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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 50000 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 $CaCrO_4 \cdot 2H_2O$, 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.

Keywords: Microstructure; Chromium; Granulated blast furnace slag; Portland cement; Waste management

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 $(CrO_4)^{2-}$ and dichromates $(Cr_2O_7)^{2-}$, 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 ($FeSO_4{\bullet}7H_2O$, $Na_2S_2O_5$ or $Na_2S_2O_4$) [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 $Cr(OH)_3$.

The others ionic substitutions observed in cement hydrates were in calcium aluminate hydrates (ettringite [$6CaO{\bullet}Al_2O_3{\bullet}3SO_3{\bullet}32H_2O$] 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 $3CaO{\bullet}Al_2O_3{\bullet}CaSO_4{\bullet}nH_2O$ (also named calcium aluminium monosulfate or monosulfate) [14]. Monosulfate come from the group of layered calcium aluminate hydrates (Afm-phases) whose general formulae is $3CaO{\bullet}Al_2O_3{\bullet}CaX{\bullet}nH_2O$ and $3CaO{\bullet}Al_2O_3{\bullet}CaY_2{\bullet}nH_2O$ with X=SO_4^{2-}, CO_3^{2-}, CrO_4^{2-} $^{-\text{and Y=OH}-}$, 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 $Cr(OH)_3$ 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 ($Ca(OH)_2$) 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, $Ca_2MgSi_2O_7$, to gehlenite, $Ca_2Al_2SiO_7$, composition) and merwinite ($Ca_3Mg(SiO_4)_2$) 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

Table 1
Chemical composition of materials

Oxides (%mass)	CaO	SiO_2	MgO	Al_2O_3	MnO	Fe_2O_3	K_2O	TiO_2	Na_2O	P_2O_5	LOI	Total
GGBFS	37.31	36.77	13.91	7.77	1.02	0.85	0.43	0.36	0.31	−0.01	−1.49	97.25
OPC	62.49	19.75	2.62	4.41	0.05	2.92	0.89	0.17	0.28	0.23	1.90	95.77

550 m^2/kg. This variation is mainly due to the different methods of crushing. The pozzolanic activity index of slag is at least 100%. The surface area of ordinary type I cement is approximately 350 m^2/kg and varies from 250 to 550 m^2/kg for types II to III. The density of GGBFS is less variable with value close to 2.9 compared to 3.15 for OPC. The density (ASTM C188-89) of the slag studied is 2.915 and 3.090 for OPC.

The GGBFS studied here comes from Algoma Steel (Sault Ste-Marie, Canada). This slag, cooled quickly, is largely in a glassy form with a small proportion consisting of merwinite and of solid-solutions of the melilite family. An ordinary type I cement (OPC) was used in this study. The chemical compositions of the solid materials are given in Table 1.

3. Methods

3.1. Chromium binding isotherms

The chromium binding isotherms method was adapted according to the procedure of Delagrave et al. [31] to quantify the capacity for Cr(VI) absorption by different binders.

The test was divided into two series. The first series was prepared with unhydrated GGBFS or OPC powders. The second series of tests was made on crushed samples of OPC and GGBFS pastes already hydrated at water to binder ratio of 0.4. This series was set up in order to simulate the contact between already hydrated materials and solution rich in Cr ions. The cylindrical paste samples (diameter=2.3 cm and height=5 cm) were cast in hermetic containers and stored at 100% relative humidity for 80 days. The pastes were crushed in order to pass the 2-mm sieve. The powder was put under vacuum in a desiccator for 7 days. Thus 4 materials were tested in this study; 2 materials in a powder state (GGBFS and OPC) and 2 crushed materials which were hydrated beforehand during 80 days (Hydrated GGBFS and Hydrated OPC).

Approximately 10 g of tested materials was introduced into 50 ml of solution of various Cr(VI) concentrations (10, 20, 40, 50, 100, 250, 500, 750, 1000, 2000, 3000, 4000, 5000, 8000, 10 000, 15 000, 20 000, 25 000 and 50 000 mg/L) made up of chromic acid (CrO_3). The uses of chromic acid were chosen because the plating baths in chromium electroplating have about this composition and considering that this use of chromium chemical is the most important. The immersion solution was alkaline and made up of 1 g/L of NaOH and 4.65 g/L of KOH. This solution was alkaline in order to accurately reproduce the conditions within hydrated cementing materials. Distilled water was also tested as the immersion solution for samples immersed in high Cr concentrations to provide information on the Cr fixation in neutral environment. These mixtures were placed in polyethylene bottles suspended in a temperature bath maintained to within 1 °C at 25 °C for 28 days. After this period, solution samples were filtered through 0.22-μm membrane filters and were acidified with HCl for cation analyses (Cr) in a Perkin Elmer Aanalyst 100 Atomic Absorption Spectrophotometer (AAS). All solutions were kept at 4 °C until analysis. The 28 days required to reach equilibrium were retained in accordance with Delagrave et al. [31] whose data clearly show that equilibrium had been achieved with powdered cement paste samples and a chloride solution after 3-week exposure period. Perkins and Palmer [14], who studied the solubility of chromate hydrocalumite, adopted a reaction time of 14 days and mention that this time is well after the 2 days necessary to reach the steady-state concentrations of species being analysed. In order to verify the time necessary to attain equilibrium-state, a supplementary sample of already hydrated material was immersed in the alkaline-based immersion solution for 157 days instead of 28 days. This sample was named “Hydrated GGBFS:157 days (alkaline)” and its performance was tested in solutions up to 1000 mg/L of Cr(VI).

