Pergamon

Available online at www.sciencedirect.com
SCIENCE @ DIRECT®

Cement and Concrete Research 33 (2003) 1039–1045

CEMENT AND CONCRETE RESEARCH

Hydration study of limestone blended cement in the presence of hazardous wastes containing Cr(VI)

M.A. Trezza*, M.F. Ferraiuelo

Facultad de Ingeniería, Universidad Nacional del Centro, Av. del Valle 5737, Olavarria (B7400JWI), Buenos Aires, Argentina

Received 29 June 2001; accepted 19 December 2002

Abstract

Considering the increasing use of limestone cement manufacture, the present paper tends to characterize limestone behavior in the presence of Cr(VI). The research reported herein provides information regarding the effect of Cr(VI) from industrial wastes in the limestone cement hydration.

The cementitious materials were ordinary Portland cement, as reference, and limestone blended cement.

The hydration and physicomechanical properties of cementitious materials and the influence of chromium at an early age were studied with X-ray diffraction (XRD), infrared spectroscopy (FTIR), conductimetric and mechanical tests. Portland cement pastes with the addition of Cr(VI) were examined and leaching behavior with respect to water and acid solution were investigated.

This study indicates that Cr(VI) modifies the rate and the components obtained during the cement hydration.

Keywords: Hydration; Characterization; X-ray diffraction; Waste management; Chromium

1. Introduction

The disposal of wastes containing heavy metals may cause environmental problems, mainly in nontreated industrial water. One of the best elimination methods is transforming these wastes into water-insoluble materials, reducing the damage by leaching.

The cementitious matrix has been demonstrated to be an adequate place to confine industrials wastes due to its density, and its thin intercommunicated pore system. Owing to the high pH value of pore water of Portland cement paste, these materials may turn into insoluble hydroxides [1] or eventually into intermediate phase by substitution of Ca ions by metals through diffusion mechanisms involving mainly the aluminate lattice.

The chromium is one of the heavy metals that may damage people's health. It is generated from different industrial effluents principally from electrochemical processes and leather tanning industries.

Different investigations have analyzed the effect of chromium on the different Portland cement phases [2–6] and its solidification in the cementitious matrix [7–13]. Pera et al. [8] reported that the solidification of Cr^{6+} in hydraulic binders occurs by the following mechanisms which can be compatible at the same time: addition, substitution (Cr-C-S-H, Cr–ettringite) or precipitation of new components. The results obtained show that ordinary Portland cement is the most efficient binder.

The chromium solidification can be mainly related to the formation of Ca–Cr aluminates and the existences of phases as $Ca_4Al_6O_{12}CrO_4$ and $Ca_6Al_4Cr_2O_{15}$ were reported [2]. Some authors consider that the ettringite phase is related to this mechanism by the substitution of Al by Cr(III) and/or SO_4^{2-} by CrO_4^{2-}. Modified *Cr–ettringite*, $3CaO\cdot Al_2O_3\cdot 3CaCrO_4\cdot 32H_2O$ [14–16] was observed in the XRD test.

In this study, the limestone blended cement hydration in the presence of Cr(VI) is introduced. Limestone fillers cause a hydration acceleration of Portland cement at early ages and produce the formation of calcium carboaluminate as results of the reaction between $CaCO_3$ from limestone and C_3A from cement. Fedman et al. [17] reveal that the reaction between C_3A and $CaCO_3$ takes place by solid state mechanism. The addition of $CaCO_3$ modifies the vigorous initial reaction of C_3A with the water due the rapid formation of a barrier of hydrated calcium carboaluminate

---

* Corresponding author. Tel./fax: +54-2284-451055.
E-mail address: mtrezza@fio.unicen.edu.ar (M.A. Trezza).

0008-8846/03/$ – see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0008-8846(03)00008-5

($C_3A{\cdot}CaCO_3{\cdot}xH_2O$) developed on the surface of C_3A grains. Consequently, the interaction between Cr and C_3A in the Cr–ettringite formation will be also modified in the limestone presence.

This investigation attempts to discuss the capacity of limestone Portland cement to confine Cr(VI) as a consequence of industrial wastes effluents incorporated. The formation and stability of monocarboaluminate and Cr–ettringite phases in limestone blended cement hydrated in the presence of Cr(VI) were studied. Chromium waste was simulated with 0.1 M of potassium dichromate solution.

