

Waste with chrome in the Portland cement clinker production

M.A. Trezza^{a,*}, A.N. Scian^{b,1}

^a *Facultad de Ingeniería-UNCPBA, Av. del Valle 5737, B7400JWI Olavarría, Argentina*

^b *Centro de Tecnología de Recursos Minerales y Cerámica, CONICET, UNLP, C^{no} Centenario y 506, 1897 Gonnet, Argentina*

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Abstract

Hazardous wastes, coming from industries are usually used in the Portland cement production in order to save energy, costs and/or stabilize toxic substances and heavy metals inside the clinker. This work focuses on the effect produced on the Portland cement clinker when it is obtained using tanned leather shavings whit chrome salts as part of the process. The raw materials were clinkered in laboratory with different percentages of shavings, which contained 2% of Cr₂O₃. DTA–TG of the raw mixtures was performed to evaluate the thermal behavior changes that can take place during the clinkering process, analyzing the crystalline phases obtained by XRD. The milling behavior of clinkers was studied, analyzing also the refractoriness variation on those clinkers. The chrome retention was evaluated by leaching tests. The structural modification determined by the chrome presence in the silicate structure brought consequences in the hydration speed, mechanical resistance and pore distribution. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

The tannery industry produces a great variety of wastes. In particular, the solid wastes coming from the leather tanning with trivalent chrome salts (scraps leather and shavings) need a special attention, due to the amount produced and the controlling agencies requirements for those wastes. This problem becomes more serious because of the great extent of this industry in Argentina, which processes 12 millions of bovine hides by year, generating an average 50,400 t of scraps and shavings [1], having a calorific value between 6700 and 7000 J/g.

Looking for solutions to these environmental problems the solidification/stabilization (S/S) technique was developed in order to improve the waste manipulation and specially to reduce their toxic components mobility. The Portland cement matrix and other puzzolanic materials have demonstrated to be a suitable place for the S/S of heavy metals, inorganic substances and organic compounds.

“Stabilization” means the techniques to reduce the potential toxicity of a waste product by converting its pollutants into a substance with lower solubility than before being processed, making it less movable or less toxic. The “solidification” on the other side, encapsulates the waste in a monolithic unit of high structural integrity. S/S refers then to the techniques or processes that simultaneously stabilize and solidify the waste considered.

The problem of the wastes with chrome (VI and III) has been extensively treated with this technique taking advantage of the hydration reaction of the Portland cement. Usually wastes are artificially incorporated to the mixing water in big quantities.

The experience in this field indicates that chrome is easily incorporated to the β-C₂S¹ and common Portland cement pastes, but this affects the characteristics and the hydration products of it [2–4]. In this regard it is well known that it retards the beginning and the end of the setting [5] as it restrain the β-C₂S hydration [6]. The S/S has been mainly related with the formation of Ca–Cr complexes [7], having also reported the formation of the phases such as: Ca₄Al₆O₁₂CrO₄ and Ca₆Al₄Cr₂O₁₅ [8]. Some authors consider that the ettringite (3CaO·Al₂O₃·3CaSO₄·32H₂O, AFt

* Corresponding author. Tel.: +54 2284 451055; fax: +54 2284 451055.

E-mail addresses: mtrezza@fio.unicen.edu.ar (M.A. Trezza), sciana@cetmic.unlp.edu.ar (A.N. Scian).

¹ Tel.: +54 221 4840247.

¹ Cement nomenclature used are C: CaO, S: SiO₂, A: Al₂O₃, H: H₂O, C₃S: 3CaO·SiO₂, C₂S: 2CaO·SiO₂, C₃A: 3CaO·Al₂O₃ and so on.

phase) participates in these mechanisms by substitution of Al (III) by Cr (III) and/or SO_4^{2-} by CrO_4^{2-} . Modified ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaCrO}_4\cdot 32\text{H}_2\text{O}$) has been detected by XRD [9–12]. Pera et al. [12] explains that the Cr (VI) immobility takes place by one or a combination of the following mechanisms: addition (Cr–C–S–H), substitution (Cr-ettringite, monochromealuminate) or precipitation of new compounds (calcium chromate, Na–Cr–AFt). The immobility efficiency of the heavy metals in the Portland cement matrix is connected with the microstructure of the hydrated paste, especially with the pore size distribution and porosity [13]. The incorporation of tannery shavings contaminated with Cr_2O_3 to the clinkering process is studied in this work, which not only contributes to the pollutant S/S but also brings part of the thermal energy required by the process due to the combustion of the organic part composing the shavings. Little is known in this regard but it was reported that the Cr_2O_3 goes into solid solution of the C_3S when it is incorporated in percentages up to 1.56 wt.% at 1450°C [14], others authors pointed out that its presence restrain the alite formation [15], consequently it has always influence on the C_3S structure and reactivity [16]. The results showed us that chrome would be incorporated to the vitreous and/or crystalline phase formed during reactions at high temperatures; then the Portland cement hydration would continue with the S/S process.