The influence of the binder characteristics and the immersion solution composition was studied at two Cr concentration levels (lower and higher initial Cr(VI) concentrations). This precision was adopted for an easier comparison between the different binders and to determine the maximum capacity of Cr(VI) incorporation in the solid phases. Two kinds of immersion solution were tested. First, an alkaline-based solution was tested to simulate the alkaline character of the concrete pore solution. Some samples were also run in a water-based solution to simulate near neutral conditions often find in a hydrologic environment.

The amount of bound chromium was calculated according to Eq. (1) where C_b was the bound chromium content (mg Cr/g sample), C_0 and C_1 were initial and equilibrium chromium concentration (mg/L), V was the volume (L) of the chromium solution and W was the sample weight (g).

$$C_b = \frac{(C_0 - C_1) \times V}{W} \tag{1}$$

3.2. Titration method for Cr(VI) determination

The Cr(VI) concentration was obtained by a chromic acid titration method [32,33] using ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) as titrating solution. The ferrous sulfate is often used as metal reducing agent in chemical fixation and solidification of wastes containing Cr(VI). In this method, the barium 4-(phenylamino) benzenesulfonate is used as a colorimetric indicator for the determination of Cr(VI) by the titration of ferrous ions. With the solution to be titrated, phosphoric acid H_3PO_4 (85% quality USP) and some drops of indicating solution (diphenylamine sulphonate of barium: 0.16%) are added. The phosphoric acid (H_3PO_4) is used to ensure the complexation of Fe(III) already in solution. Titration by acidified ferrous sulfate heptahydrate is carried out quickly until a mauve color is obtained and then more slowly until a final green color is obtained. The acidification of the titrating solution ensures a low pH (<3) making it possible [4]. The mechanism for the reduction reaction of Cr(VI) to Cr(III) using ferrous sulfate as the reducing agent is [34] as follows:

$$6Fe^{2+} + CrO_4^{2-} + 13H_2O \rightarrow 6Fe(OH)_3 + Cr_2O_3 + 8H^+ \tag{2}$$

3.3. X-ray diffraction (XRD) and scanning electron microscopic analyses (SEM)

Powered samples of GGBFS and OPC which were in contact with Cr(VI) alkaline solutions (0, 3000, 15 000 and 50 000 mg/L) were studied in order to identify Cr-bearing phases. The samples of GGBFS and OPC in contact with a distilled water-based solution of Cr(VI) at 50 000 mg/L were also studied. Powered samples (dried at 60 °C) of the reacted solid were analysed by a Siemens D5000 X-ray diffractometer using Cu Kα radiation generated at 20 mA and 40 kV. Specimens were step-scanned as random powder mounts from 5° to 55° 2θ at 0.02° 2θ steps integrated at 1.2-s $step^{-1}$. The same samples were also observed under a JEOL LSM-840A Scanning Electron Microscope equipped with an energy dispersive X-ray analysis system (EDXA).

3.4. Pore solution extraction method

Paste samples were made with a ratio of contaminated solution (50 g/L of Cr(VI)) to binder materials of 0.4. The paste samples were cast in hermetic containers and stored at 100% relative humidity. After 28 days of curing, pore solutions were extracted by the high-pressure method first described by Longuet et al. [35] with a maximum applied pressure of 1130 MPa. Chemical analyses were carried out on the solutions and total Cr was analysed by atomic absorption and Cr(VI) by titration as previously described.

4. Results and discussion

4.1. Influence of the binder characteristics and the immersion solution composition

Tables 2 and 3 present the experimental results of chromium binding isotherm. The chromium binding isotherms for the four stabilizing materials (OPC, GGBFS, already hydrated or not) are presented in Figs. 1 and 2. The

Table 2
Initial Cr(VI) and final total Cr concentrations of the immersion solutions with percentage relative error

