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Evaluation of the degree of Cr ions immobilization by different binders

Josée Duchesne*, Guylaine Laforest

Département de Géologie et de Génie Géologique, Université Laval, Quebec, QC, Canada G1K 7P4

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Abstract

Disposal of industrial solid wastes can cause environmental risks due to the mobility of toxic elements. Stabilization/solidification (s/s) is an effective tool in the treatment of various wastes; however, there is a lack of chemical fixation on the concentrations of Cr. Thus, Cr, in particular Cr^{6+}, remains free in the leachate. Some phases of the blast furnace slag seem to be able to exert a solubility control on chromium. This study evaluates the effect of various binders on the fixation of Cr ions. Static leaching tests were conducted at two different water–solid ratios as a means to distinguish elements that have solubility controls. The results show that Cr content decreases very quickly to obtain values near 0.03 ppm soon after the contact between the contaminated solution and the different binders. The sample containing only the slag was the most effective. Cr was evenly distributed in the C–S–H as detected by scanning electron microscope (SEM).

Keywords: Waste management; Chromium; Granulated blast furnace slag; Cement; Heavy metals

1. Introduction

Disposal of industrial solid wastes in a hydrologic environment can cause environmental risks due to the mobility of toxic trace elements. As new toxicology information is developed and more sensitive analytical procedures become available, the allowable leachate concentrations for many elements have fallen to levels that were barely measurable a few years ago. With the placement of more stringent limits by many countries on the trace element content and leachability of materials used as lakefill, landfill, and construction material, ever-increasing volumes of solid wastes may be relegated to monitored disposal sites. It is increasingly important to find simple and inexpensive treatments to remove undesirable elements from industrial solid wastes.

Stabilization/solidification (s/s) is a very effective tool in the treatment of various wastes [1]. Recent researches showed that there is lack of chemical fixation on the concentrations of Cr in cement-based s/s technology [2–6]. Thus, Cr, in particular Cr^{6+}, remains free in the leachate. According to Duchesne [2], and Allan and KuKacka [7], some phases of the blast furnace slag seem to be able to exert a solubility control on chromium. This is particularly interesting considering that blast furnace slag is itself a by-product of the iron industry.

According to several researchers [3,5,8], the addition of blast furnace slag can fix Cr but also Cr^{6+}. Kindness et al. [5] noticed that in the presence of blast furnace slag, Cr^{6+} is reduced to Cr^{3+} that can precipitate under the stable and insoluble form $Cr(OH)_{3(s)}$. The Cr^{3+} can also substitute for Al^{3+} in most of the calcium aluminate hydrates formed by the hydration of slag. The blast furnace slag has a reducing potential that would create an environment where the Eh values will be weaker than in a system composed mainly of Portland cement [5,9]. There are also economical and environmental advantages to use blast furnace slag in replacement of Portland cement. In fact, the utilization of slag permits energy savings considering that the production of Portland cement needs between 2900 and 6000 MJ by metric ton, while the production of ground granulated blast furnace slag (GGBFS) requires only 25% to 33% of this amount.

The purpose of this study is to evaluate the effect of various binders on the concentration of Cr in leachates. Reactions were conducted at two different water–solid ratios (3:1 and 6:1) as a means to distinguish elements in the leachates that have solubility controls versus those that do not. GGBFS, a by-product of iron manufacture, was chosen to stabilize undesirable elements. The performance

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* Corresponding author. Tel.: +1-418-656-2177; fax: +1-418-656-7339.

E-mail address: josee.duchesne@ggl.ulaval.ca (J. Duchesne).

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of blast furnace slag to decrease undesirable elements is compared to other cementitious materials: ordinary Portland cement (OPC) and a ternary blend.