2. Experimental

2.1. Materials

2.1.1. Raw material

The raw material used in this work corresponds to an industrial mix provided by a local cement industry. Its chemical analysis, made by X-ray fluorescence is shown in Table 1.

The material was also characterized by XRD. The crystalline phases observed on the majority were calcite (CaCO_3) and quartz (SiO_2). Muscovite [$\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$] was detected among the minority crystalline constituents.

2.1.2. Shavings

The chemical analysis of the main components of the shavings used in this study showed the presence of 2% chrome, expressed as Cr_2O_3 . The ashes, obtained at 1000°C , were characterized by XRD, and Na_2SO_4 was also found as it can be observed in Fig. 1.

The characterization by infrared spectroscopy (FTIR) permitted to corroborate that observed by XRD. The IR spectrum

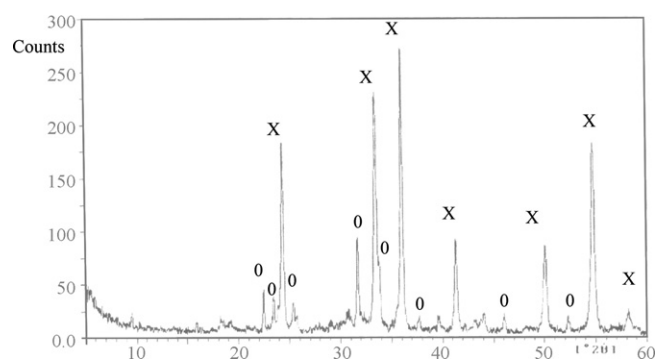


Fig. 1. XRD of the ashes of shavings with chrome. Cu $\text{K}\alpha_1$ radiation [X = Cr_2O_3 , 0 = Na_2SO_4].

of the leather shaving ashes compared with the spectra of pure Cr_2O_3 and Na_2SO_4 ones, pointing out a total coincidence.

2.2. Preparation of the samples

2.2.1. Preparation of clinkers samples

Due to the high percentage of chrome and the toxicity of these shavings they were incorporated in low proportions to the cement raw materials to stabilize it. The percentages of the study were fixed in 0.4, 0.6 and 0.8% (V1, V2, V3) of shavings in weight as it is shown in Table 2. A sample with 6% of shavings (V4) was prepared to study the tendency.

To prepare the different samples the shavings and the raw material were quantitatively weighed and they were dried mixed; 0.4% of ashes were added in V4, the equivalent to 6% in weight of shavings.

The samples were transformed into pellets and then clinkered in a furnace-muffle, with a heating rate of $10^\circ\text{C}/\text{min}$ up to 1450°C , and maintaining this temperature during 1 h. Cooling rate was also controlled to ensure that the suitable hydraulic phases remain at ambient temperature.

The different synthesized clinkers were milled in a Herzog HSM 100 oscillating mill with vanadium steel chamber. Equal quantities of each clinker were milled at equal times to make the test comparative. The milling time was selected in order to that the specific surface may remain within the range used in ordinary Portland cements.

On the milled clinkers the following tests were performed: specific surface by the Blaine method (IRAM 1623, ASTM C-204), measurement of Pyrometric Cone Equivalent (PCE) (IRAM 12507, ASTM C-24), differential thermal analysis (DTA–TG), X-ray diffraction (XRD) and infrared spectrometry

Table 1
Centesimal composition of the raw materials, as oxides

CaO	43.52
SiO_2	14.28
Al_2O_3	3.12
Fe_2O_3	2.37
K_2O	0.69
Na_2O	0.03
SO_3	0.49
LOI	34.9

Table 2
Percentage of waste incorporated and designation of the samples

Designation	Shavings, % (w/w) (g shavings/100 g raw materials)
V0	0
V1	0.4
V2	0.6
V3	0.8
V4	6.0 ^a

^a Equivalent to 0.4% de shaving ashes.