[Cr(VI)] (mg/L)	Final [Cr] (mg/L)								
	Hydrated OPC		Hydrated GGBFS			OPC		GGBFS	
Solution	Alkaline	Water	Alkaline	Alkaline	Water	Alkaline	Water	Alkaline	Water
Time	28 days	28 days	157 days	28 days	28 days	28 days	28 days	28 days	28 days
10	UDL		0.6±13.8	UDL	0.5±17.8	0.3±28.4		UDL	
20	0.1±62.9		0.5±16.4	UDL	0.1±64.5	0.5±18.5		UDL	
40	0.5±18.8		0.5±17.9	UDL	UDL	0.8±10.4		UDL	
50	0.7±12.1		0.4±20.9	UDL	UDL	1.1±7.7		UDL	
100	2.0±4.3		0.7±12.7	UDL	UDL	2.5±3.5		UDL	
250	9.5±0.9		0.2±52.4	UDL	UDL	8.5±1.0		UDL	
500	29±0.3		12±0.7	UDL	UDL	14±0.6		UDL	
750	34±0.3		67±0.1	22±2.5	25±0.4	20±0.4		UDL	
1000	205±1.3	24±0.4	111±0.1	164±0.9	64±0.7	30±0.6	UDL	4.3±30.6	UDL
2000	499±0.4	138±0.6		703±1.4	425±12.7	33±0.5	UDL	2.6±19.9	UDL
3000	933±0.8	382±1.1		1406±0.8	789±6.8	29±0.6	UDL	192±0.5	UDL
4000	1418±0.4	839±6.4		2134±0.4	1203±4.5	68±1.3	UDL	432±0.5	19±23.2
5000	2052±0.7	1355±4.0		2836±0.8	1454±3.7	143±0.6	41±10.8	840±0.3	133±3.3
8000	3714±0.4	3086±1.4		5761±0.5	5133±0.6	1075±2.7	391±0.7	3203±0.4	1113±1.4
10 000	5367±1.3	3954±1.2		7482±0.6	7405±0.7	2536±0.7	1795±1.6	7998±0.5	2631±0.6
15 000	5421±1.4	3670±1.9		12 934±0.6	12 337±0.4	4402±1.5	1327±3.3	8602±0.8	10 364±0.4
25 000	12 429±1.9	11 949±1.2		21 324±0.7	20 312±1.1	4653±0.8	2064±3.6	21 401±1.1	20 664±0.7
50 000	21 314±1.7	22 456±1.0		42 261±1.1	39 536±1.2	20 313±2.0	18 325±1.3	48 339±2.0	38 770±1.2

UDL: Under detection limit.

Table 3
Initial and final Cr(VI) concentrations of the immersion solutions with percentage relative error

[Cr(VI)] (mg/L)	Final [Cr(VI)] (mg/L)								
	Hydrated OPC		Hydrated GGBFS			OPC		GGBFS	
Solution	Alkaline	Water	Alkaline	Alkaline	Water	Alkaline	Water	Alkaline	Water
Time	28 days	28 days	157 days	28 days	28 days	28 days	28 days	28 days	28 days
1000	174±1.3	*		*	*	*	*	*	*
2000	436±1.1	*		*	*	12±9.6	*	*	*
3000	835±0.6	*		719±0.7	*	*	*	*	*
4000	1299±0.4	*		1232±0.4	*	24±5.0	*	*	*
5000	1928±0.6	*		2108±0.6	*	82±1.8	35±3.6	415±0.9	56±3.9
8000	3550±0.7	2884±0.2		4712±0.6	4137±0.7	929±0.6	332±1.4	2893±1.2	912±0.6
10 000	4747±1.8	3907±1.0		7415±1.6	6999±1.6	2421±0.5	1607±0.7	8040±1.5	2263±0.6
15 000	5903±1.7	3487±1.1		13 579±6.5	10 873±4.6	4772±1.9	1287±0.8	8874±7.4	10 175±0.7
25 000	12 497±0.7	12 230±1.3		22 368±5.9	19 409±12.2	4686±1.9	1965±1.6	20 637±2.4	20 929±6.0
50 000	19 052±6.0	22 665±5.9		40 870±5.5	41 972±11.0	16 990±6.2	20 190±12.1	47 665±5.4	42 117±11.0

* No change of color observed.

amount of bound chromium is expressed as a function of the equilibrium free chromium concentration. Fig. 1 shows the results for the samples immersed in low initial Cr(VI) concentrations (10 to 1000 mg/L). This figure indicates that the amount of bound chromium increases with the chromium ion concentration of the immersion solution for all binder materials. The chromium ions were totally fixed by the GGBFS sample. The OPC sample has almost totally fixed the Cr ions but trace concentrations were still analysed in that solution.

The hydrated GGBFS sample has bound less Cr ions than the non-hydrated sample but more than the hydrated OPC. The hydrated binders were less effective than the non-hydrated one. However, the time of reaction seems most of the time a positive factor as shown by the sample of hydrated GGBFS that reacted for a period of 157 days which bound more Cr ions than the same sample after only 28 days of reaction. At low initial Cr ions concentration, a water-based solution seems to be more effective than the alkaline-based solution at least for the hydrated GGBFS sample.

