

The Effect of Cement Hydration on the Release Mechanism of Soluble Chromates

M. Magistri¹, T. Cerulli¹, D. Padovani¹, F. Cella¹, A. Lo Presti²
¹Mapei S.p.A., Milan, Italy; ²University of Milan, Milan, Italy

The presence of soluble chromates in Portland clinker represents a serious problem in cement manufacturing: several patents have been presented dealing with the production of chromates-free cements. AFm phase and ettringite play an important role in the release of chromates. The immobilisation/release mechanism of soluble chromates has been studied, considering the hydration of synthetic C₃A in presence of sulphates and the synthesis of AFm phases directly in solution, by chemical reaction of alkaline aluminates and Ca²⁺. The effects of the presence of cement additives, fineness, type of calcium sulphate have been taken into account. Surprisingly, we have evidence that several factors (e.g. some cement additives without red-ox properties) can strongly modify the amount of soluble chromates released in solution by cementitious systems, we suppose by their effect on the equilibria between AFm phase and ettringite. These results have been verified on clinkers and cements of industrial production.

1. Introduction

The raw material for grey Portland cement manufacturing can contain Cr(III). Due to the highly oxidizing and alkaline conditions of the kiln, during clinker production it is partially converted to hexavalent chromium and probably fixed as alkaline or calcium chromate (Na₂CrO₄, K₂CrO₄, CaCrO₄). As a result, the Portland clinkers and cements contain soluble chromates (usually in the range of 5 – 20 ppm or mg/kg, while the total chromium can reach the 200 ppm) that are reported to cause skin irritation (allergic contact dermatitis). This is the reason why the European Community has recently introduced the obligation (Directive 2003/53/EC) to maintain the level of soluble chromates below 2 ppm [1]. The reduction of soluble chromates (obtained with the addition of stannous or ferrous salts during cement grinding) has a great impact on cement industry, and some European Company reports a total cost of about 10-15 million €/year.

The interactions between hexavalent chromium and cement hydration have been studied from the point of view of heavy metals immobilization and waste managements. AFm phases and ettringite are reported to be able to immobilize chromates [2, 3]. H. He and H. Suito studied the immobilization of Cr(VI) by calcium aluminates and sulphoaluminates [3]. By hydrating tricalcium aluminate in chromium containing solution they

found a complete fixation of chromium after six hours. The main hydration products were C_3AH_6 and C_4AH_{19} and it was possible to verify (using a microprobe analysis) that the chromium was present only in the C_4AH_{19} . The authors concluded that this phase is responsible for the immobilization and that the chromate takes the place of one of the hydroxide ions in the coordination sphere of aluminium. It is also known that the chromate, having the same charge and a similar ionic radius of sulphate, can have a similar behavior and give ettringite-like structures. The chromate analog of ettringite has been studied by several authors. Teramoto and Koie [4], studying the effect on cement hydration of several hazardous elements, noted the formation of an ettringite-type phase containing chromate. Poellman et al. [5] synthesized a chromate substituted ettringite and studied the solid solutions of sulphate and chromate ettringite. Perkins, in his Ph.D. work [6], synthesized the chromate analogous of ettringite and measured its solubility after a set of dissolution and precipitation experiments. On this basis, he evaluated the solubility product and several thermodynamic properties (free energy and enthalpy of formation).

Only a few works have applied the same concept to the release of chromates from cement itself [7] and the results obtained are the following:

1. The amount of chromates released from a clinker and from a cement produced with the same clinker can be very different: the presence of gypsum has a great influence.
2. Pure tricalcium aluminate fully immobilizes hexavalent chromium from an aqueous solution while a mixture of C_3A and gypsum does not.
3. The immobilization of chromates by C_3A is reversible: if the amount of sulphates in solution increases, the chromium already immobilized is newly released.

In this paper we present further results. We started by verifying the effect of fineness, type and amount of gypsum and presence of additives on chromium immobilization by pure C_3A . Afterwards we took into account the release of chromates from a real cement and finally we present an hypothesis about the chromate immobilization/release mechanism.

2. Experimental

All chromium concentrations are expressed in mass ppm Cr(VI) (mg/kg). The quantification were performed with visible spectroscopy (Thermo Evolution 300 UV-Visible Spectrophotometer), after acidification of aqueous solutions and reaction with diphenylcarbazide. The absorbance at 540 nm is proportional to the concentration of Cr(VI). The calibration curve was prepared with solutions of potassium dichromate. In the case of clinker and cement, the determination of soluble chromates was performed by adding under magnetic stirring 50 g of cement to 50 g of distilled water. After 15' the suspension is filtered under vacuum, diluted

and analyzed. The European Standard Test Method EN 196-10 (determination of water soluble Cr(VI) content of cement) is based on a similar procedure and reports a standard deviation for reproducibility of $\pm 0,40$ ppm for cements with 0-5 ppm soluble Cr(VI). According to our experience, we can consider a reproducibility of $\pm 0,50$ ppm for cements containing 0-20 ppm Cr(VI).