Characterization of raw material and the hydration products was performed using infrared spectroscopy based on Fourier Transform (FTIR) and X-ray diffraction (XRD). Mechanical properties, leachability and ionic conductivity were also tested.

2. Experimental program

2.1. Materials

A normal Portland cement (C0) and a limestone-blended cement (C20), obtained from the same Portland clinker by an intergrinding process in the cement plant, were used. The potential composition of clinker was 58.2% of C_3S, 17.6% of C_2S, 1.7% of C_3A and 13% of C_4AF. The limestone content by mass was 0% in C0, and 18.1% in C20, according to the data supplied by the cement produced. Cements have the same strength class (CP40) and the specific surface were 321 and 383 m^2/kg for C0 and C20, respectively.

Adequate amounts of C0 and C20 were hydrated with a w/c ratio 0.4 in the reference samples. In the study, the water was substituted by 0.1 M of potassium dichromate solution, in order to obtain a large concentration of Cr(VI) as an industrial effluent. Samples were sealed during hydration time. Grinding with acetone stopped the hydration process. Table 1 shows the conditions and hydration time of each test. The denomination given to each sample is also mentioned.

2.2. XRD and FTIR studies

The samples were characterized by XRD using a Philips PW 3710 diffractometer with copper anode. The infrared measurements were recorded with a Nicolet FT-IR Magna 500 spectrophotometer using the KBr pellets technique.

Table 1
Identification of tested samples

	Hydrated with	Hydration time						
		1 h	1 day	3 days	14 days	30 days	90 days	180 days
C0	Water	H1	H2	H3	H4	H5	H6	H7
	Chromium	H8	H9	H10	H11	H12	H13	H14
C20	Water	H22	H23	H24	H25	H26	H27	H28
	Chromium	H29	H30	H31	H32	H33	H34	H35

2.3. Mechanical properties

Compressive strength was determined on 40 × 40 × 160-mm specimens. In all cases, the average value of three specimens is reported. Mechanical properties were obtained at 3, 7 and 28 days of curing.

2.4. Ionic conductivity test

A Jenway 4010 conductimeter was used; conductivity was measured at 1-min intervals during the first 5 min and then every 5 min until test time (300 min). A ratio $w/c = 10$ was used, but water was replaced by the Cr(VI) solution in the studied sample.

2.5. Leachability

Leaching test were carried out on the 1, 3 and 6 months hydrate pastes using the toxicity characteristic leaching procedure (TCLP) [4,18]. A sample was ground to a powder with a particle size < 0.5 mm and leached in water and in acetic acid solution ($pH \cong 3$). Two hundred milliliters of water or solution was added to the 10-g sample in a bottle. The bottle and its contents were agitated in a rotary shaker for 18 h. The leached solution was analyzed and the Cr(VI) concentrations are reported here.

Cr(VI) was determined by colorimetrical tests using a Lasa20 (0.03–1.0 mg/l chrom) equipment.

3. Results and discussion

3.1. XRD and FTIR studies

For this study, samples of different cements were hydrated with $w/c = 0.4$ and kept in sealed flasks during 1 h and 1, 3, 14, 90 and 180 days.

Figs. 1 and 2 show the X-ray diffractograms of clinkers at different times. H10 sample presents peaks of CH and ettringite diminished with respect to the ones of H3, showing also a clear CH presence, indicating higher hydration in the H1–H7 series than in the H8–H14 ones. The same happened when C20 was used. H31 presents peaks of CH and ettringite diminished with respect to H24, indicating higher hydration in the H22–H28 series with respect to the H29–H35 series, hydrating in the Cr(VI) presence. We can assume that the presence of chromium slows down the hydration of limestone cement as well as C0 at all hydration times.

