

The release mechanism of hexavalent chromium

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Abstract: we are studying the release mechanism of hexavalent chromium and the possible interferences with the hydration of the clinker phases. It has already been discovered that the amount of soluble chromates released by a clinker is greatly influenced by the presence of gypsum. Thus in practice the use of a clinker with less than 2 ppm of soluble chromates does not necessarily guarantee a cement which is free of chromates. In some cases hydrated aluminate may completely incorporate chromate anions in their structure while ettringite on the other hand does not have the same effect: this has been verified by studying the hydration of pure C_3A and of C_3A /gypsum using water which contains chromates.

We have decided to continue with this study: firstly examining the immobilization/release of chromates by synthetic C_4AF , pure and in the presence of gypsum and secondly studying the immobilization effect of hydrated aluminate and ettringite verified by the chemical reaction of sodium aluminate, aluminium sulphate and calcium salts in a chromate containing aqueous solution.

In our opinion a more in depth examination of the relationship between the hexavalent chromium and the hydration of Portland cement may give interesting information about clinker chemistry and perhaps lead to alternative methods to eliminate soluble chromates.

Introduction

Since the beginning of 2005 all cements sold in Europe (produced or imported) have to comply to the EU Directive 2003/53/EC that limits the content of soluble chromates to a maximum of 2 ppm, expressed in Cr(VI). This regulation simply certifies what has already been known for a long time: hexavalent chromium is dangerous to people's health and, in the specific case of the cement and building industries, may cause irritation of the skin (allergic contact dermatitis). The problems of determination and reduction of soluble chromates are of great interest, and this can be verified looking at the several technical papers and patents that have been presented on this topic during the last years (1, 2). In our opinion the interaction between the release of hexavalent chromium and the hydration of Portland cement is also of great importance: the study of the release mechanism of soluble chromates may lead to a better understanding of the hydration chemistry and could offer us an alternative way to comply with the requirement of the European Community.

The amount of Cr(VI) released into solution

The release of hexavalent chromium from a cement when it is mixed with water is very rapid and begins with the hydration of the more reactive phases of the clinker. After a few minutes from the mixing of cement and water the amount of soluble chromates has already reached its maximum. It is a common fact that a cement may release an amount of soluble chromates higher than the clinker from which is made. The reason lies in the fact that some clinker phases in the absence of gypsum react with water giving hydrated products that may immobilize chromate ions, where as in the presence of gypsum the same phases react to form ettringite which has a lower tendency to immobilization. In a previous work (3) this fact was demonstrated by preparing pure tricalcium aluminate (by

heating a mixture of lime and alumina) that was hydrated with water containing hexavalent chromium. By filtering off the water, it was possible to verify that all the chromium disappeared from the solution and was captured in the hydration products. In the same way, after the hydration of a mixture of C₃A and gypsum with water containing chromates, it was demonstrated that the hydration products of tricalcium aluminate in the presence of gypsum were unable to immobilize the same amount of chromium.

Aluminates hydration effect on Cr(VI) release

We decided to carry on with this work and report here the results obtained after trials performed with the following targets:

- verify the effect of tetracalcium alluminoferrite on the immobilization of chromates;
- verify the reversibility of the immobilization of chromates by hydrated aluminates;
- study in detail the mechanism of chromates immobilization.

It is well known that in Portland clinker there are two main phases based on aluminium and characterized by instantaneous reactivity with water: tricalcium aluminate (C₃A) and tetracalcium aluminoferrite (C₄AF). It is possible to prepare pure C₄AF by heating a mixture of analytical grade CaO, Al₂O₃ and Fe₂O₃ in appropriate amounts to 1300°C. The product of the reaction is then ground (totally passing through a 90 micron sieve) and characterized by X-ray diffraction.

Following the procedure already used for the tricalcium aluminate (see ref. 3) half of the tetracalcium aluminoferrite was hydrated in water containing chromates. The second half was mixed with gypsum and then hydrated in the same water as reported in the table 1.