2.1 Tricalcium aluminate. Pure tricalcium aluminate was prepared by heating at 1400°C a mixture of analytical grade CaO and Al₂O₃ in stoichiometric amount and characterized by X-Ray diffraction (PANalytical X'Pert Pro theta-theta diffractometer, Cu K α radiation). Three samples of C₃A were ground in a mortar at different fineness, expressed in terms of particles size (samples A < 180 μ m, B < 90 μ m, C < 63 μ m).

2.1.1 Effect of fineness. The following experiment was performed: 2,5 g of C₃A were added under magnetic stirring to 50 g of water containing Cr(VI). At fixed interval, the suspension was sampled with a syringe, filtered and the amount of chromium in the solution analyzed. For each sample (A, B and C) we used a starting chromium concentration of 1000 ppm, prepared by dissolving the corresponding amount of potassium dichromate in distilled water.

2.1.2 Effect of sulphates and additives. We chose three different kinds of calcium sulphate: β -hemihydrate, gypsum and anhydrite. The solubility kinetics of each sample were evaluated by measuring continuously the electrical conductivity (conductivity-meter WTW LF 538) of a suspension of 10 g of calcium sulphate in 200 g of distilled water at 23°C.

2,5 g of C₃A were mixed with a different amount of each type of calcium sulphate and then added, under stirring, to a 50 g solution of 10 ppm Cr(VI). After 10 minutes the suspension was filtered and the hexavalent chromium in solution evaluated.

We repeated the same experiment (with calcium sulphate dihydrate) by adding in the water 1% triethanolamine and 5% trisodium citrate (mass percent respect to C₃A).

2.2 Clinker and cement. We obtained a sample of ordinary Portland clinker from an Italian cement company. The chemical composition was evaluated according to the EN 196-2 Standard Test Method and the mineralogical composition was calculated according to Bogue and estimated with XRD/Rietveld refinement (GSAS software [8]).

2.2.1 Effect of fineness, sulphates and presence of additives. Four samples of the clinker were ground in a ball mill to different fineness, evaluated with specific surface measurement (Blaine, according to EN 196/6 Standard Test Method). For each fineness, several samples of cement were prepared by mixing the clinker with different amounts of gypsum and the level of soluble chromates evaluated. Some experiments were repeated by adding in the water 0,1% triethanolamine and 0,5% trisodium citrate.

2.3 Study on the immobilization/release mechanism. We performed the following synthesis: 5 g of calcium nitrate tetrahydrate are dissolved in 70 ml of distilled water. The solution is then poured in a three-necked, round bottomed flask. The flask is equipped with a dropping funnel and a pH meter. The third neck is connected to an automatic titrator. The pH is adjusted to 12 with a few ml of a calcium oxide suspension (40 g/l). Under magnetic stirring, a solution of 4 g sodium aluminate in 200 ml water is slowly added with the dropping funnel, while the pH is kept constant at 12 with a suspension of 40 g/l of CaO automatically dropped by the titrator. This correction is necessary because the sodium aluminate, due to its amphoteric character, tends to lower the pH. The precipitate is then filtered under vacuum, washed with water, quenched with methyl alcohol and dried. The same procedure is repeated adding 4 g of potassium chromate in the flask together with the calcium nitrate. Both precipitates are characterized by X-ray diffraction (XRD), thermogravimetric analysis (thermo-microbalance Netzsch mod. TG 209 *F1 Iris*), chemical analysis and infra-red spectroscopy (Nicolet 6700 FT-IR, ADR mode).

