

Immobilization of chromium (VI) evaluated by binding isotherms for ground granulated blast furnace slag and ordinary Portland cement

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Abstract

The interaction mechanisms of the Cr(VI) ion in presence of GGBFS and OPC were evaluated by chromium binding isotherms and by pore solution analysis. The chromium in the final leaching solution was measured and the solid samples were investigated by SEM and by XRD. GGBFS was more efficient than OPC in fixing Cr ions at lower initial concentrations. However, from an initial Cr(VI) concentration of 2000 and 5000 mg/L, OPC was more efficient.

For an initial Cr(VI) concentration of 50 000 mg/L, around 145 mg Cr/g was fixed by OPC and only 8 and 55 mg Cr/g were fixed by GGBFS in alkaline and water-based immersion solutions, respectively. The Cr-bearing phases identified by XRD and SEM are: CaCrO_4 and $\text{CaCrO}_4 \cdot 2\text{H}_2\text{O}$, C–S–H and calcium aluminate phases. The pore solution chemistry indicates that a value around 92% of chromium was retained by GGBFS and 87% by OPC.

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1. Introduction

Waste disposal has become a major concern in the industrial world [1] because this practice can cause environmental risk due to the mobility of toxic trace elements [2]. There is increasing public interest in finding ecological solutions for safe disposal of by-products that might be suitable for incorporation into cementitious materials and concrete [3]. Moreover, chemical fixation and solidification is a very effective tool and is becoming a standard process in liquid and hazardous waste treatment and disposal [4,5].

The processes of stabilization/solidification (S/S) aim to carry out a mineralogical control of the metals to be stabilized. Several studies have shown that there is a lack of chemical fixation of the concentrations of Cr(VI) in cement-based S/S technology [2,5–8]. Thus Cr, in particular Cr(VI),

remained free in the contaminated solution when ordinary Portland cement (OPC) was used without a reducing agent. Some phases of the ground granulated blast furnace slag (GGBFS) seem to be able to exert a solubility control on chromium [1,6,7,9–11]. This is particularly interesting considering that GGBFS is itself a by-product of the iron industry.

Chromium can be found in three valency states: +2, +3 and +6. At low levels, chromium is an essential element for animal metabolism, but at levels close to 0.1 mg/g of the body weight, it can be lethal [12]. Chromium(III) and Cr(VI) are the more frequent states. The Cr(VI) is a severe toxic contaminant of natural waters, sediments and soils. Chromium(VI) is acidic, forming chromates $(\text{CrO}_4)^{2-}$ and dichromates $(\text{Cr}_2\text{O}_7)^{2-}$, the other valences are basic. Chromates are used or generated by some industrial process like electroplating, pigments and allied products, leather tanning and textiles, pulp production and ore and petroleum refining. The effects of chromates are principally on the skin and mucous membrane [4]. The traditional technique of

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stabilization of Cr(VI) is initially to reduce it in Cr(III) in an acid medium using a reducing agent ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Na}_2\text{S}_2\text{O}_5$ or $\text{Na}_2\text{S}_2\text{O}_4$) [5]. Chromium(III) is then precipitated, in a basic medium, the hydroxide is almost completely insoluble. This technique is difficult and expensive since one must pass by two stages, and a reducing agent must be used. GGBFS seems to have the capacity, without addition of reducing agent and the acidification step, to reduce Cr(VI) to Cr(III) and simultaneously solidify the residue. Then, as with the traditional technique mentioned before, the Cr(III) will precipitate as the stable and insoluble form $\text{Cr}(\text{OH})_3$.

The others ionic substitutions observed in cement hydrates were in calcium aluminate hydrates (ettringite [$6\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 32\text{H}_2\text{O}$] and monosulfate hydrate) and calcium silicate hydrate (C–S–H) [13]. The predominant hydrated calcium alumina-sulfate phase present in mature Portland cement pastes is sulfate hydrocalumite $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot n\text{H}_2\text{O}$ (also named calcium aluminium monosulfate or monosulfate) [14]. Monosulfate come from the group of layered calcium aluminate hydrates (Afm-phases) whose general formulae is $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaX} \cdot n\text{H}_2\text{O}$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaY}_2 \cdot n\text{H}_2\text{O}$ with $\text{X}=\text{SO}_4^{2-}$, CO_3^{2-} , CrO_4^{2-} –and $\text{Y}=\text{OH}^-$, Cl^- , NO_3^- [14,15]. The Cr(VI), which primarily occurs as CrO_4^{2-} in alkaline solutions [11,14,16], can be substituted for the SO_4^{2-} in ettringite [17] and in monosulfate [13,14]. The identical charges, the similar structures and nearly the same thermochemical radii should readily substitute in the crystal structure of many SO_4 -minerals [14,17,18]. The substitution of Cr(III) for Al(III) in most of the calcium aluminate hydrates formed by the hydration of GGBFS also becomes possible [6].