This effect is a consequence of the interaction between chromium and Portland cement components

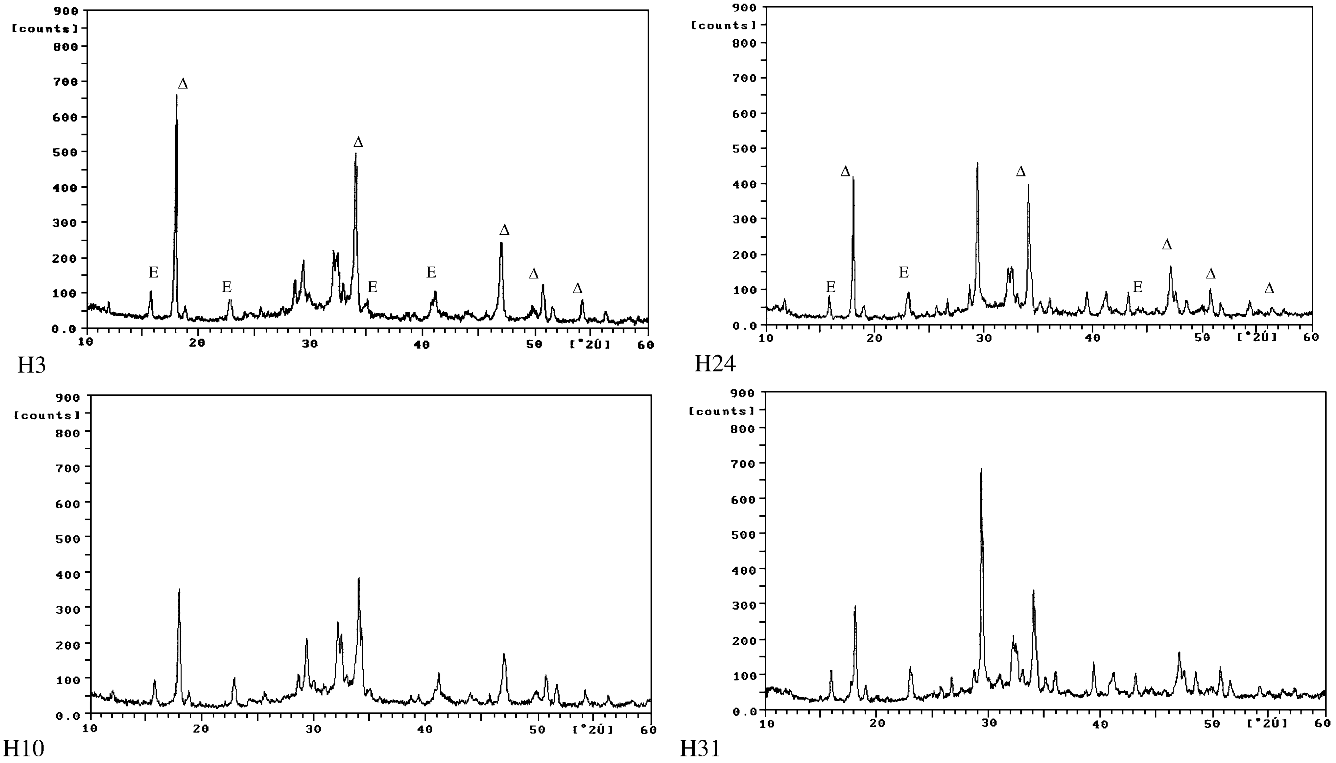

Fig. 1. X-ray diffractograms for C0 and C20 with and without Cr(VI) at an early age. Δ = CH, E = ettringite.

and it was reported by Bensted and Prakash Varma [14,15]. These authors reported that CrO_4^{2-} can substitute SO_4^{2-} forming a yellow chromium–ettringite: $Ca_6[Al(OH)_6]_2(CrO_4)_2\cdot 26H_2O$ since many ions of CrO_4^{2-} tend to assemble in the ettringite phase during ordinary Portland cement hydration.