(IR). Chrome (VI) lixiviation analysis was included according to the toxicity characteristics leaching procedures (TCLP).

Those tests were carried out using a NETZCH STA 409, DTA–TG equipment, a PHILIPS PW 3710 diffractometer and a NICOLET spectrophotometer, FTIR–Magna 500. The Cr (VI) was colorimetrically determined using a METROLAB 1700 photo-colorimeter.

The measure of compression resistance were carried out using a modified J.J. INSTRUMENTS machine, and by the porosimetry study were used a Carlo Erba Instrumental mercury intrusion porosimeter.

2.2.2. Preparation of hydration samples

The different samples with tannery waste additions were hydrated following the $w/c = 0.4$ relation. At different study ages (1, 3, 7, 28, 60 and 180 days) pastes were milled in the presence of acetone and analyzed by XRD and IR. The study was completed following the early hydration (first 48 h) using a differential calorimeter.

Standard probes were also prepared to measure compression resistance at different ages (7, 14 and 28 days). Besides, porosimetry studies of mercury intrusion and DTA–TG were performed on 28 days aged probes.

3. Results and discussion

3.1. In the clinkers samples

3.1.1. Specific surface area

The different clinkers were milled as it was indicated in Section 2.2.1 and their specific surface area was measured by a Blaine permeabilimeter; the results are shown in Table 3. The clinker behavior during milling is closely related with the texture and crystalline structure of the phases formed during clinkering [17]. Consequently the higher values of the specific surface area of the samples with chrome shavings compared with that of the reference sample showed that the milling was easier for the first ones. We can say that clinker with chromium have structures with bigger percentage of amorphous phases and requires in general less milling energy that the reference sample without chrome.

Our previous works on this subject make us think that the chrome oxide incorporated through the shavings had determined some modifications in the crystalline structure that led to an easier milling even if it is not a function of the percentage added [18]. The maximum value of specific surface area was obtained for the V2 sample, and afterwards it could be observed that this

Table 3
Blaine specific surface area of different clinkers

Sample (m ² /kg)	Specific surface area (m ² /kg)
V0	302
V1	317
V2	320
V3	315
V4	311

effect decreased, even for V4 sample where the chrome oxide percentage incorporated is 10 times higher. The system shows so an effect when adding up to a certain amount of impurities (up to 0.6% in this case), showing then that this effect changed round when adding higher percentages.

Nevertheless, it must be also considered that the shavings are mainly formed by combustible material (about LOI 93%, on dried base) and the shavings were incorporated to the raw material. In consequence, after clinkering it is likely to obtain a highly porous clinker that makes milling easier, which what the milling easiness would not be only related with the crystalline phases formed. However, this effect, if it exists, even though it can have an influence, is not either a function of the added percentage of shavings.

3.1.2. Analysis of the clinkers by XRD/IR

After analyzing the diffractograms and IR spectrums of the different clinkers no differences were observed that could indicate the formation of new phases related with or inhibited by chrome.

However, when analyzing comparatively the diffractograms it is worth highlighting the inversion of the relative intensities found for 2θ values (Cu $K\alpha_1$ radiation) of the C_3S main peaks. It is also important to observe the position shift of these peaks to lower angles (higher d) when going from V0 to V4, this is to say when increasing the percentage of impurities incorporated to the system. Table 4 shows the mentioned shifts.

The 2θ values corresponding to the four more important peaks of C_3S obtained for all samples with shavings were lower than that of the reference sample and even if they are not directly related with the percentage added they are necessarily determined by its presence. Fig. 2 shows the variation of the spacing corresponding to the plane (225) expressed as with a 2θ angle (Cu $K\alpha_1$ radiation) versus the percentage of shaving added.

This modification of the cell parameters is attributed to the addition of chrome impurities to the silicate nets, forming a solid solution with them that would indicate the pollutant stabilization.