2. Materials and methods

2.1. Materials

2.1.1. GGBFS

GGBFS is a waste product in the manufacture of iron composed mainly of calcium silicate and aluminosilicate. If allowed to cool slowly, it crystallizes to give a material having no cementing properties. If cooled rapidly, it forms a glass, which is a latent hydraulic cement. The crystalline part of slag is mainly distributed between the solid solution of the melilite family [from akermanite ($Ca_2MgSi_2O_7$) to gehlenite ($Ca_2Al_2SiO_7$) composition] and merwinite [$Ca_3Mg(SiO_4)_2$] minerals. The chemical composition of the blast furnace slag shows little variation in a plant and is homogenous from particle to particle [10]. The North American blast furnace slags are composed mainly of CaO (38%), SiO_2 (36%), MgO (12%), and Al_2O_3 (11%). Fe_2O_3, SO_3, MnO, and K_2O remain in the major constituents but at small proportions (1%) [7,10]. The content in MgO can vary from different areas. In fact, in North America, the typical MgO content is approximately 12%, while the average concentration in European countries is only 6% [11]. The blast furnace slag studied here comes from Algoma Steel (Sault Ste-Marie, Canada). This slag, cooled quickly, is largely under a glassy form with a weak proportion constituted of a melilite solid solution that is formed, more precisely, of akermanite ($Ca_2MgSi_2O_7$) and gehlenite ($Ca_2Al_2SiO_7$). The chemical composition of this blast furnace slag is presented in Table 1. The surface area of most GGBFS varies from 340 to 550 m^2/kg [10]. This variation is mainly due to the different methods of crushing [10]. The density is less variable with a value close to 2.9. The density of the slag studied is 2.915 (ASTM C188-78).

2.1.2. OPC and ternary blend

Two types of cements were used in this study. The first one is an ordinary type I cement. The second cement is a ternary blend composed mainly of clinker, GGBFS, and silica fume. The chemical compositions of these cements are given in Table 1.

Table 1
Chemical composition of materials

Oxides (% mass)	GGBFS	Type I cement	Ternary cement
CaO	37.31	62.49	56.27
SiO_2	36.77	19.75	25.9
MgO	13.91	2.62	3.83
Al_2O_3	7.77	4.41	5.13
MnO	1.02	0.05	0.23
Fe_2O_3	0.85	2.92	2.61
K_2O	0.43	0.89	0.76
TiO_2	0.36	0.17	0.37
Na_2O	0.31	0.28	0.33

2.2. Methods

2.2.1. Static leaching test

A series of batch leaching experiments was performed by reacting samples of cementitious material at 3:1 and 6:1 water—solid ratios in 60-ml high-density polyethylene containers. The containers were mounted horizontally on a Plexiglass carousel that was suspended in a temperature bath maintained to within 0.5 °C at 25 °C. The carousel was rotated between 10 and 20 rpm for 90 days.

The cementitious materials tested were the GGBFS (sample named “L”), the Ternary blend (sample “CT”), and mixtures of OPC with GGBFS at a ratio by mass of 50:50 (sample “L50”) and 25 :75 (sample “L75”). The cementitious materials were put in contact with synthetic solutions containing 20 or 40 ppm Cr. A solution was also prepared with both 20 ppm Cr and 20 ppm Mo.

A sufficient number of replicate samples for each water–solid mix were reacted to provide all the solution samples required for each sampling period for chemical analyses. Solution samples were obtained at time intervals and filtered through 0.22-μm membrane filters. Samples were acidified with 1.0 ml of 1:1 HCl for cation analyses (Cr and Mo) on a Perkin Elmer Aanalyst 100 Atomic Absorption Spectrophotometer (AAS). All solutions were kept at 4 °C until analysis.

2.2.2. Scanning electron microscopic (SEM) analyses

The different binders were put in contact with a 3000-ppm Cr solution to identify Cr-bearing phases. Powder samples of the reacted solids in contact with the 3000-ppm Cr solution were dried at low temperature, mounted using double-sided conductive adhesive tapes and observed under a JEOL JSM-840A SEM equipped with an energy dispersive X-ray analysis (EDXA) system.

3. Results and discussion

3.1. Static leaching test results

Fig. 1 presents the effect of various binders on the Cr concentrations of the leachates. First, one can note the very drastic fall of the Cr concentrations, which were 20 ppm at the beginning. The results show that the Cr content decreases very quickly to obtain values near 0.03 ppm after only 7 days of contact between the contaminated solution and the solids. Later on, Cr concentrations fall below the detection limits. The sample containing only GGBFS is the most effective. It suppresses Cr content below the detection limits after 56 days of reaction. The quantity of GGBFS in the mixtures has an effect on the removal of chromium ions from the solution.