Fig. 2 shows the results for the samples immersed in the high initial Cr(VI) concentrations (1000 to 50 000 mg/L) for all the stabilizing materials. Contrary to the results presented in Fig. 1, the samples derived from OPC are more effective at incorporating chromium ions irrespective of the immersion solution. In fact, the free Cr concentrations of the solution in contact with OPC are two times less than those in contact with GGBFS. For an initial Cr(VI) concentration of 50 000 mg/L, around 145 mg Cr/g was fixed by the OPC sample, irrespective of the immersion solution. For the GGBFS sample in contact with a Cr(VI) bearing solution of 50 000 mg/L, only 8 mg Cr/g and 55 mg Cr/g were fixed in alkaline-based and water-based immersion solutions, respectively. The immersion solution has a limited influence on the amount of Cr ions fixed: water-based solutions seem marginally more effective at fixing Cr ions than alkaline-based solutions. Moreover, anhydrous samples behave better than those already hydrated. For an initial Cr(VI) concentration of 50 000 mg/L, around 140 mg Cr/g was fixed by the hydrated OPC sample irrespective of the immersion solution. For the hydrated GGBFS sample, in the

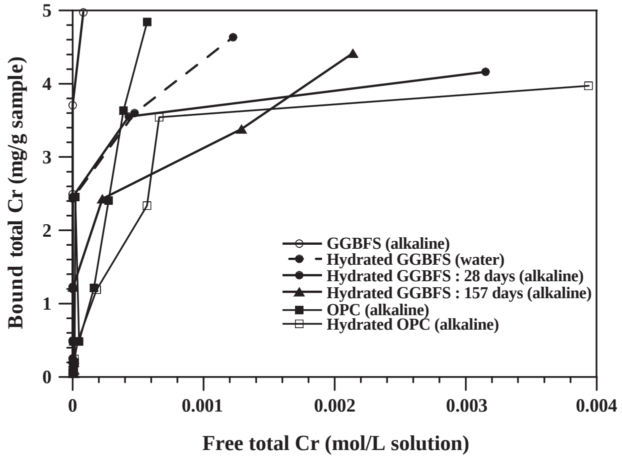

Fig. 1. Influence of binder characteristics and immersion solution on chromium binding capacity until 1000 mg/L.

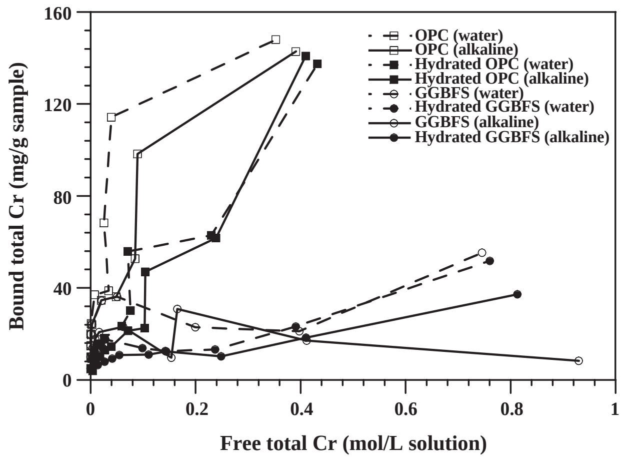

Fig. 2. Influence of binder characteristics and immersion solution on chromium binding capacity between 1000 to 50 000 mg/L.

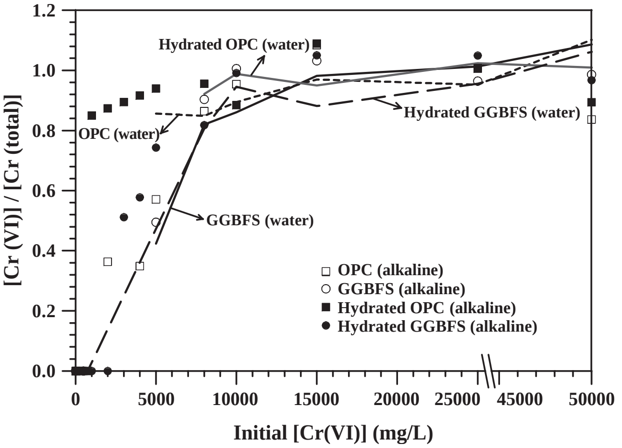

Fig. 3. The residual Cr(VI) in solution of leaching.

same initial Cr(VI) concentration of 50 000 mg/L, only 37 mg Cr/g and 52 mg Cr/g were fixed in alkaline-based and water-based immersion solution, respectively.

The equilibrium time fixed at 28 days according to literature was verified by comparison between the results obtained from the sample “Hydrated GGBFS: 157 days (alkaline)” and the sample “Hydrated GGBFS: 28 days (alkaline)” shown in Fig. 1. The sample which reacted for 28 days offers a better performance in solutions with initial concentrations of about 10 up to 750 mg/L. At 1000 mg/L, the sample which reacted for 157 days had fixed more Cr than the sample which reacted for 28 days. These results can be explained by the tendency of the GGBFS to be less effective at fixing Cr at higher initial concentrations and that the reaction time may highlight this fact. It should be considered that the results come from experimental tests and that the values obtained (111 and 168 mg/L) are close. The proximity of values obtained after 28 and 157 days allows us to confirm that the 28-day period is an acceptable reaction time to evaluate chromium fixation.