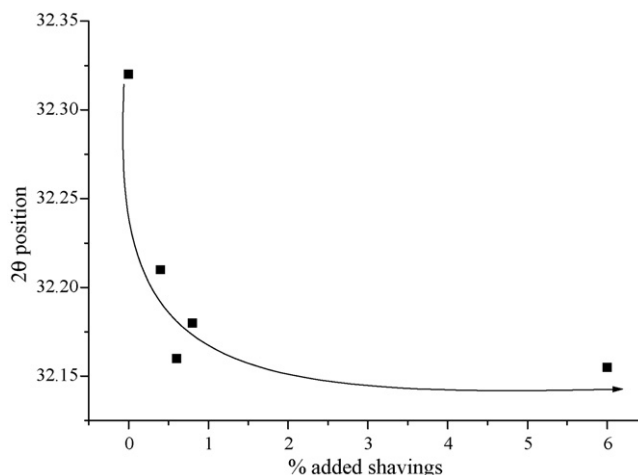


Fig. 2. The 2θ angle shift, corresponding to the (225) plane vs. % of shavings in the clinker.

Table 4
Position in 2θ (XRD– $\text{CuK}\alpha_1$) of the main peaks of the tricalcium silicate (C_3S) for the different samples

	2θ	I. relativity (%)	2θ	I. relativity (%)	2θ	I. relativity (%)	2θ	I. relativity (%)
Bibliography	29.530	75	32.283	85	32.708	75	34.442100	100
V0	29.530	72	32.320	100	32.680	95	34.470	78
V1	29.455	51	32.210	100	32.615	77	34.390	84
V2	29.420	70	32.160	100	32.550	96	34.335	97
V3	29.420	86	32.180	95	32.555	100	34.360	93
V4	29.400	52	32.155	86	32.560	100	34.345	79.5

3.1.3. Pyrometric cone equivalent (PCE)

Measuring only the PCE does not give much information about the nature of the clinkering or the characteristics of the phases formed. However, it can help to know, in a comparative way, the effect of the impurities on the firing process.

The reference sample has a PCE of 1525°C ; this indicates that the mixing reaches a softening and the cone goes down at that temperature. As regards the samples with addition of shavings we obtained the results showed in Table 5.

As it can be observed in Table 5 the addition in small amounts of shavings (0.4%, V1 sample) seems not to affect the PCE, but if the percentage added is greater (up to 0.6%, V2 sample) they act as melting decreasing the temperature to 1520°C . This effect, which is not a function of the percentage of impurities, could be the reason of the crystallinity differences found especially for V2–V3 and one of the facts that determined the easier milling.

In the V4 case (6%) the effect was the opposite one, this can be attributed to the fact that, when increasing noticeably the percentage of impurities like Cr_2O_3 , mayor melting point is achieved and greater diffusional difficulties are generated caused by the great addition of a highly refractory oxide.

3.1.4. Thermal analysis (DTA–TG)

Differential thermal analysis and thermogravimetric analysis were performed in reverse order (heating–cooling) and under the same thermal conditions than those used for elaborating clinkers on the different crude dust samples with and without the addition of shavings. The following was the temperature program used:

From 20 to 1450°C — $10^\circ\text{C}/\text{min}$ rate, maintaining this temperature during 1 h. Then from 1450 to 1350°C — $30^\circ\text{C}/\text{min}$ rate, and 1350°C to room temperature— $10^\circ\text{C}/\text{min}$ rate.

In the DTA–TG diagram for the reference sample (Fig. 3), during heating a first endothermic peak of great magnitude appears at 910°C corresponding to the limestone decomposition.

Table 5
Pyrometric cone equivalent

Sample	PCE ($^\circ\text{C}$)
V0	1525
V1	1525
V2	1520
V3	1520
V4	1535

As soon as the decarbonation has been overcome and always during heating, the reaction zone of CaO with silicates and aluminosilicates appears as an endothermic band within the 950 – 1000°C zone. In the samples analyzed it is not well defined as a peak because these reactions in solid state are mostly of diffusional control. Flat and wide bands are generated instead of peaks.

When temperature goes on increasing an endothermic peak at 1349°C is observed for V0, caused by the melted phase formation (clinkering).

During cooling in the DTA curve only one exothermic sharp peak at $1286,6^\circ\text{C}$ could be observed in the reference sample, due to the solidification of the liquid phase formed during clinkering [19].

The DTA–TG studies on the samples with different additions show the same general aspect but with slight shifts in the clinkering and crystallization temperatures, as it is shown in Table 6.

The carbon dioxide release of the carbonates depends not only on the temperature but also on the particle diameter of the limestone; consequently, the presence of doublets or triplets in Table 6 would indicate grains of different diameters that decompose at different temperatures.