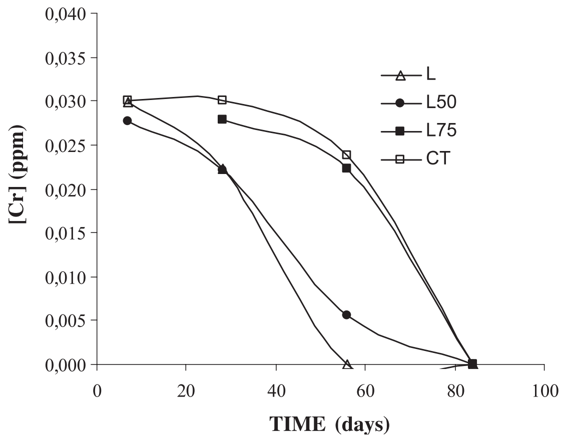

Fig. 1. Effect of the binder on the Cr concentrations in the leachates (water–solid ratio=3:1, solution Cr=20 ppm) L=100% GGBFS; L50=50% GGBFS+50% OPC; L75=75% GGBFS+25% OPC; CT=100% Ternary blend.

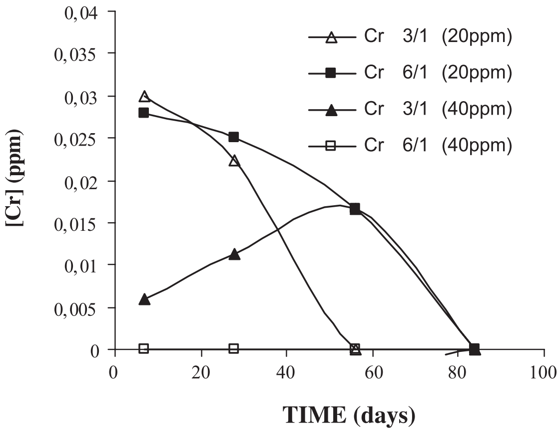

Fig. 3. Effect of the initial Cr content on the Cr concentrations of the leachates in contact with GGBFS.

In fact, the ternary blend, which contains less slag according to its MgO content, offers the weakest performance but not in a significant way. It should be noted that all the binders studied were powerful in reducing the Cr concentrations of the contaminated solution. After only 7 days of reaction, the initial Cr concentration of 20 ppm was lower or equal to 0.03 ppm. A very small quantity of GGBFS makes it possible to obtain chemical fixation of Cr ions.

Figs. 2, 3, and 4 present the final Cr concentrations of the leaching solutions in contact with 100% of slag. The concentration of elements in solution can be controlled by the solubility of secondary precipitates or of their availability to the leachate solutions and by their diffusive flux into solution from the leaching of the primary phases over time. To assess the mobility of toxic trace elements and the environmental risk that may be imposed in a hydrologic environment, it is necessary to distinguish between these two classes of elemental behaviour. If a mineral solubility control exists for an element, its concentration in water can be readily predicted with chemical equilibrium models. If the concentration of an element is controlled by its rate of release, more sophisticated hydrochemical transport models are required. To differentiate between these two classes of elemental behaviour, Reardon et al. [12] recommended conducting leaching tests on a particular waste material at least at two different water–solid ratios. They point out that if an element's concentration does not double when the water–solid ratio is halved, there must be a solid phase control on its concentration in solution. The tests were carried out with two solid–liquid ratios to make it possible to conclude on the presence or not of mineralogical control.

Fig. 2 shows that Cr ions are almost completely included in the solid phases and are thus independent of the initial water–solid ratio. The molybdenum ions are not completely stabilized by the GGBFS even after 84 days of reaction. However, as revealed in each term, concentration values measured at the water–solid ratio of 3:1 are always lower than double of those observed at the 6:1 ratio. We can conclude that a solid phase present in the slag or in the slag hydration products has a solubility control on both Cr and Mo concentrations.

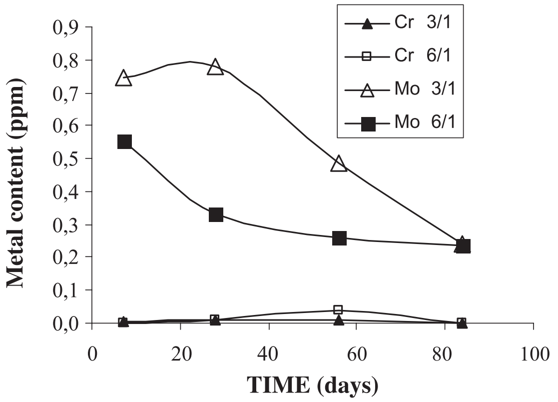

Fig. 2. Concentration of metals (Cr or Mo) in solution for samples of GGBFS in contact with solution containing 20 ppm Cr and 20 ppm Mo.