4.2. Chromium (VI) fixation

The relation between Cr(III) and Cr(VI) is shown in Fig. 3 by the ratio of Cr(VI)/Cr(total). The ratio of residual Cr(VI) and total Cr in the final solution increase with increasing initial Cr(VI) concentrations and tend to 1 for an initial Cr(VI) concentration near 50 000 mg/L. The samples of OPC and GGBFS seem to present approximately the same capacity to fix Cr(VI) in alkaline-based immersion solution. The same tendency was observed for samples in water-based immersion solution, with the exception of initial Cr(VI) concentration values between around 5000

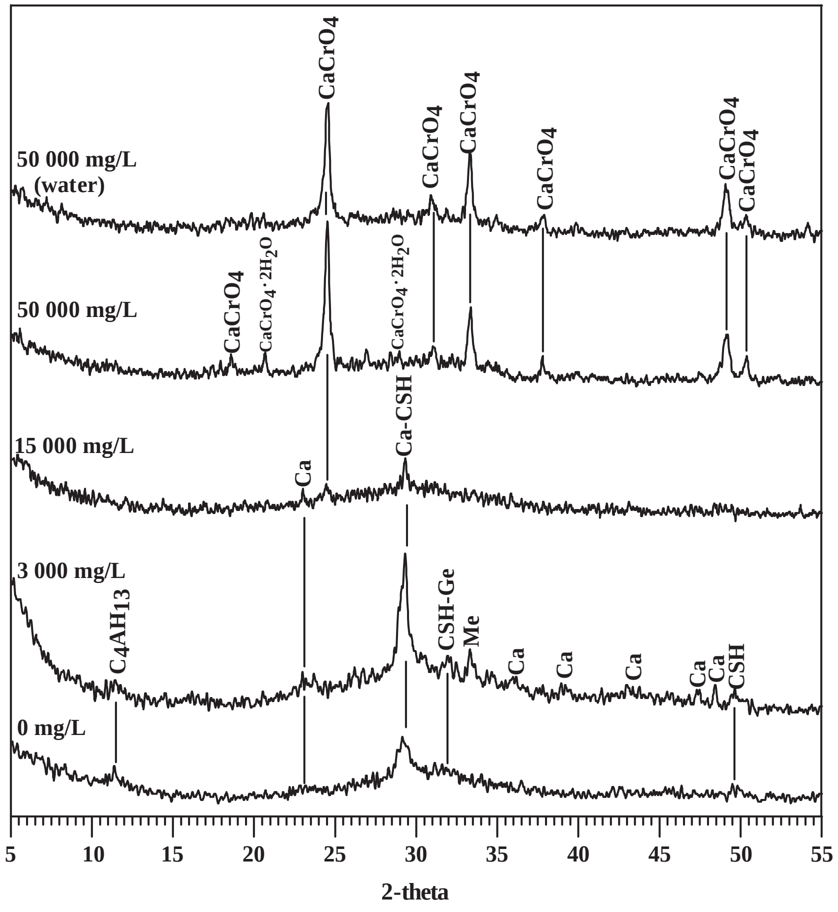

Fig. 4. XRD results of GGBFS in contact with a 0, 3000, 15 000 and 50 000 mg/L of Cr(VI) solution for 28 days (λ=1.54184 Å CuKα).

and 8000 mg/L. For this concentration range, the immersion solution contains less Cr(VI) in the presence of GGBFS. In the case of previously hydrated samples, GGBFS was more effective at fixing Cr(VI) than OPC and this was irrespective of the immersion solution.

4.3. X-ray diffraction (XRD) and scanning electron microscopic analyses (SEM) results

The XRD results come from solid samples recovered from the chromium binding isotherms test. Fig. 4 presents the evolution of the XRD patterns obtained on GGBFS samples, and this figure clearly shows the appearance of the chromatite phases ($CaCrO_4$), a Cr-bearing phases, starting at Cr concentrations of 15 000 mg/L. This phase is better defined in the samples immersed in the 50 000 mg/L solution. At this higher concentration, results obtained are effectively identical for the alkaline and the water-based immersion solutions. The formation of calcium chromium oxide hydrate ($CaCrO_4 \bullet 2H_2O$) is observed in the GGBFS sample immersed in the 50 000 mg/L alkaline-based solution. The presence of C–S–H can be note on samples immersed in 0, 3000 and 15 000 mg/L of Cr. It is probable that some Cr ions were incorporated in this C–S–H. Calcite ($CaCO_3$) was also identified at these concentrations. The XRD lines associated with the hydrocalumite (C_4AH_{13}) phase appear in the GGBFS sample immersed in water without Cr ion. The hydrocalumite line can also be observed in the sample with 3000 mg/L but the line is broad. This may be due to the incorporation of chromium ions in this calcium aluminate phase.

Fig. 5 presents the evolution of the XRD patterns obtained on OPC samples. The presence of chromatite was identified only on samples immersed in 50 000 mg/L of Cr. The chromatite lines are wider than those identified in presence of GGBFS (Fig. 4). The intensity of the chromatite lines is increased for the OPC sample immersed in the water-based solution. A new line appears at a *d*-spacing of (4.034 Å) and is still not identified. The line associated with the hydrocalumite (C_4AH_{13}) phase appears in the solution without Cr ions. This hydrocalumite line is still present in the 3000 mg/L sample but its intensity decreases dramatically. This line has widened probably due to the incorporation of Cr ions in the calcium aluminate phases. The portlandite ($Ca(OH_2)$), which is the major phase in samples until 15 000 mg/L, disappears in samples immersed in 50 000 mg/L solution.