The slight decrease of clinkering temperature compared with the reference sample, and the solidification temperature variation that decreases as function of the percentage of shavings added, indicates a shift of the clinker formation temperature and the temperature until the melted phase remains. This determines the structural modifications detected by XRD, different PCE

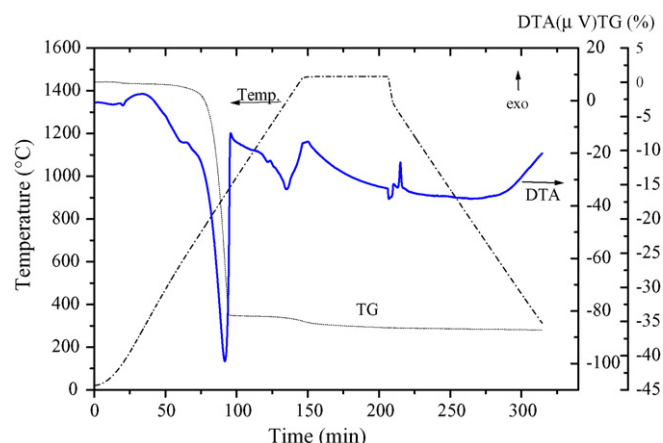


Fig. 3. DTA–TG–DTG diagrams for reference (V0).

Table 6
Reaction temperatures for different samples

Sample	Decarbonation temperature (°C)	Reaction temperature (exothermic, °C)	Clinkerization temperature (°C)	Solidification temperature (cooling, °C)
V0	910.0	1233.0	1349.0	1286.6
V1	911.1	1235.7	1346.8	1287.6
V2	897.5 (T)	1238.1	1348.0	1287.3
V3	910.1	1232.3	1346.5	1286.9
V4	858.8 (D)	1235.4	1341.5	1281.0

D: doublets; T: triplets.

temperatures and which consequently cause the specific surface variation of the milled material compared with the reference sample.

3.1.5. Leaching

The leaching chrome was evaluated on the different samples of the synthetic clinkers after 18 h extraction with a pH 5 leaching solution.

All the chrome was oxidized to Cr (VI). The Cr (VI) reacts with the 1,5-diphenylcarbazide to form 1,5-diphenylcarbazone, which forms a red complex (0.01–0.50 mg/l chrome) [20,21], then the Cr (VI) was colorimetrically determined.

When performing this study on the shavings in their natural state, the leaching percentages were of 1.17% over all the chrome existing. Taking into account that all the chrome present in the sample is found as Cr (III), the low solubility of this specimen in the leachant liquid can be justified obtained value.

The results obtained for the clinkers are briefly shown in Table 7, where also the chrome retained percentages as function of the additions made for each sample has been calculated.

The percentages of chrome leaching in the clinkers overcome those obtained for the natural shavings, this indicates the presence of a greater quantities of soluble chrome. This is due to the clinking process in which the oxidant atmosphere (electric furnace) would determine the oxidation of Cr (III) to Cr (VI). Whereas, in the industrial process and as consequence of the partial reducing atmosphere (combustion), the clinker goes out of the fire zone with Cr (III) and Cr (VI) as part of the equilibrium.

Anyway, the percentages of chrome retained are high enough to consider the cements matrix as a suitable place for the S/S of this metal.

In Argentina, the 24.053 Law regulated by the Decree 831/93 [22] states in the annex VI the stipulated limits for the chemical parameters of waste mud containing dangerous substances. This parameter will be determined on the leaching obtained after putting under the extraction processing a mud sample, which it is explained in the same annex. The aim of this test is to reproduce

the most adverse condition under which the pollutant studied would be and that would eventually pass to the leaching. The maximum limit is 5 mg Cr/l of leachant. Though cement is not a waste, these limits were used as reference since there is not a particular legislation.

The last column Table 7 shows the leaching results as mg of chrome/l of leachant in order to establish if the leached chrome tenors are or not within the limits permitted.

In our case the values remain always under the limit permitted, even for V4. This indicates that the addition of shavings with chrome coming from tannery wastes to the clinking process is a suitable way for the S/S of this waste product.