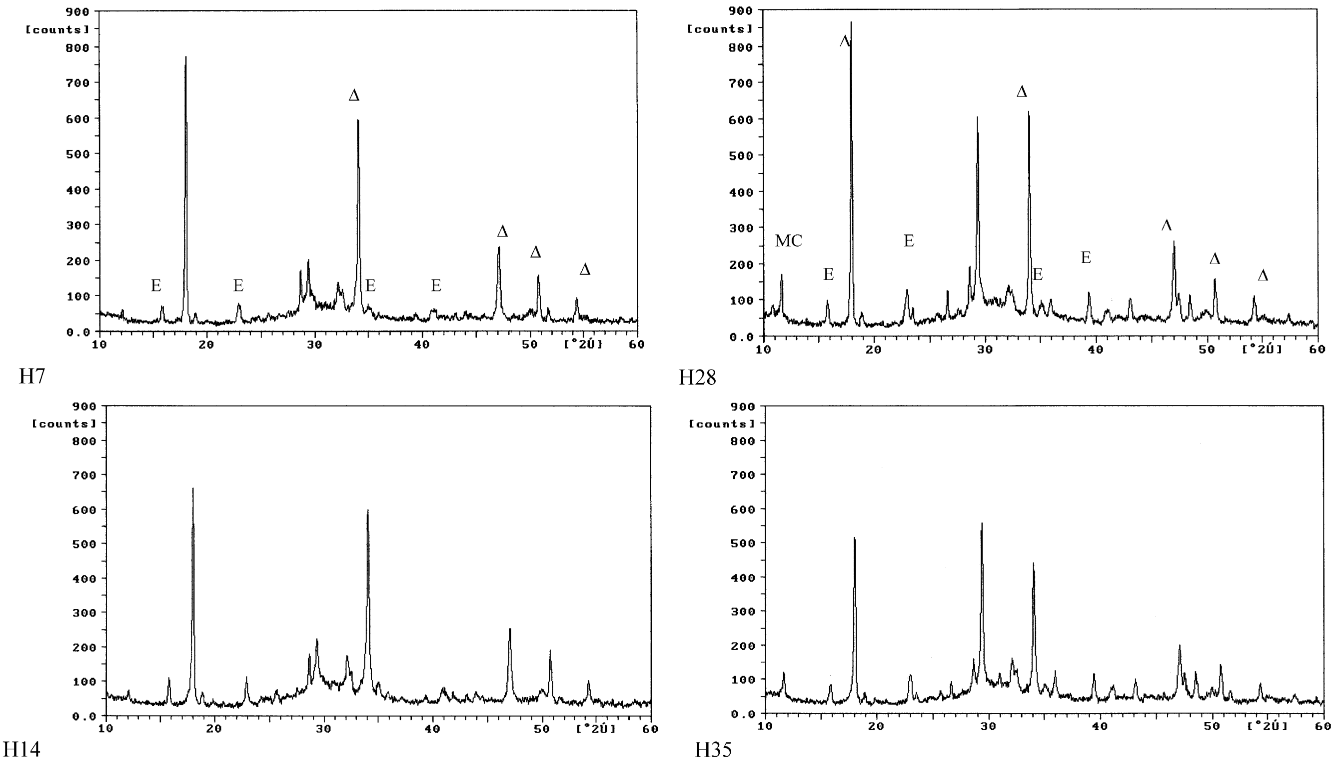

Fig. 2. X-ray diffractograms for C0 and C20 with and without Cr(VI) at 180 days. Δ = CH, E = ettringite, MC = monocarboaluminate.

As ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$), Cr–ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaCrO_4 \cdot 32H_2O$) and bentorite ($3CaO \cdot Cr_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) phases have a similar crystalline structure, their XRD patterns show great similarities. Particularly chromium–ettringite has $d = 5.70$, 4.71 and 3.52 Å as differential peaks. However, bentorite only shows an XRD pattern with slight displacement of the peaks in relation to ettringite being just a peak of $d = 3.60$ Å, which was absent in the other two phases [8]. Thus, when these investigations are carried out in pastes of commercial cement, they do not always reveal any presence of crystalline compounds that incorporate chromium [19].

In this work, it was possible to identify phases with chromium incorporation. Table 2 shows the main diffraction peaks obtained for some study samples of limestone blended cement. H27 shows a displacement of the main diffraction peaks of ettringite but H34, hydrated in the presence of Cr(VI), shows a clear Cr–ettringite formation.

Cr–ettringite is a crystalline and stable phase, so Cr(VI) was stabilized in limestone blended cement after 90 days.

In limestone blended cement, the incorporation of CO_3^{2-} to the system must also be considered. For normal carbonation the hydrated calcium aluminate [20] becomes calcium carboaluminates, probably for exchange of CO_3^{2-} by OH^-. Then the carboaluminate becomes $CaCO_3$. However, there is not much knowledge about the stability of those Cr phases or about the intermediate solid solutions (Al, Cr).