GGBFS has a reducing potential that creates an environment where the Eh values (–200 to –400 mV) will be weaker than in a system composed mainly of Portland cement (100 to 200 mV) [6,19]. Indeed, the activity field (conditions of particular Eh and pH) of the GGBFS is found in the zone of stability of chromium, i.e. when chromium is found in the $\text{Cr}(\text{OH})_3$ form. With regard to Portland cement, its field of activity is located in the chromates (CrO_4)^{2–} zone which are a very soluble form of Cr(VI).

There are also economical and environmental advantages to use GGBFS to replace OPC. The utilization of GGBFS permits energy saving, given that the production of Portland cement needs 4000 MJ by metric ton while the production of GGBFS requests only 25% to 33% of this amount. Thus, the saving of energy coupled with the re-use and the valorization of the GGBFS are interesting for the environment.

The purpose of this study was to give information on chromium interaction mechanisms with GGBFS and OPC by isotherm adsorption analysis and by pore solution extraction.

2. Materials

GGBFS is a waste product in the manufacture of iron composed mainly of calcium silicate and aluminosilicate.

More precisely, the slag comes from fusion of the fluxing agent (limestone or dolomite) with the gangue (silico-aluminous residues of the iron ore) and then coke ash in the blast furnace. The slag is a liquid formed at 1400–1600 °C and composed of the undesirable substances of low density which float above the mild steel and the un-melted burden [20–22]. The chemical characteristics of the slag vary depending on its state. The slag is inert in a crystalline state but it is reactive in a vitreous state and in this condition produces compounds having binding properties. The slag can also be granulated. In fact, there are several types of slags which are classified according to their respective modes of cooling.

Air-cooled slag is cooled slowly in a pit and is then crushed. This type of slag is sometimes used as aggregate but has practically no binding properties since its crystallization is more complete. The granulated blast furnace slag is most common, wherein powerful water jets or air blasts cool and fragment the molten slag which is then plunged under water. The result is an amorphous granular material whose variable binding capacity is a function of, among other things, its degree of vitrification. The chemical composition also makes it possible to classify different slags. The blast furnace slag used in the design of the mixtures of concrete is a ferrous slag.

GGBFS is used at up to 70% cement replacement in concrete. Hydration of the slag cements showed that these products give the same hydrates as ordinary type 1 Portland cement. The hydration of the slag cements forms less portlandite ($\text{Ca}(\text{OH})_2$) and in parallel releases less heat. The C–S–H produced by the slag has a lower Ca/Si ratio than C–S–H produced by Portland cement [19,23–25]. These C–S–Hs have a greater capacity for fixing alkalis and other metals. The slag reacts slowly with water (approximately 28 days) but its hydration can be activated chemically, thermally or mechanically. Under conditions which allow slower reacting slag to react, the long-term strength of concretes made with slag is higher than those obtained with only Portland cement [22,26,27]. Moreover, the presence of slag decreases the penetration of the aggressive agents by decreasing the permeability. This characteristic of the slag increases the durability of the concrete and would support the long-term capture of heavy metals in the solidified matrix.

The crystalline part of slag is mainly distributed between the solid-solution of the melilite family (from akermanite, $\text{Ca}_2\text{MgSi}_2\text{O}_7$, to gehlenite, $\text{Ca}_2\text{Al}_2\text{SiO}_7$, composition) and merwinite ($\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$) minerals. The chemical composition of the GGBFS shows little variation within a plant and is homogenous from particle to particle. North American GGBFS is composed mainly of CaO (38%), SiO_2 (36%), MgO (12%) and Al_2O_3 (11%) [1,20,26,28,29]. The content in MgO oxide varies from different areas. The typical MgO content in North America is approximately 12% whereas the average concentration is only 6% in the European countries [30]. The surface area of most GGBFS varies from 340 to

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