Fig. 6 presents the SEM results for the same samples studied by XRD. The SEM investigation has confirmed the presence of chromium ions in the C–S–H. Chromium ions

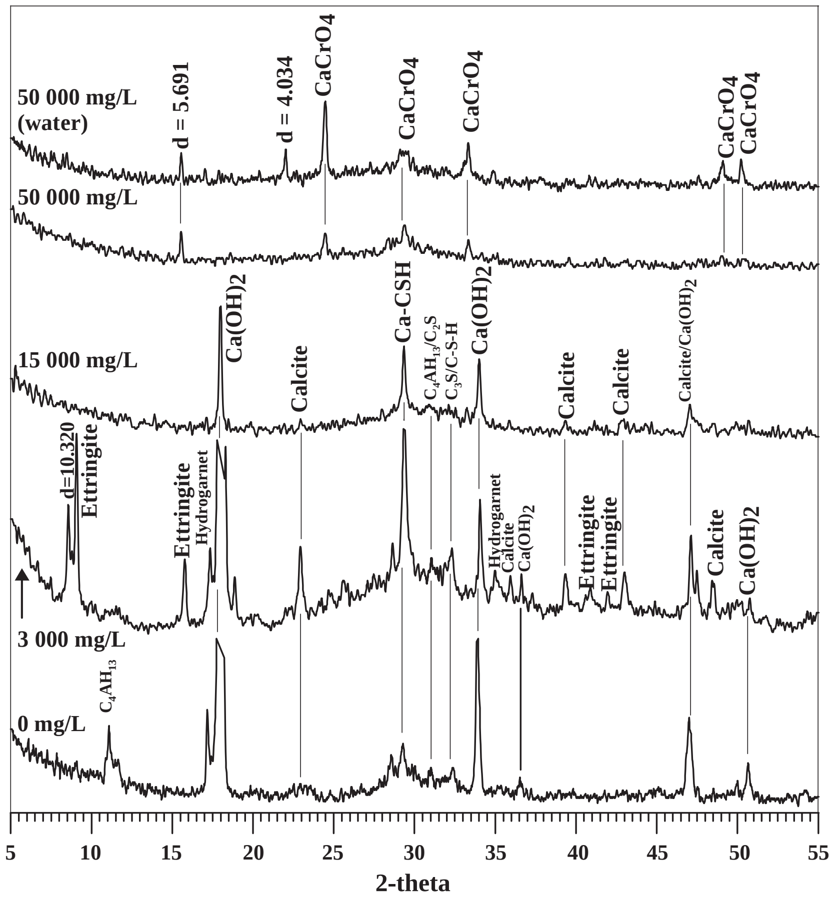

Fig. 5. XRD results of OPC in contact with a 0, 3000, 15 000 and 50 000 mg/L of Cr(VI) solution for 28 days (λ=1.54184 Å CuKα).