The limestone presence presupposes the carboaluminates formation during the cement hydration. Table 3 shows the XRD identification of monocarboaluminate in the study sample. The calcium monocarboaluminate, the most stable phase, has been identified in the reference hydration samples. In H33 to H35 samples, it is not clear if the monocarboaluminate is present before 180 days. In consequence, the Cr(VI) presence retards the monocarboaluminate formation in limestone blended cement. The displacements in the cell parameters, with regard to the reported phase, at early age can be attributed to a partial incorporation of chromium in C20 hydrated phases.

Quantitative analysis were carried out in C20 samples, from XRD spectra using one of the main peaks of limestone $2\theta = 29°$, in order to determine the limestone percentage incorporated to the hydration phases.

Table 2
Main diffraction peaks of ettringite and associated phases expressed as d(Å)

Bentorite	Ettringite	Chromium–ettringite	H27	H34
5.59	5.61	5.70	5.60	5.66
		4.71		4.75
3.89	3.87	3.91	3.86	3.90
3.60	3.48	3.52	3.47	3.49
3.23	3.24			

Bentorite: $3CaO \cdot Cr_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$.
Cr–ettringite: $3CaO \cdot Al_2O_3 \cdot 3CaCrO_4 \cdot 32H_2O$.
Ettringite: $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$.

Table 3
Identification of monocarboaluminate by XRD expressed as d(Å)

Monocarboaluminate	H26	H27	H28	H33	H34	H35
7.60	7.58	7.58	7.57	7.60	7.68	7.56
3.80	3.87	3.86	3.87	–	–	3.77
2.86	2.89	2.90	2.79	2.88	2.80	2.88
1.66	1.69	1.69	1.67	1.66	1.69	1.68

The results expressed as limestone percent consumed in function of hydration time are shown in Fig. 3.

The limestone incorporation obtained in this work is coincident with the ones reported by Bonavetti et al. [21], but when the hydration is in the Cr(VI) presence, this incorporation happens before (3 days) and the percentage of limestone incorporated is smaller in the period previous to 6 months. This ratified the previous discussion with regard to the calcium monocarboaluminate formation. In the H29–H35 samples (see Table 3), this compound appears only at 180 days (H35 sample) coincident with the highest limestone consumption.

This confirms that the Cr(VI) presence in limestone cement hydration retards the monocarboaluminate formation.

Hydration was also studied by FTIR spectroscopy, the results corroborated those obtained by XRD but did not introduce new indications of chromium phase formation.

As shown in Fig. 4, the biggest hydration advance in reference sample with regard to those with Cr(VI) is ratified by the band in 3645 cm^{-1} corresponding to OH^- group of the $Ca(OH)_2$, the one which is absent in H29 but not in H22.

The calcium monocarboaluminate presence is assigned in FTIR by the typical band $\nu 3$ CO_3^{2-}, split in 1365–1426 cm^{-1} and a shoulder in 1066 cm^{-1} assignable to $\nu 1$ CO_3^{2-}, indicating that the symmetry of the group CO_3^{2-} in the calcium monocarboaluminate is not purely D3h, becoming in this mode another characteristic peak of the hydrate [22,23]. A deformation of $\nu 3$ CO_3^{2-} is seen with the hydration time but this is not a clear proof of the formation of this compound.

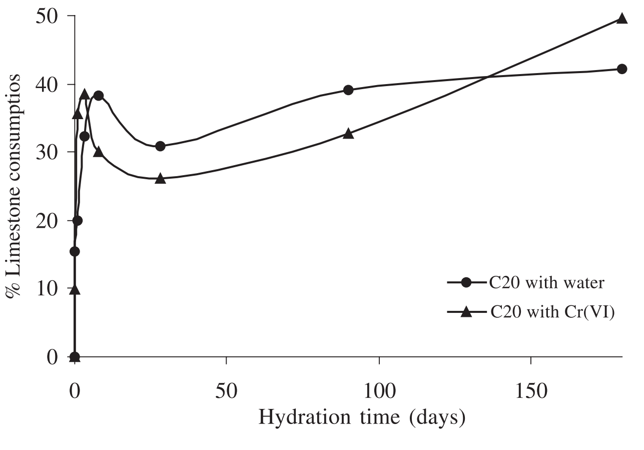

Fig. 3. Variation of percentage lime consumption with hydration time.