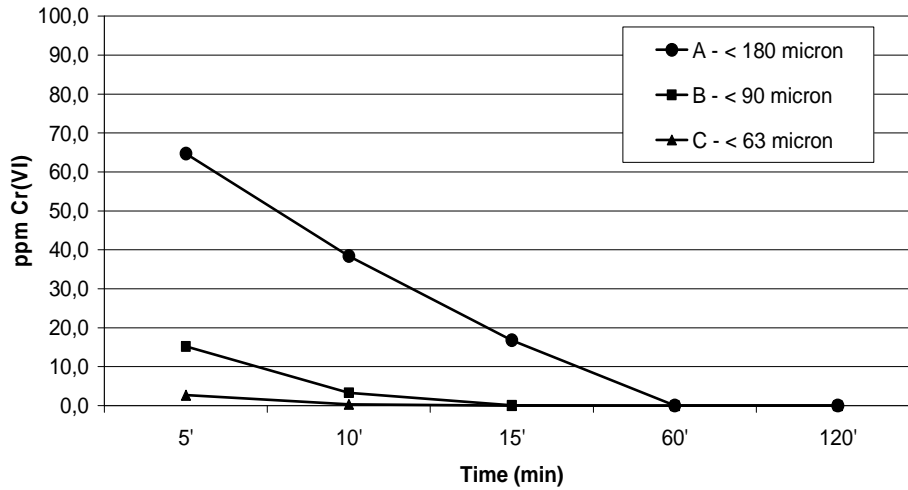
3. Results and discussion

3.1 Pure tricalcium aluminate. Graph 1 shows clearly that the higher the fineness of tricalcium aluminate, the faster the reaction of immobilization. Sample C captured the whole amount of Cr(VI) after 10 minutes, while sample A required 1 hour. In our opinion the finer C₃A is more reactive and produces, after the same time, a higher amount of hydrates immobilizing more chromium. In presence of gypsum the situation is different. First of all, it is well known that different types of calcium sulphate are characterized by different solubility kinetics [9].

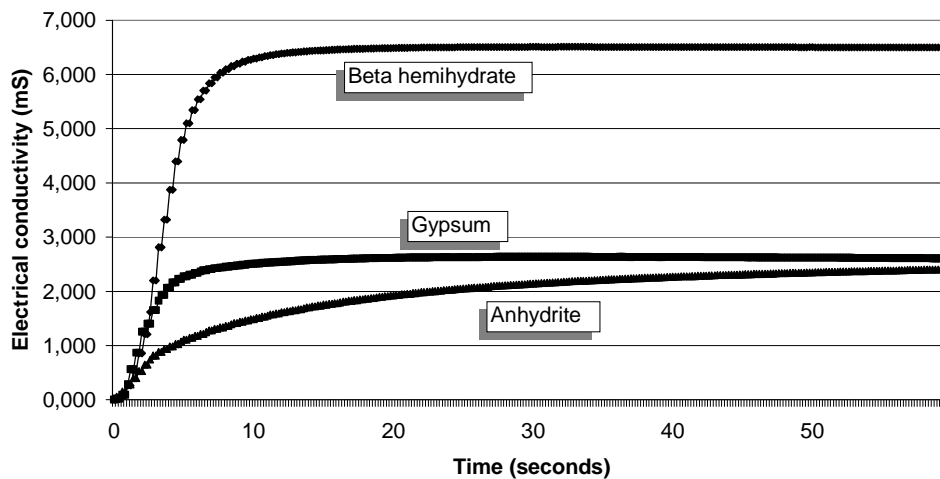
The quantity of ions (Ca²⁺ and SO₄²⁻) that goes into water solution in function of the time is different. A comparison of the solubility kinetics of the sulphates used is represented in graph 2.

It can be clearly seen that the β-hemihydrate has a faster solubility kinetic than gypsum and anhydrite. The results of chromates immobilization are reported in graph 3. By increasing the amount of calcium sulphate,