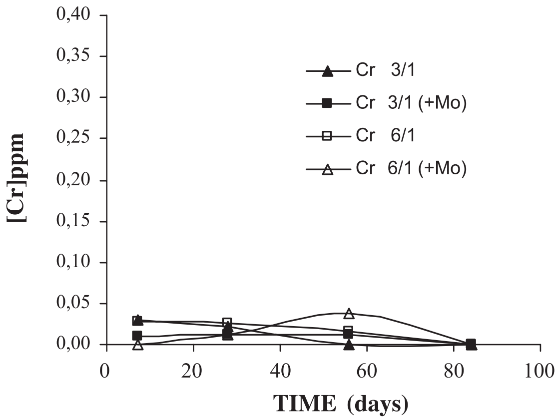

Fig. 4. Effect of Mo ions on the Cr concentrations of the leachates in contact with GGBFS.

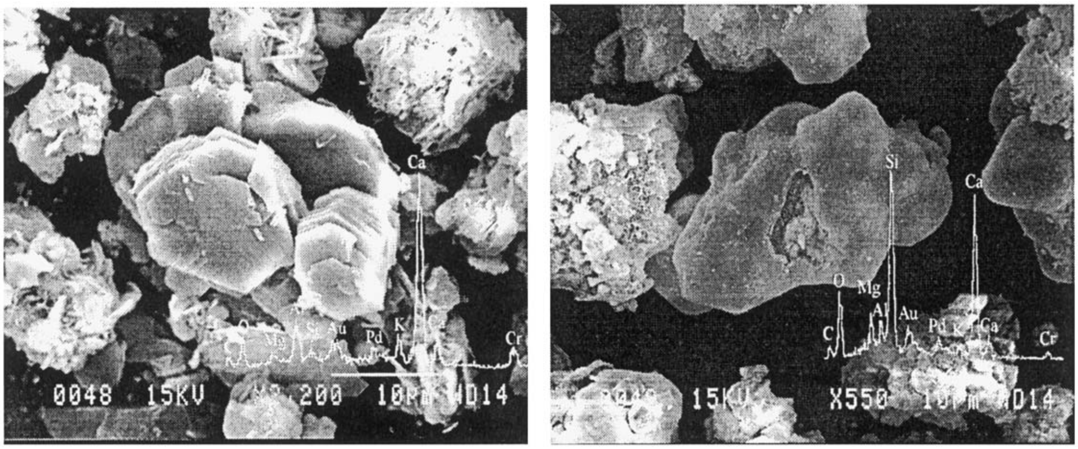

Fig. 5. SEM micrographs of solid samples in contact with a 3000-ppm Cr solution. (left) Ordinary Portland type I cement; (right) GGBFS.

Fig. 3 presents the effects of the initial Cr concentrations on the quantity of Cr ions included in the solid phases. These results were obtained for samples composed exclusively of GGBFS. The use of GGBFS allows reducing a Cr concentration of 40 ppm to a value close to 0.03 ppm after 7 days of reaction. Cr ions are almost completely incorporated in the solid phases for all samples.

Fig. 4 presents results with regard to the influence of the presence of another ion in solution. In fact, the molybdenum ions were introduced to verify if another ion of similar behaviour would have a negative influence on the fixation of Cr ions. According to data obtained, there is no ionic competition between molybdenum and chromium ions, at least with the concentrations studied.

3.2. SEM analysis results

Fig. 5 (left) is a micrograph of the OPC in contact with a 3000-ppm Cr solution. In this case, Cr ions are mainly detected in the hydrated calcium aluminate phases. Aluminate phases are abundant and well distributed over the sample. We can also observe the formation of calcite crystals without measurable chromium content using the EDXA technique. Chromium ions can be detected in the C–S–H but in small proportion and at some isolated places over the sample.

Fig. 5 (right) shows a micrograph of the GGBFS sample after contact in a high-concentration chromium ion solution. Cr was evenly distributed in the sample as detected by the energy dispersive X-ray analyser. The C–S–H is the host of the chromium ions. Aluminate phases were not detected in the GGBFS sample.