3.2. The hydration samples

3.2.1. Differential calorimetry

In Fig. 4 the calorimetric curves corresponding to the studied series are presented, where it can be comparatively observed the differences between them and with the reference. The first peak is generated as soon as water is put in contact with the

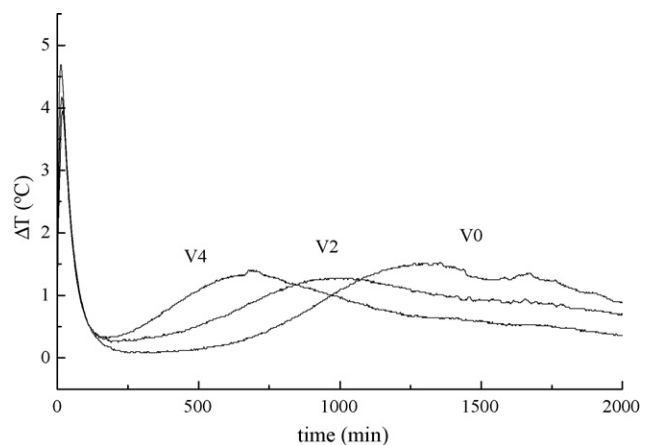


Fig. 4. Calorimetric curves corresponding to V0, V2 and V4 samples.

Table 7
Chrome lixiviation

Samples	Incorporated chrome, ppm (mg Cr/kg clinker)	Lixivate chrome, ppm (mg Cr/kg clinker)	Retained chrome (%)	Cr/l, mg (mg chrome/l of lixiviation liquid)
V1	84.15	Nd	–	0.17
V2	126.31	41.42	67.21	0.824
V3	168.42	37.98	77.45	0.7597
V4	1263.16	242.55	80.80	4.851

clinker. Heat developed corresponds to the wetting and surface solubilization of the particles. Water is saturated by calcium hydroxide produced by the C₃S hydrolysis and calcium aluminate. Together with the dissolution of these ions, the alkaline hydroxides of the clinker are quickly dissolved. Kinetics of this process is fast and the control is chemical.

The little differences observed in this first hydration stage can be attributed to a lower surface activity as the specific surface decreases; however, there is no exact correlation in this aspect. This stage is of chemical control and even though it is strongly connected with the reaction surface exposed as it has already mentioned, it cannot be ignored the effect produced by the presence of impurities incorporated.

It can be observed then a period of apparent inactivity, known as dormant period. This stage determines that the cement remains in plastic state for some hours. From a chemical point of view, it is caused by the need to have a determined concentration of ions in solution before starting the precipitation of the hydration products. The end of the dormant period determines the beginning the setting of Portland cement as it is defined by test methods where the time at which the pure cement paste shows a resistance to particular deformation arbitrarily defined [23] (for example, by the Vicat test).

The differences found for different samples are remarkable as regards the duration of this sleeping period. As the amount of shavings with chrome added increases, this period significantly decreases, pointing out so a decrease of the time when the setting starts, what has a great technological importance.

Previous to the second maximum of the hydration curves, an acceleration period can be observed that determines in its maximum point the end of the formation processes of hydrate nuclei and the beginning of the gain of paste resistance due to the growing and crossing of the hydrates formed. For this reason this maximum is frequently correlated with the final set [24]. This process chemically controlled is caused by the formation of hydration products from silicates.

Apparently [25], the CH crystallizes from the solution, while the C–S–H is develops at de surface of the C₃S grain and forms a coating covering them. Thus, when the hydration goes on, the thickness of the hydrate layer increases and forms a barrier, between the material without hydrating and the water. For this reason the water must diffuse to reach the anhydrous material and the ions diffuse in the opposite direction to reach the growing zones, this determines a deceleration period chemically and diffusively controlled. The movement of ions through the C–S–H layers determines the reaction rate of this stage, which is controlled by diffusion. These processes are lower as the layer

thickness increases; consequently, they are completed at a very long delay. This stage determines the resistance gain rate.

For the cases studied the appearance of the second maximum in the calorimetric curves of Fig. 4 (final set) moves forward as the chrome percentage added increases, clearly indicating a greater initial resistance gain rate compared with the reference. The chrome presence undoubtedly accelerates the early hydration processes probably caused by the viscosity decrease of the gels formed (what allows a greater diffusion rate) or by the generation of nucleation points from which hydrate crystals grow up and this phenomenon is function of the percentage added.

3.2.2. Analysis by XRD/IR

When the XR diffractograms and IR spectra of the clinkers hydrated at different ages are analyzed, no significant differences and nor formation of phases different from the reference were detected in the samples with shaving. The hydration rate was comparatively followed according to the height of the Ca(OH)₂ main peak formed during hydration of silicates. By this technique and at the studied ages they were no differences detected in the mechanism and/or hydration rate as consequence of the addition.