Graph n°1: Cr(VI) immobilization - C₃A

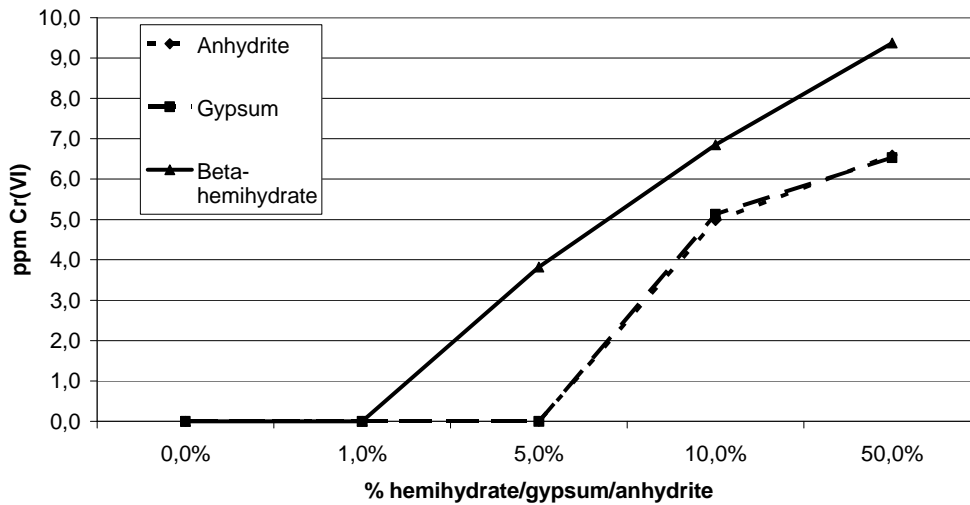


Graph n°2: solubility kinetics of calcium sulphates



less chromium is immobilized in the hydration products and this is more evident with the β -hemihydrate: the faster the solubility process of the sulphate, the higher the amount of chromium that remains in solution. In our opinion the explanation of this behavior lies in the fact that the presence of sulphate leads to the production of ettringite that has a weak effect on chromates immobilization [3, 7]. The production of ettringite is higher when more sulphate is available in solution, and the amount of sulphate in solution is depending on the quantity of calcium sulphate and on the solubility kinetics. This is the reason why the β -hemihydrate allows more chromium to remain in solution.

Graph n°3: Cr(VI) immobilization - $C_3A + SO_4^{2-}$

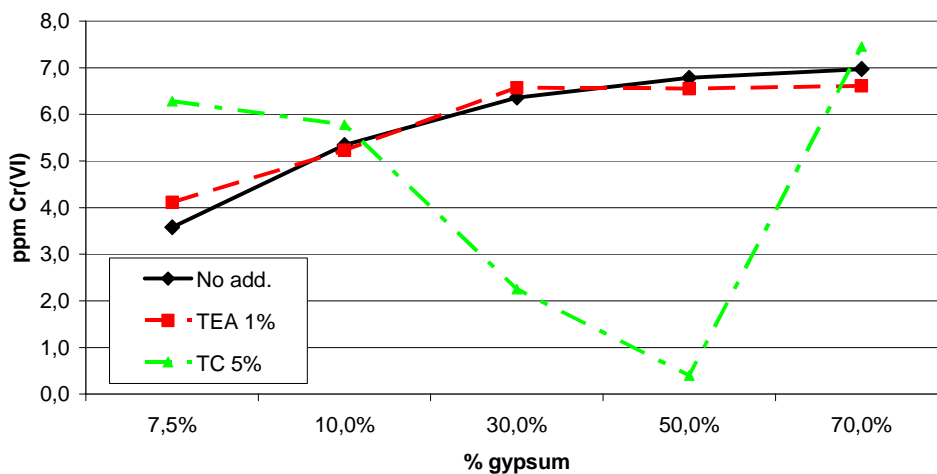


Since the use of chemical additives that influence the hydration of tricalcium aluminate should have a strong effect on the immobilization of chromates, we decided to investigate the effect of the following chemicals:

1. triethanolamine (TEA): is a well known raw material for the formulation of grinding aids. It is reported to have a strong accelerating effect on the hydration of C_3A both increasing the amount of hexagonal hydrates and promoting the conversion to the cubic form [10].
2. trisodium citrate (TC): is used as a set retarder and to modify the rheological and mechanical properties of Calcium Aluminate Cement thanks to its effect on the hydration of aluminate phases [11].

The results of hexavalent chromium immobilization by C_3A /gypsum in presence of TEA and TC are shown in graph 4. TEA seems to have no influence on Cr(VI) immobilization, while TC gives very different results depending on the amount of gypsum. We can suppose that TEA increases