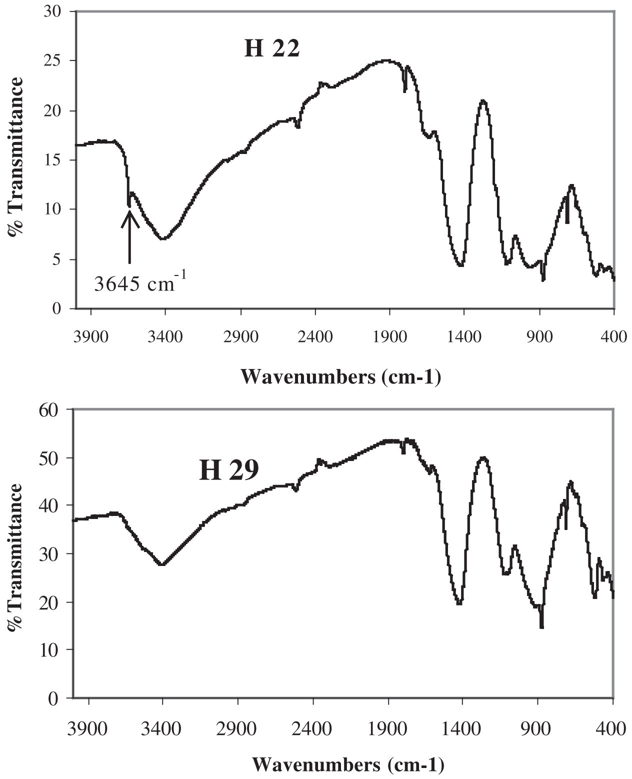

Fig. 4. FTIR spectra of H22 and H29.

3.2. Mechanical properties

The effect of the Cr(VI) presence on the compressive strength of pastes with and without limestone at 28 days is reported in Fig. 5.

At 28 days, C0 exhibited a lower value of compressive strength in Cr(VI) presence than in the corresponding reference (23%). This result coincides with that reported by Wang and Vipulanandan [18]. In C20 pastes, the compressive strength loss in the Cr(VI) presence was approximately 20%, with regard to C20 pastes without Cr(VI).

Reference paste suffered the highest decrease of compressive strength at 28 days in the Cr(VI) presence. The best results obtained for limestone pastes with Cr(VI) are possibly related to Cr phases formed at an early age.

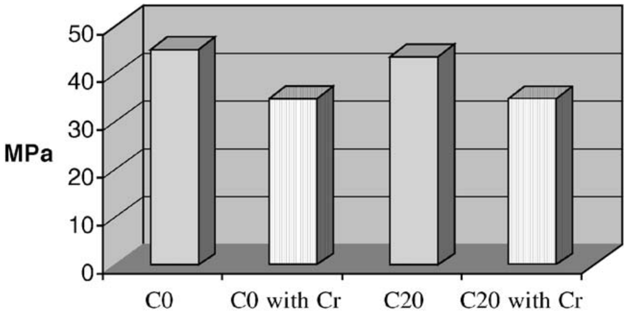

Fig. 5. Compressive strength of paste at 28 days (MPa).

3.3. Ionic conductivity test

As soon as cement is in contact with water, the superficial dissolution of cement starts and the ions go into the solution so the conductivity increases. Since the concentration of ions starts increasing, the conductivity also increases and reaches a maximum in a very short time (approximately 1 min) [24].

At that moment, the liquid phase becomes saturated with respect to Ca^{2+} and OH^{-} ions coming from silicate hydrolysis and the variation of the ionic conductivity depends only on the migration of these ions. Due to the slow nucleation mechanism of portlandite, from saturation and up to the precipitation, the process goes on until it has reached a balance with minimum variations of conductivity values [25].

Fig. 6 shows the variation of ionic conductivity with the hydration time obtained for C0 and C20 hydrated with Cr(VI) solution. The limestone incorporation is the cause of the smallest ionic conductivity in the C20 sample with regard to C0 at all times. Since $CaCO_3$ is practically insoluble in water, its contribution to the ionic conductivity is null and, in consequence, there exists a small quantity of ions in the solution for the substitution of almost 20% of cement for limestone fillers.

When C0 and C20 were hydrated in Cr(VI) solution, the measured conductivity was lower to the one calculated as it was expected according to the Kohlrausch's law (of the independent migration of ions), already used by other authors in this system [25]. This would show that there exist other ions or a bigger number of them that remain in the solution with regard to the pattern at the same age. In consequence, the hydration products are not precipitated at the same speed than in the reference ones. It can be inferred that early hydration is retarded, coinciding with that observed by XRD and FTIR.