3.2.3. Leaching

Taking into account that the hydrated cement is the normal state of the material in contact with the environment, chromium leaching from different samples were evaluated after 60 days hydration with w/c = 0.4. The test conditions mentioned in 3.1.5 were kept. The results are shown in Table 8.

For all the samples, the leaching values (mg Cr/l of leachant) were below the limits accepted and discussed for the clinkers.

The results obtained do not represent the possible transference of ions Cr⁺⁶/Cr⁺³ from the concrete structure to the ground as this will depend on the characteristics of the soil and the surrounding conditions. Also it must be considered that the test conditions are much more aggressive than the ones which the concrete in service could suffer.

3.2.4. Compression resistance

The resistance compression results, obtained like the media of five tests, aged 7, 14 and 28 days are shown in Table 9.

At 7 days the reference showed a resistance value far higher than the other samples with chrome addition and this fact remained at 14 days even when the differences are lower. Within the group of samples with chrome it was observed that resistance increases with the percentage of shavings added when this addition is made in small amounts. However, when the percentage is

Table 8
Chrome lixiviation on samples hydrated for 60 days

Samples	Incorporated chrome, ppm (mg Cr/kg clinker)	Lixivate chrome, ppm (mg Cr/kg clinker)	Retained chrome (%)	Cr/l, mg (mg chrome/l of lixiviation liquid)
V1	84.15	28.69	66	0.29
V2	126.31	40.84	68	0.41
V3	168.42	61.44	64	0.61
V4	1263.16	398.50	68	3.98

Table 9
Compression resistance of the samples after different hydration times (MPa)

Days	V0	V1	V2	V3	V4
7	28.6	23.2	25.4	26.0	23.2
14	33.1	27.2	27.6	27.1	25.0
28	33.8	33.7	37.5	43.2	34.2

very high the effect was the inverse and consequently V4 showed a resistance value lower than that expected.

This lower resistance at early ages did not seem probable from the results obtained by differential calorimetry which showed a greater early hydration rate with the increase of the percentage of shavings and greater than V0. Besides, all samples with additions had greater specific surface (see Section 3.1.1), what usually helps the first hydration processes. Obviously, this effect only affects the beginning and end of setting and it does not mean any correlation with the resistance at longer ages.

At 28 days of hydration the samples showed an increase on mechanical resistance from V1 to V3, even though the V0 and V1 values were almost similar. For V4 the values feel again but they stayed over V0. So the same tendency than that of 7 days remained, this is to say that the resistance increased with the percentage of shavings added (V1 to V3) and V4 showed a lower resistance value and similar to V1.

In other studies [18] a similar phenomenon was observed, the impurities added to the system generate a mineralizer effect that improves the system properties with the percentage added, but up to a certain degree where the effect becomes the contrary one.

3.2.5. Porosimetry

The porosimetry tests were performed on hydrated samples ($w/c = 0.4$) for 28 days. Many authors [26,27] agreed that the pore size distribution is the better criterion for evaluating the characteristics of the capillary holes bigger than 50 nm diameter in a hydrated cement paste. This porosity is detrimental to the resistance and impermeability, while the holes smaller than 50 nm have greater influence on the contraction by drying and the creep. The tested samples did not practically show macroporosity between 30 and 5 μm (30,000 and 5000 nm radius).

Fig. 5 shows the porosity results of the different tested samples within the range 5–10,000 nm (50–100,000 Å) and the 25 nm radius line were remarked (50 nm diameter).

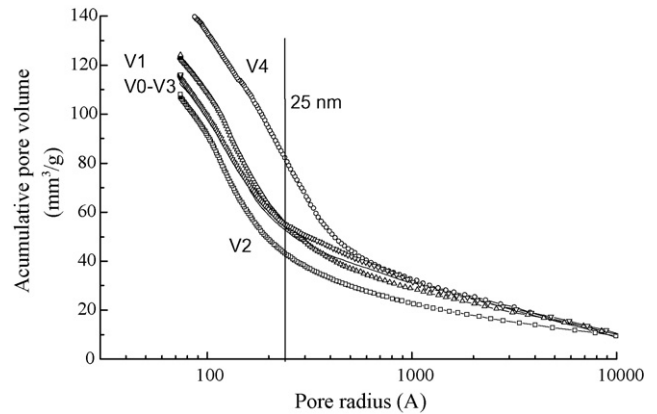


Fig. 5. Pore size distribution of V0, V2, V3 and V4 samples hydrated for 28 days.