Graph n°4: Cr(VI) immobilization - C_3A/SO_4^{2-} + additives

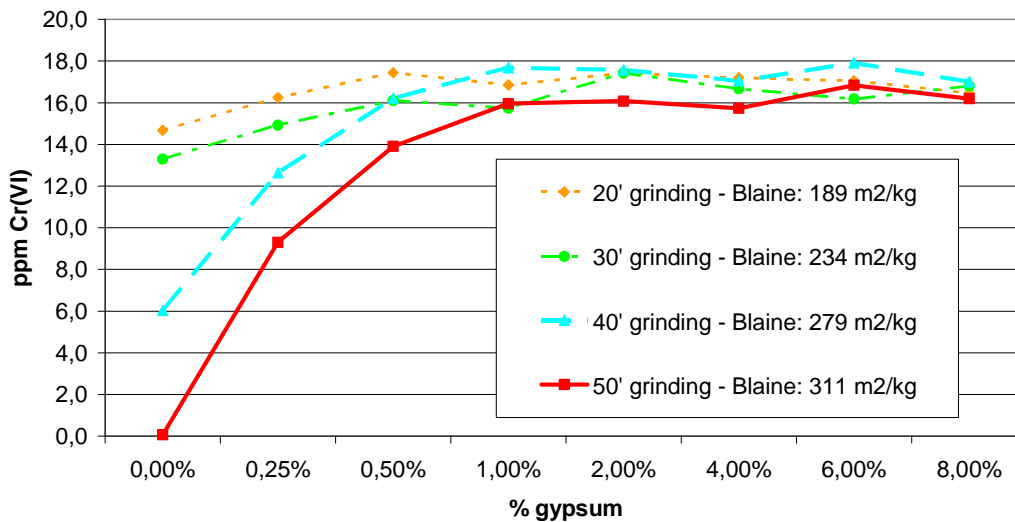


the reaction of C_3A , but does not modify significantly the amount of ettringite produced. The interpretation of the behavior of TC is difficult. We can suppose that it influences both the hydration of C_3A and the solubility kinetics of gypsum, leading to different results at different ratios TC/gypsum.

3.2 Real clinker and cements. First of all, it can be useful to focus our attention on the characteristic of the clinker, summarized in table 1. The first thing to note is the high alumina ratio ($Al_2O_3/Fe_2O_3 = 2,4$) that leads, as confirmed by the XRD analysis, to an amount of C_3A that is quite high. The cement type I produced with this clinker releases in solution between 10 and 20 ppm of soluble chromates, according to the EN 196-10

Chemical Analysis		Bogue calculation		XRD/Rietveld	
Loss on Ignition	0,21%	C_3A	12,2%	C_3A	17,1%
SiO_2	20,60%	C_4AF	7,8%	C_4AF	2,2%
Al_2O_3	6,26%	C_3S	63,8%	C_3S	69,2%
Fe_2O_3	2,57%	C_2S	10,9%	C_2S	8,7%
CaO	65,83%				
MgO	1,30%				
Free CaO	0,46%				
SO_3	0,73%				

Graph n°5 - Cr(VI) release from cement vs % of gypsum



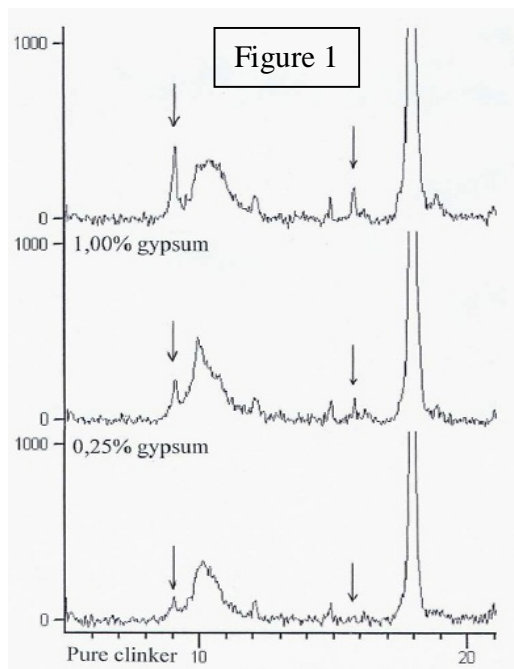
standard test method, that is a high value. Thanks to the high content of C_3A and to the relevant amount of soluble chromates, this clinker is ideal in order to confirm what we have found working with the pure phase.

The effect of fineness and gypsum is summarized in the graph 5.

The main features of the graph are the following:

1. the pure clinker (0,00% gypsum) releases a quantity of Cr(VI) that is strongly dependent on the fineness: the finer is the clinker, the higher the amount of immobilized Cr(VI). The sample ground 50' does not release chromates in solution.
2. The increase in the amount of gypsum tends to increase the release of chromium. This effect is more evident at the highest fineness (samples ground 40' and 50').
3. When the amount of gypsum is above 1,00% the effect of the fineness can be considered lost and the Cr(VI) released is $16,8 \pm 0,7$ ppm.

A comparison between graph 5, 1 and 3 allows us to conclude that the release of hexavalent chromium from a real clinker has several analogies with pure C_3A . In a clinker, a higher fineness means a higher reactivity of all the phases, including C_3A . The result is that the release of chromates is lower when the clinker is finer, thanks to the immobilizing effect of aluminates hydrated that are produced in a major amount when the reactivity of C_3A is higher. The increase in the percentage of gypsum