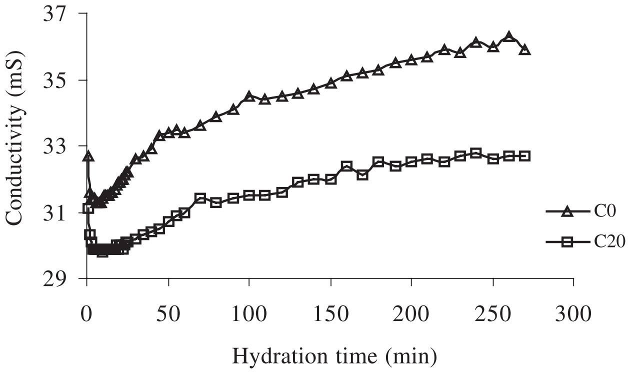

Fig. 6. Variation of electrical conductivity of cement pastes with hydration time.

Table 4
Concentration of Cr(VI) obtained by leaching at different times

Time	Water leaching		Acid leaching	
	ppm	% retained	ppm	% retained
C0				
1 month	208	90.0	604	71.0
3 months	50	97.6	420	79.8
6 months	72	96.5	430	79.3
C20				
1 month	128	93.9	650	68.8
3 months	124	94.0	510	75.5
6 months	132	93.7	630	69.7

Initial concentration = 2080 ppm.

3.4. Leachability

The results of leachability tests carried out in water and at pH = 3 solution for the hydrated C0 and C20 with Cr(VI) at different times, are shown in Table 4.

For the C0, the quantity of Cr(VI) leached diminishes with the hydration time. More hydration phases with high specific surface produced the biggest densification of microstructure, so more ions are caught and are chemically stabilized [7]. For all hydration times, the Cr(VI) retained is higher when the tests are carried out in water than in a solution of pH = 3.

In C20 pastes, the chromium percentage retained after leaching in water remains practically constant for all hydration times, being lower than for C0. However, considering that C20 has a percentage of substitution of 20%, in consequence, the quantity of available cement is smaller. It shows a bigger efficiency of Cr(VI) retention for cement, in the presence of limestone. This agrees with that observed previously, the formation of hydration products at early ages and the crystalline Cr–ettringite that incorporates chromium determine this behavior. The same situation is repeated for leaching at pH = 3.

The chromium percentages retained in cement structures reached high percentages in all samples. This shows that, in this studied condition and the time test, limestone cement shows a high capacity of Cr(VI) retention. When the cement matrix is used to confine Cr(VI) waste, it reduces the negative impact that this wastes have on environment and health.

4. Conclusions

- ✓ Limestone blended cement incorporates partially chromium through the chromium–ettringite formation.
- ✓ The calcium monocarboaluminate formation is also influenced by the Cr(VI) presence. Its formation is slower and the formation of intermediate phases at early ages that possibly incorporate chromium was detected.
- ✓ Chromium presence retards limestone Portland cement hydration, especially at early ages. XRD, FTIR spectroscopy and ionic conductivity test corroborated this phenomenon.
- ✓ In limestone blended cement, the presence of Cr(VI) reduced the compressive strength less than that in ordinary Portland cement.
- ✓ Leaching tests carried out in water and pH = 3 solution showed that limestone Portland cement matrix is an adequate place as well as ordinary Portland cement to confine Cr(VI).