In the zone lower than 25 nm radius (250 Å) the samples can be grouped in three types of behavior: (i) V2 sample presents the lower porosity, (ii) V4 sample with a great amount of pores lower than 25 nm radius and (iii) the V0, V1 and V3 set presenting similar characteristic between them and intermediate as regards the previous ones but with a slight tendency to greater microporosity for V1.

Over 50 nm all the samples have similar behavior except for V2 that showed lower values.

3.2.6. Differential thermal–thermogravimetric analysis (DTA–TG)

The 28 days hydrated samples ($w/c = 0.4$) were analyzed by DTA–TG at a heating rate of 10 °C/min up to 700 °C.

Table 10 shows the results obtained for the different samples analyzed.

Two endothermic peaks well defined were detected, corresponding to the hydration of the C–S–H gels (first peak), and to the CH decomposition (second peak). The first one was observed in the 130–200 °C zone [28–30] like a wide band that shifts to greater temperatures with the presence of chrome; according to the references [31] the rounded shape observed in this peak (not showed as graphic) is typical of substances that loose water without suffering a significant structural change [24]. This change was accompanied by a great mass loss. When comparatively observing the results obtained, it was only registered a slight variation of the mass lost by the different samples at these temperatures. The mass loss corresponding to the gel dehydration is greater in the series with shavings than in V0; however, the

Table 10
DTA–TG data of 28 days hydrated samples

Sample	Δm (%) (total)	First peak DTA (C–S–H) (°C)	Second peak DTA (CH) (°C)	First peak TG (C–S–H)		Second peak TG (CH)	
				Δm (%)	T (°C)	Δm (%)	T (°C)
V0	24.21	135.7	531	13.6	125.8	10.6	524.9
V1	25.97	142.5	533.1	15.6	125.6	10.4	527.0
V2	26.10	138.0	532.5	15.6	125.8	10.5	526.3
V3	24.92	141.4	528.9	14.8	129.1	10.1	523.0
V4	25.03	143.0	529.3	15.1	129.0	10.0	522.7

Δm = mass variation.

amount of gel formed is not a function of the percentage of impurities present. There is no correlation, at this point, because the specific surface area of the original hydrated materials also plays an important role.

The second endothermic peak observed at about 530 °C is attributed to the crystalline CH decomposition produced by the hydration of the silicate phases of the clinker [31,32]. The mass loss that goes with this decomposition can be related with the advance of the hydration. In this case there are no significant differences between the different tested samples.

In Table 10, the temperatures of the DTA peaks are slightly higher than the TG ones due to the thermal inertia of the process.

In general, the results obtained in the DTA–TG tests at 28 days of hydration, did not allow detecting any difference that could be related with the other parameters analyzed.

4. Conclusions

The lixiviation tests showed that the addition of shavings with chrome coming from tannery wastes to the clinkering process is a suitable way to the S/S of this pollutant.

However, it is evident that in the clinkering process part of the Cr (III) oxidizes to Cr (VI) with the subsequent increase of the mobility of this ion as it can be deduced from the retention percentages both in the clinkers and in the hydrates samples. In spite of this, the immobilization reached maintains the values of leached chrome under the permitted limits.

The addition of leather shavings containing chrome in the raw materials used in the production of Portland cement clinkers produce modifications in the crystalline characteristics of the main phases of the clinker. That causes a modification of the cell parameters of the main crystalline phases indicating that chrome enter in the net producing a stabilization of this pollutant.

The hydration study of the clinkers obtained with the addition of shavings with chrome showed an acceleration of the initial hydration speed (first 48 h) affecting the beginning and the end of the setting time. This change increases with the percentage of the shavings added.

The resistance obtained for pastes at 7 and 14 days show a variation as function of the percentage added but with values lower than the reference. At 28 days the tendency remains, but the values observed are greater than the reference. V4 must be excluded of the tendency observed, which showed an anomalous behavior with resistances that decrease in relation with V3 and are similar to the reference with time.

When the percentage of shavings added is 0.6% (V2) there were better distribution and pore volume results. Apart from that there was not a correlation between this parameter and the percentage added, and the compressive strength at 28 days.

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