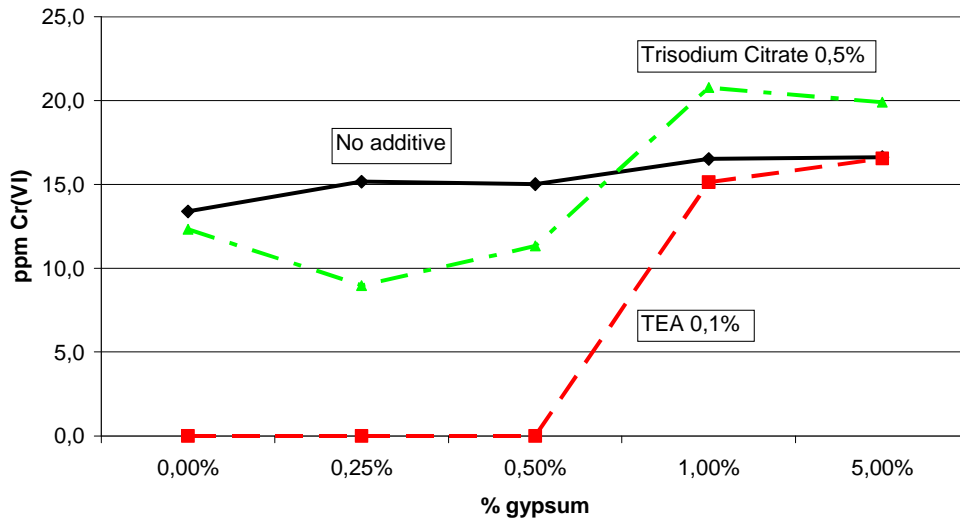


added causes the formation of more ettringite and less aluminates hydrated and then the release of chromates is higher. The sample ground 50', especially when mixed with amounts of gypsum below the 1,00%, has given the most interesting results, as shown in the graph 5: the C_3A is very reactive and the release of chromium is strongly dependent on the amount of gypsum. A small variation of this parameter can have a strong influence on soluble chromates. This is the reason why we chose this sample for further analysis and we measured the XRD pattern (see figure 1) after 24 h of hydration of the pure clinker and the cements made with 0,25%, and 1,00% of

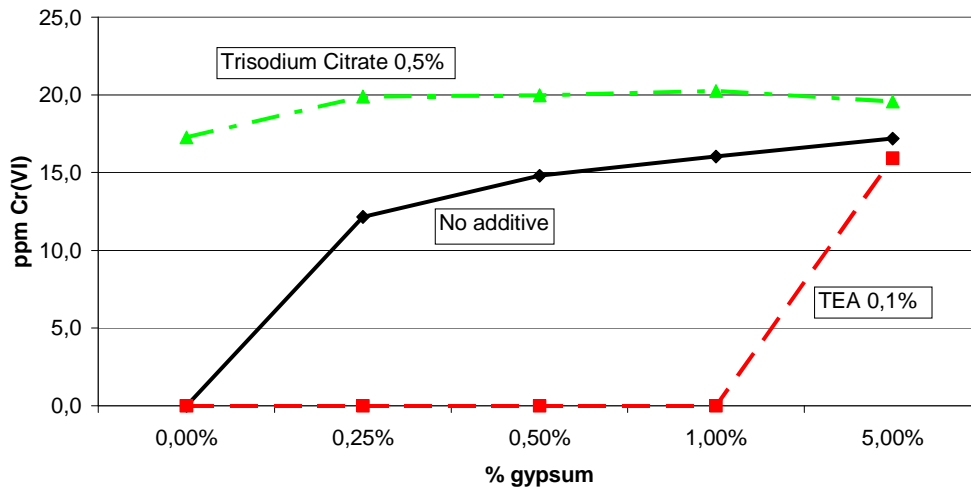
gypsum. Even though a precise quantification of the phases would be highly imprecise due to the presence of the amorphous hydrate, it can be seen, as expected, an increase in the amount of ettringite (peaks at nearly 9 and 16 °2Theta) in correlation with the amount of gypsum.

In graphs 6 and 7 is represented the effect of additives (TEA and TC) on the release of Cr(VI) by the same clinker with different amounts of gypsum. Graph 6 refers to the clinker sample ground for 20', graph 7 refers to clinker ground 50'. TEA can reduce the release of chromates at low percent of gypsum. Increasing the fineness, the amount of gypsum