References

[1] A.E. Lavat, M.A. Trezza, Estudio de la inmovilización de metales pesados en la matriz cementicia, 1st International Congress of Concrete Technology, AATH, Buenos Aires, Argentina, 1998, pp. 337–350.
[2] D. Stephan, H. Maleki, D. Knöfel, B. Eber, R. Härdtl, Influence of Cr, Ni and Zn on the properties of pure clinker phases: Part II. C_3A and C_4AF, Cem. Concr. Res. 29 (5) (1999) 651–657.
[3] D. Stephan, H. Maleki, D. Knöfel, B. Eber, R. Härdtl, Influence of Cr, Ni and Zn on the properties of pure clinker phases: Part I. C_3S, Cem. Concr. Res. 29 (4) (1999) 545–552.
[4] O.E. Omotoso, D.G. Ivey, R. Mikula, Quantitative X-ray diffraction analysis of chromium (III) doped tricalcium silicate pastes, Cem. Concr. Res. 26 (9) (1996) 1369–1379.
[5] J.H. Chen, Y.Y. Wang, C.C. Wan, D.C. Liou, MAS/NMR studies of the hydrations process of β-C_2S in the presence of chromium, Cem. Concr. Res. 24 (2) (1994) 319–324.
[6] C. Tashiro, J. Oba, The effects of Cr_2O_3, $Cu(OH)_2$, ZnO and PbO on the compressive strength and the hydrates of the hardened C_3A paste, Cem. Concr. Res. 9 (2) (1979) 253–258.
[7] C.-K. Park, Hydration and solidification of hazardous wastes containing heavy metals using modified cementitious materials, Cem. Concr. Res. 30 (3) (2000) 429–435.
[8] J. Pera, G. Thevenin, M. Chabannet, Design of a novel system allowing the selection of an adequate binder for solidification/stabilization of wastes, Cem. Concr. Res. 27 (10) (1997) 1533–1542.
[9] G. Kakaki, S. Tsivilis, A. Tsialtas, Hydration of ordinary portland cement from raw mix containing transition element oxides, Cem. Concr. Res. 28 (3) (1998) 335–340.
[10] V. Alunno Rosseti, F. Medici, Inertization of toxic metals in cement matrices: effects on hydration and hardening, Cem. Concr. Res. 25 (6) (1995) 1147–1152.
[11] M. Frías, M.I. Sánchez de Rojas, N. García, M.P. Luxán, Contribution of toxic elements: hexavalent chromium in materials used in the manufacture of cement, Cem. Concr. Res. 24 (3) (1994) 533–541.
[12] M. Frías, M.I. Sánchez Rojas, Determination and quantification of total chromium and water-soluble chromium contents in commercial cements, Cem. Concr. Res. 25 (2) (1995) 433–439.
[13] S. Sprung, Trace elements—concentration build-up and measure for reduction, Zem.-Kalk-Gips (Wisebaden) 41 (5) (1988) 251–257.
[14] J. Bensted, S. Prakash Varma, Studies of ettringite and its derivatives: Part II. Chromate substitution, Silic. Ind. 37 (12) (1972) 315–318.
[15] J. Bensted, S. Prakash Varma, Studies of ettringite and its derivatives, Cem. Technol. 3 (2) (1971) 73–76.
[16] A. Macias, A. Kindness, F.P. Glasser, Impact of carbon dioxide on the immobilization potential of cemented wastes: chromium, Cem. Concr. Res. 27 (2) (1997) 215–225.
[17] R. Fedman, V. Ramachandran, P. Sereda, Influence of $CaCO_3$ on hydration of C_3A, J. Am. Ceram. Soc. 48 (1) (1965) 25–30.

[18] S. Wang, C. Vipulanandan, Solidification/stabilization of Cr(VI) with cement: leachability and XRD analyses, Cem. Concr. Res 30 (3) (2000) 385–389.

[19] A. Macías, S. Goñi, A. Guerrero, E. Fernández, Inmovilización/solidificación de residuos tóxicos y peligrosos en matrices de cemento, Mater. Constr. 49 (254) (1999) 5–16.

[20] H.F.W. Taylor, The Chemistry of Cement, vol. II, Academic Press, New York, 1964.

[21] V. Bonavetti, V. Rahhal, E.F. Irassar, Studies on the carboaluminate formation in limestone fillers blended cement, Cem. Concr. Res. 31 (1) (2001) 853–859.

[22] J. Bensted, S. Prakash Varma, Some applications of infrared and Raman spectroscopy in cement chemistry: Part 3. Cem. Technol. 5 (5) (1974) 440–442.

[23] J. Bensted, S. Prakash Varma, Infrared and Raman spectroscopy in cement chemistry—miscellaneous applications. World Cem. Technol. 8 (1) (1977) 16, 18–20.

[24] N.B. Singh, R. Sarvahi, N.P. Singh, Effect of superplasticizers on the hydration of cement, Cem. Concr. Res. 22 (5) (1992) 725–735.

[25] S. Maximilien, J. Pera, M. Chabannet, Study of the reactivity of clinkers by means of the conductimetric test, Cem. Concr. Res. 27 (1) (1997) 63–73.