4. Conclusion

This study presents the effect of various binders on the Cr ion fixation. Static leaching test were conducted at two different water–solid ratios (3:1 and 6:1) as a means to distinguish elements in the leachates that have solubility controls versus those that do not. GGBFS was chosen to stabilize undesirable elements. The performance of GGBFS is compared to other cementitious materials, such as ordinary Portland–slag mixtures cement and a ternary blend.

The results show that all the binders were effective in reducing Cr ions from solution. The sample containing only GGBFS is the most effective. It suppresses Cr content below the detection limits. Cr ions are almost completely included in the solid phases and independently of the initial water–solid ratio. The molybdenum ions are not completely stabilized by the GGBFS, but this phase has a solubility control on Mo ions. Furthermore, no ionic competition between molybdenum and chromium ions was observed. In the GGBFS sample, Cr ions are dispersed in the C–S–H. For the OPC, Cr ions are linked to hydrated calcium aluminate phases.

Acknowledgements

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References

[1] J.R. Conner, Guide to Improving the Effectiveness of Cement-Based Stabilization/Solidification, Portland Cement Association, Skokie, IL, USA, 1997.

[2] J. Duchesne, Réduction des concentrations en Cr et en Mo dans des lixiviats générées par des poussières de four de cimenterie, in: J. Méhu, G. Keck, A. Navarro (Eds.), Stabilisation des Déchets and Environnement 99, Société alpine de publications, Grenoble, 1999, pp. 21–25.

[3] A. Macias, S. Goni, J. Madrid, J.M. Diez, E. del Castillo, Potential of blast furnace slags to immobilize toxic wastes, in: V.M. Malhotra (Ed.), 6th CANMET ACI/JCI International Conference on Fly ash, Silica Fume, Slag and Natural Pozzolans in Concrete, American Con-

crete Institute and Electric Power Research Institute, Farmington Hills, MI, USA, 1990, pp. 277–325.

[4] J.N. Diet, P. Moszkowick, A. Navarro, Solidification de boues d'hydroxydes métalliques par des ciments portland: comportement du ciment en présence de boues d'hydroxyde de chrome, in: J.M. Thomas, F. Thomas (Eds.), Actes du Congrès International sur les Procédés de Solidification et de Stabilisation des déchets, Société Alpine de Publications, Grenoble, 1997, pp. 207–212.

[5] A. Kindness, A. Macias, F.P. Glasser, Immobilization of chromium in cement matrices, Waste Manage. 14 (1994) 3–11.

[6] A. Bouchelaghem, M.C. Magnie, J.Y. Cojan, Stabilisation des déchets à base de liants hydrauliques: des principes théoriques à la mise en oeuvre industrielle, in: J.M. Cases, F. Thomas (Eds.), Actes du Congrès International sur les Procédés de Solidification et de Stabilisation des déchets, Société Alpine de Publications, Grenoble, 1997, pp. 119–125.

[7] M.L. Allan, L.E. KuKacka, Blast furnace slag-modified grouts for in situ stabilization of chromium-contaminated soil, Waste Manage. 15 (1995) 193–202.

[8] S.K. Srivastava, V.K. Gupta, D. Mohan, Removal of lead and chromium by activated slag—A blast-furnace waste, J. Environ. Eng. (ASCE) 123 (1997) 461–468.

[9] W.A. Klemm, Ettringite and Oxyanion-Substituted Ettringites—Their Characterization and Applications in the Fixation of Heavy Metals: A Synthesis of the Literature, Research and Development Bulletin RD116W, Portland Cement Association, Skokie, IL, USA, 1998.

[10] R.D. Hooton, La réactivité et les produits d'hydratation du laitier de haut fourneau. Matériaux complémentaires en cimentation pour le béton, in: R.D. Canmet (Ed.), Centre d'édition du gouvernement du Canada, Ottawa, Canada, (1989) 277–325.

[11] H.F.W. Taylor, Cement Chemistry, Academic Press, London, 1990.

[12] E.J. Reardon, C.A. Czank, C.J. Warren, R. Dayal, H.M. Johnston, Determining controls on element concentrations in fly ash leachate, Waste Manage. Res. 13 (1995) 435–450.