Graph n°6: Cr(VI) release - Clinker + additives - 20' grinding



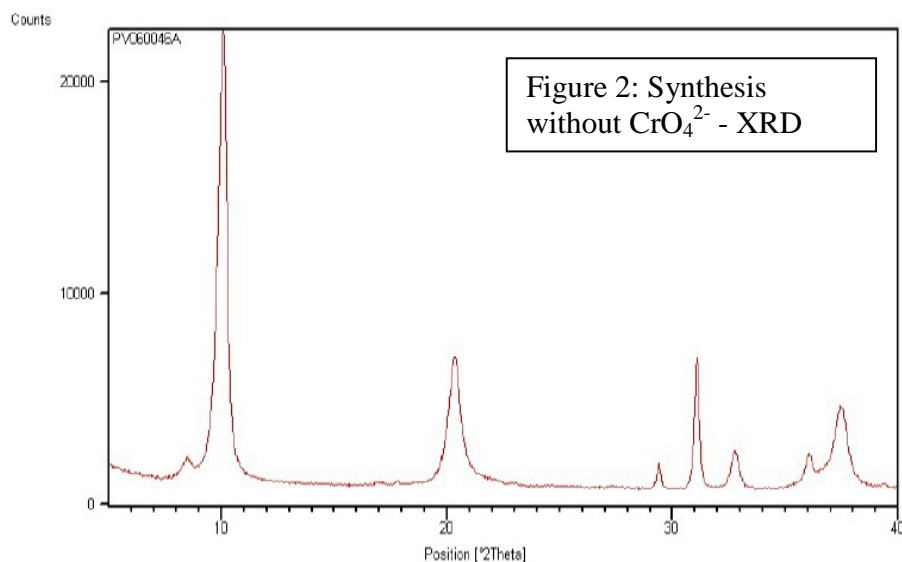
Graph n°7: Cr(VI) release - Clinker + additives - 50' grinding



that allows the release of Cr(VI) is higher. TEA accelerates the hydration of C_3A and the immobilization of Cr(VI), but above a certain quantity of gypsum (that increases with fineness) the immobilization effect is lost. We can suppose that this is the minimum quantity of gypsum that produces enough ettringite to allow chromates release. The effect of TC is similar (at low fineness) to what happens with pure C_3A . With the sample ground 50' the release of chromates is higher, and this can be explained considering

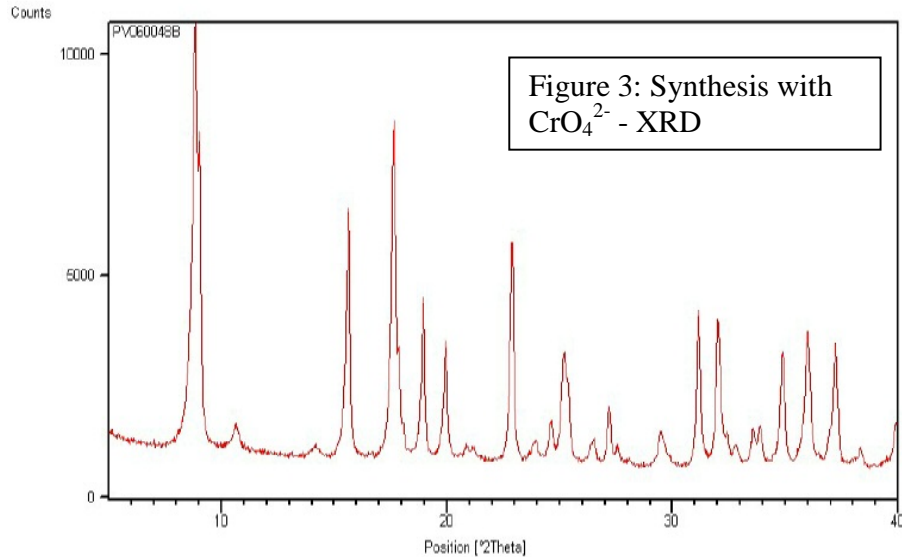
a retarding effect of TC on the hydration of C_3A . In our opinion the different reactivity at different grinding time can be explained considering that the mineralogical composition of the finest particles changes with fineness. Based on our knowledge, this is the first case of modification of the amount of soluble chromates of a real cement obtained with additives without red-ox properties.

3.3 Study on the immobilization/release mechanism. As soon as the cement is mixed with water, an amorphous and colloidal gel layer is formed. This gel is rich in alumina, calcium, sulphate and silica and the nucleation and growth of the crystalline hydration products starts from it. The parameters that control type and morphology of the hydration products are several and can be described by thermodynamic and kinetic considerations (solubility products, solubility kinetics of the anhydrous phases, diffusion of ions through the gel). In our opinion a simpler way to



investigate which type of modification the presence of chromate has on the hydration product can be a synthesis in aqueous solution at a fixed pH of hydrated aluminates in presence of chromates. By adding sodium aluminate ($Na_2O \cdot Al_2O_3$) to a solution of Ca^{2+} (or Ca^{2+} and CrO_4^{2-}) the less soluble product will precipitate first, according to the solubility product. This allows us to concentrate on thermodynamic aspects. Regarding the precipitate in absence of chromate, the XRD (see figure 2), TGA (46,1% total loss weight) and chemical analysis (24,3% Ca^{2+} , 7,6% Al^{3+} , molar ratio $Ca^{2+}/Al^{3+} = 2,09$) are coherent with aluminates hydrated of general formula C_4AH_x .