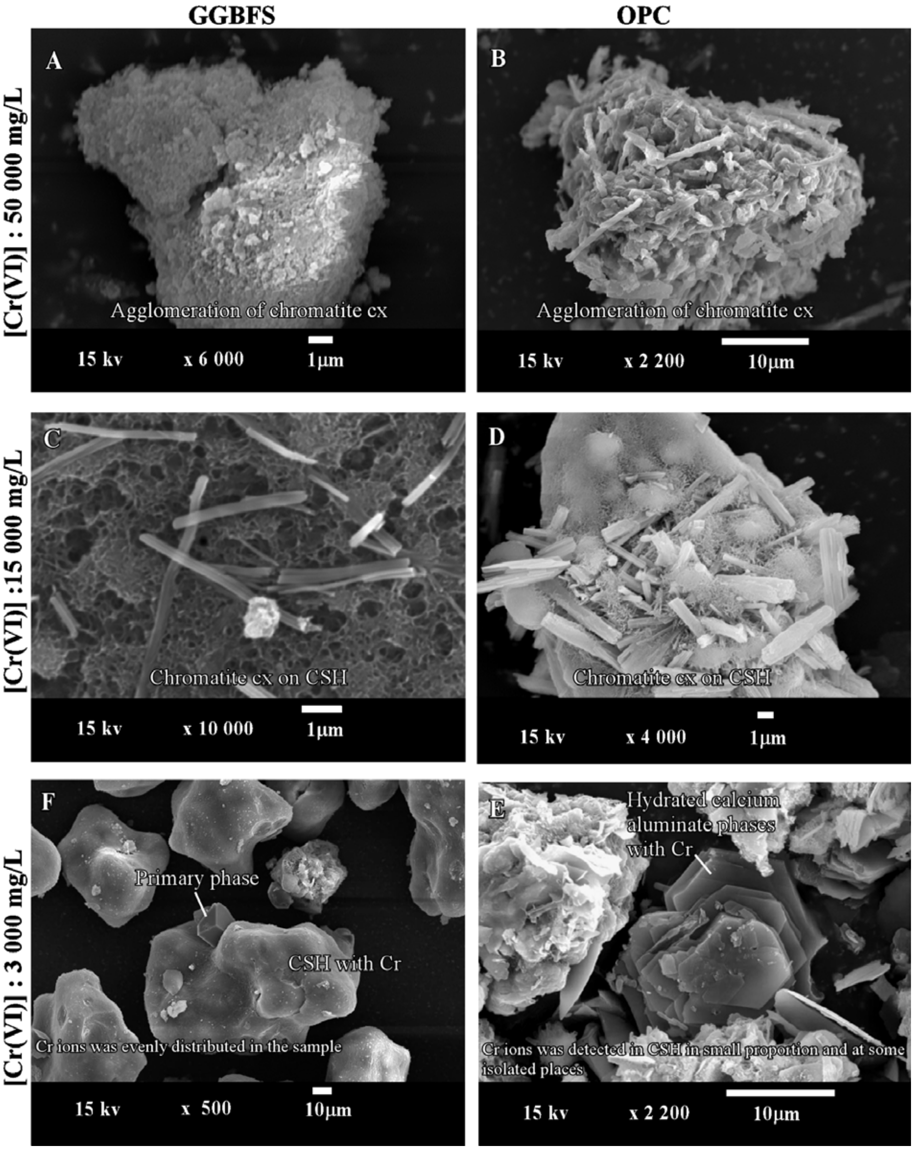

Fig. 6. SEM micrographs of solid samples in contact with a 0, 3000, 15000 and 50000 mg/L of Cr(VI) solution for 28 days.

were evenly distributed in the C–S–H of the GGBFS sample immersed in the 3000 mg/L solution. In the OPC sample immersed in the same solution, chromium ions were mainly found in hydrated calcium aluminate phases and sparingly in the C–S–H phases. The SEM observations have allowed the identification of the rod-shaped chromatite that appears to be more or less crystalline.

4.4. Nature of chromium fixation potential

Chromium has an amphoteric behaviour like aluminium, zinc and lead, i.e. these elements are soluble in both strongly acidic and basic solution [11]. The minimum solubility of chromium is at a pH value near 9. The increase in solubility at higher pH is generally due to the formation of an oxyanious complex such as chromate [36]. Glasser [37] points out that the precipitation of heavy metals under S/S conditions is often a two-step process. First, the metal constituent precipitates as hydrous oxide or hydroxide under the high pH conditions, but subsequently this metal constituent may react chemically with other cement components such as calcium, alumina, silica and OH^- ion to obtain a more complete precipitation [36]. Chromium(III) precipitation occurs immediately after mixing, as $Cr(OH)_3$, but this precipitation is not entirely complete due to the amphoteric nature of chromium. This behaviour is also conditioned by the oxidation state. In fact, the Cr(III), a slightly amphoteric ion, is readily precipitated as $Cr(OH)_3$ in an alkaline environment contrary to Cr(VI) [11]. The chromates $(CrO_4)^{2-}$, the more frequent form of Cr(VI) in solution, are relatively soluble at all values of pH [11]. However, with increasing time the $Cr(OH)_3$ is resorbed and substitutes for octahedrally coordinated Al in aluminate phases [36]. This explains the presence of chromium in calcium aluminate phases observed by SEM for samples of OPC at initial low concentrations of Cr(VI).

Fig. 7 presents the pH of the leaching solution as a function of the initial Cr(VI) concentration. This figure explains the better results obtained for the OPC sample at high Cr(VI) concentration. For the OPC samples, at 50 000 mg/L of initial Cr(VI) concentration, the pH values vary from 10.5 to 12.2 while for the samples with GGBFS, the pH are approximately from 6.6 to 8.3. These pH conditions for the GGBFS samples are more favourable than the OPC samples for the dissolution of chromium hydroxides ($CaCrO_4{\bullet}2H_2O$) [38]. The behaviour of chromatite ($CaCrO_4$) probably follows the same tendency to be more soluble in an acid medium. At low Cr concentration, the samples containing GGBFS have a lower pH with values close to 12 compared to samples with OPC that have pH over 13. This time, GGBFS samples present pH values more favourable concerning the low chromium hydroxide solubility point.

The presence of portlandite identified by XRD explains the maintenance of the high pH values measured in the OPC samples. The large reserve of solid portlandite ($Ca(OH)_2$) present in cement acts as a buffer so that the internal pH tends to decrease below this value [11]. At 50 000 mg/L, the portlandite was no longer detected and the pH fell to near the value of 12.2. Therefore, Ca^{2+} probably reacts preferentially with CrO_4^{2-} to form chromatite rather than portlandite [38].

