulted in only a marginal increase in the total percentage calcium leached (from 22 to 29%) strengthens the view that addition of chromium nitrate within the range 4.8–8.7% has no negative consequence on waste form stability. The results presented in Fig. 1b show that in the presence of *T. thiooxidans* the total percentage calcium leached from a cement waste form containing no added chromium nitrate waste is about 18%. Thus, the increase in the total calcium leached from 19% to just about 29% after addition of 8.7% chromium nitrate and reduction of cement proportion by 8.7%, can be said to be minor, indicating absence of a substantial loss in stability. The substantial increase in the total percentage calcium leached (from 29 to 54%) with only a 1.3-fold increase in the proportion of chromium nitrate appears to confirm that further increase in the proportion of chromium beyond the level 8.7% will result in a substantial reduction in waste form stability.

The proportional increase in the total magnesium leached with increase in the proportion of chromium nitrate within the range 4.8% and 10.7% is noteworthy. It is not clear if this trend is due to a chemical displacement of magnesium by chromium. Several workers [6,16–18] have reported both physical and chemical chromium fixations into the calcium silicate hydrate matrix. Cioffi et al. [17] for instance, reported a case of chemical stabilization for chromium in which chromium supposedly substituted aluminum. On the other hand Ivey et al. [18] suggested a chemical substitution of silicon with chromium in calcium silicate hydrate matrix. No definite conclusion can be arrived from our study on the status of aluminum in the metal substituted chemical fixation of chromium. The 3-fold increase in the leaching of aluminum with only a 1.3-fold increase in the proportion of chromium nitrate in the waste form (i.e. from 8.7 to 10.7%) points to a likely aluminum involvement in the chemical fixation of chromium. However, the marginal increase in aluminum leached when the proportion of chromium nitrate in waste form was nearly doubled (4.8 to 8.7%) appears to rule out aluminum as the substituted metal, especially when metals like magnesium had their total leached value proportionately doubled.



The observed decrease in the total percentage of magnesium and aluminum leached when the proportion of chromium nitrate was increased from 10.7 to 15.9% contrast sharply with the trends obtained for chromium and calcium. The high chromium level in the 15.9% chromium nitrate waste form was expected to result in the highest loss of stability accompanied by the leaching of the highest proportion of all the metals. The reason for the unusual trends for magnesium and aluminum is not very clear. Further investigations are required to determine if the trends have anything to do with the complex waste cement chemistry.

## 5. Conclusions

An evaluation of the leaching profiles of chromium, calcium, magnesium, and aluminum was carried out at various ratios of chromium nitrate:cement. The near doubling of chromium's proportion in the waste form from 4.8 to 8.7% resulted in only a minor change in the leaching profiles of all the metals, except magnesium in which a proportionate doubling in amounts leached was observed. Within the chromium nitrate: range 4.8 and 8.7%, addition of chromium to the waste form does not impact negatively on microbial stability. Further increase in the proportion of chromium outside this range could result in substantial decrease in the ability of the waste form to withstand microbial degradation. On the whole, the total chromium leached from the different waste forms was substantially lower in comparison to those of calcium, magnesium and aluminum.

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