The precipitate obtained in presence of chromates is completely different. The XRD (see figure 3) and the TGA (table 2) are coherent, as reported



also by Perkins [7], with ettringite-like structure of general formula $\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{CrO}_4)_3 \cdot 26\text{H}_2\text{O}$. The chemical analysis (20,8% Ca^{2+} , 5,0% Al^{3+} , 22,2% CrO_4^{2-})

Temperature (°C)	Weight loss	
	Found	Expected for $\text{C}_3\text{ACaCrO}_4 \cdot 32\text{H}_2\text{O}$
100 - 400 °C	34,0%	35,6%
500 - 900 °C	7,5%	8,2%
Total	41,5%	43,8%

shows a slight excess of Ca^{2+} and Al^{3+} and a defect of CrO_4^{2-} .

In the IR spectra the 885 cm^{-1} chromate band is present. The sum of these analysis is coherent with a mixture of a small quantity of hydrated aluminate (excess of Ca^{2+} and Al^{3+}

in the chemical analysis) and a chromium-bearing ettringite-like structure ($\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{CrO}_4)_3 \cdot 26\text{H}_2\text{O}$). This compound precipitates from an aqueous solution containing Ca^{2+} , Al^{3+} and CrO_4^{2-} at alkaline pH and this means that it has a low solubility product [6].

Following this experiment, we can propose the following release mechanism of chromates: as soon as the cement is mixed with water immediately starts the dissolution of the phases. In presence of chromate (that comes from the clinker itself) some amount of a chromium-bearing ettringite-like structure is formed first, then converted to the usual (and more stable) sulphate ettringite as the amount of sulphate in solution increases following the dissolution of gypsum, allowing the release of the chromate. This would explain the reversibility of immobilization of chromates by C_3A that we observed [7].

References

- [1] EUR-LEX, the Portal to the European Union Law: http://eur-lex.europa.eu/LexUriServ/site/en/oj/2003/l_178/l_17820030717en00240027.pdf
- [2] W.A. Klemm, Ettringite and Oxyanion-Substituted Ettringites – Their Characterization and Applications in the Fixation of Heavy Metals: A Synthesis of the Literature, Portland Cement Association, R&D Bulletin RD116, 1998
- [3] H. He, H. Suito, Immobilization of Hexavalent Chromium in Aqueous Solution through the Formation of $3\text{CaO}\cdot(\text{Al,Fe})_2\text{O}_3\cdot\text{Ca}(\text{OH})_2\cdot x\text{H}_2\text{O}$ Phase, Ettringite and C-S-H Gel, ISIJ International, Vol. 42 (2002), No.2, pp. 139-145
- [4] H. Teramoto, S. Koie, Early Hydration of a Superhigh-early-strength Portland Cement containing Chromium, Journal of the American Ceramic Society, Vol. 59, (1976), pp. 522-525
- [5] H. Poellman, St. Auer, H.J. Kuzel, R. Wenda, Solid Solutions of Ettringite. Part II: Incorporation of $\text{B}(\text{OH})_4^-$ and CrO_4^{2-} in $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$, Cem Concr Res, Vol. 23, (1993), pp. 422-430
- [6] R.B. Perkins, The Solubility and Thermodynamic Properties of Ettringite, its Chromium Analogs, and Calcium Aluminium Monochromate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCrO}_4\cdot n\text{H}_2\text{O}$), Portland State University (2000)
- [7] M. Magistri, D. Padovani, The Release Mechanism of Hexavalent Chromium, CemTech, Rome, 2006
- [8] A.C. Larson, R.B. Von Dreele, General Structure Analysis System (GSAS), Los Alamos National Laboratory LAUR 86-748, 2000
- [9] J.P. Bayoux, M. Testud, B. Espinosa, Thermodynamic Approach to Understand the $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SO}_3$ System, Congrès IX ISCC New Delhi, 11.1992, pp. 6-11
- [10] V.S. Ramachandran, Action of Triethanolamine on the Hydration of Tricalcium Aluminate, Cem Concr Res, Vol. 3, (1973), pp. 41-54
- [11] L. Amathieu, Th. A. Bier, K. L. Scrivener, Mechanisms of Set Acceleration of Portland Cement through CAC Addition, International Conference on Calcium Aluminate Cements, Edimburgh, July 2001