C–S–H precipitated from normal type I Portland cement has a Ca/Si ratio of approximately 1.8, and the addition of blast furnace slag decreases this ratio. According to Glasser [39], the surface charge of the C–S–H is dependent on its Ca/Si ratio. When this ratio is raised, the charge is positive. The charge becomes zero, and can be negative as the Ca/Si ratio decreases. This implies that the C–S–H in the presence of slag tends to attract cations contrary to C–S–H from Portland cement. This implies that the chromium ions could be more easily attracted by the C–S–H of the slag cement. The zero points of charge for the slag are situated at a pH of 2.8, the surface has a negative charge when the pH is higher than this value. More measurements need to be done to fully understand this surface charge phenomenon.

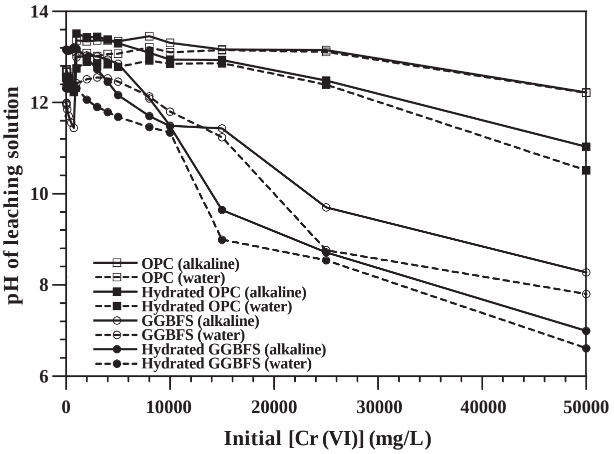

Fig. 7. pH and chromium solubility.

Table 4
Available chromium in pore solution

	Cr total (mg/L)	Cr (VI) (mg/L)
OPC paste	6367	5035
GGBFS paste	4090	3114

4.5. Available chromium ions in pore solution (pore solution extraction method)

Chemical analysis results of pore solutions extracted under high pressure from OPC and GGBFS paste samples are shown in Table 4. This method allows us to obtain more realistic results about the fixation of chromium ions in a concrete environment with a more realistic water/binder ratio. Results showed that a large part of the initial chromium ions (50 000 mg/L) are fixed in the solid phases. The concentration of Cr ions fell from 50 000 to 6370 and 4090 mg/L for OPC and GGBFS samples, respectively, i.e. 92% of chromium ions were retained by GGBFS and 87% by OPC. For both materials, the proportion of Cr(VI) compared to total Cr was similar. The water-soluble Cr(VI) in pore solution represents 76% and 79% of the free chromium in pore solution after a curing period of 28 days for GGBFS and OPC, respectively.

In the test realised at high Cr concentration (50 000 mg/L), the GGBFS sample has fixed more chromium ions than the OPC sample. This behaviour may be due to the difference in the oxidation potential between the leaching test open to the atmosphere and the present test where solid samples are in a closed environment with less oxygen present in the system. The GGBFS has a higher reducing character.

5. Conclusion

In an environment where the binders tested were immersed in Cr(VI) contaminated solution, GGBFS and OPC were both effective at fixing Cr(VI). GGBFS was more effective at lower initial Cr concentrations and OPC was more efficient from an initial Cr(VI) concentration of 2000 mg/L in alkaline-based solution and 5000 mg/L in water-based solution OPC. For an initial Cr(VI) concentration of 50 000 mg/L, around 145 mg Cr/g was fixed by the OPC sample independently of the type of solution of immersion. For the GGBFS sample, only 8 mg Cr/g and 55 mg Cr/g were fixed in alkaline-based and water-based immersion solution, respectively. The nature of the immersion solution has a limited influence on the amount of Cr ions fixed. The samples in water-based solution seem more effective at fixing Cr ions than alkaline-based solution but not in a major way. Moreover, anhydrous samples behave better than those already hydrated.

The pH values explain the better performance of OPC samples at fixing chromium ions. The pH's values of GGBFS samples (6.6 to 8.3) are more favourable to the dissolution of chromium oxide hydrate ($CaCrO_4{\bullet}2H_2O$) comparatively to OPC samples (10.5 to 12.2) because the minimum solubility of chromium is at a pH value near 9.

The Cr-bearing phases identified by XRD and SEM are the calcium chromium oxide ($CaCrO_4$ and $CaCrO_4{\bullet}2H_2O$), the C–S–H and the calcium aluminate phase (C_4AH_{13}).

The available chromium (total and (VI)) in pore solution measured by the extraction method was less from GGBFS paste. The pore solution chemistry indicates that a value around 92% of chromium was retaining by GGBFS and 87% by OPC.

The chromium oxide and hydroxide seem to exert a solubility control at higher Cr(VI) concentrations for OPC and particularly for GGBFS. The best performance of the GGBFS sample in the low initial Cr concentration may be due to its reducing properties. In fact, the GGBFS sample was more efficient to fix Cr ions in the pore solution extraction test run at high initial Cr concentration (50 000 mg/L of Cr) compared to OPC samples. In the pore solution extraction experiment, the pastes are less exposed to oxygen and the reducing properties of the GGBFS can play a major role. Further experiments should be run with control on the oxidation–reduction conditions to elucidate these results.

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