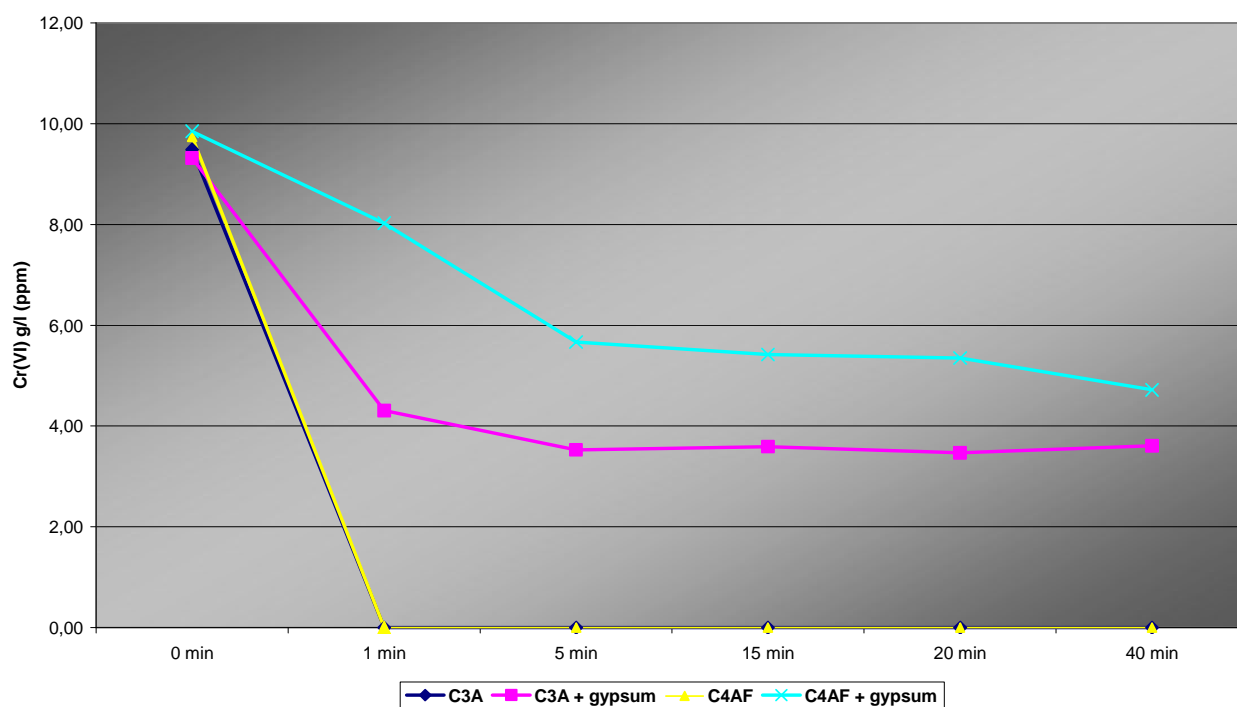
TABLE 1	C ₄ AF	C ₄ AF + gypsum
C ₄ AF	50 g	50 g
Gypsum	-	25 g
Water	250 g	250 g
Concentration of Cr(VI) in water	9,74 ppm	9,85 ppm

From a practical point of view, the C₄AF (or the mixture C₄AF/gypsum) was added to the solution of Cr(VI) kept under magnetic stirring. The suspension was sampled at fixed intervals using a syringe with a membrane filter, and the filtrate was analyzed using ionic chromatography, following a procedure used in our lab (4). The results are reported in table 2 and represented in graph 1. The data already collected in the work cited (3) for the tricalcium aluminate are reported for confrontation.

It appears that C₃A and C₄AF have the same behaviour: they can immobilize soluble chromates in their hydration products, but in the presence of gypsum the immobilization of Cr(VI) is not total. This can be explained by considering that in the presence of gypsum part of the C₃A and C₄AF react with sulphates forming ettringite.

TABLE 2	C ₄ AF	C ₄ AF + gypsum	C ₃ A	C ₃ A + gypsum
Time (min)	Cr(VI) – mg/l (ppm)	Cr(VI) – mg/l (ppm)	Cr(VI) – mg/l (ppm)	Cr(VI) – mg/l (ppm)
0	9,74	9,85	9,49	9,32
1	0,00	8,03	0,00	4,31
5	0,00	5,67	0,00	3,53
15	0,00	5,42	0,00	3,59
20	0,00	5,35	0,00	3,47
40	0,00	4,72	0,00	3,61

GRAPH 1 - Immobilisation of Cr(VI) by systems C3A/C4AF/Gypsum



Reversibility of Cr(VI) immobilization: the post-addition of gypsum

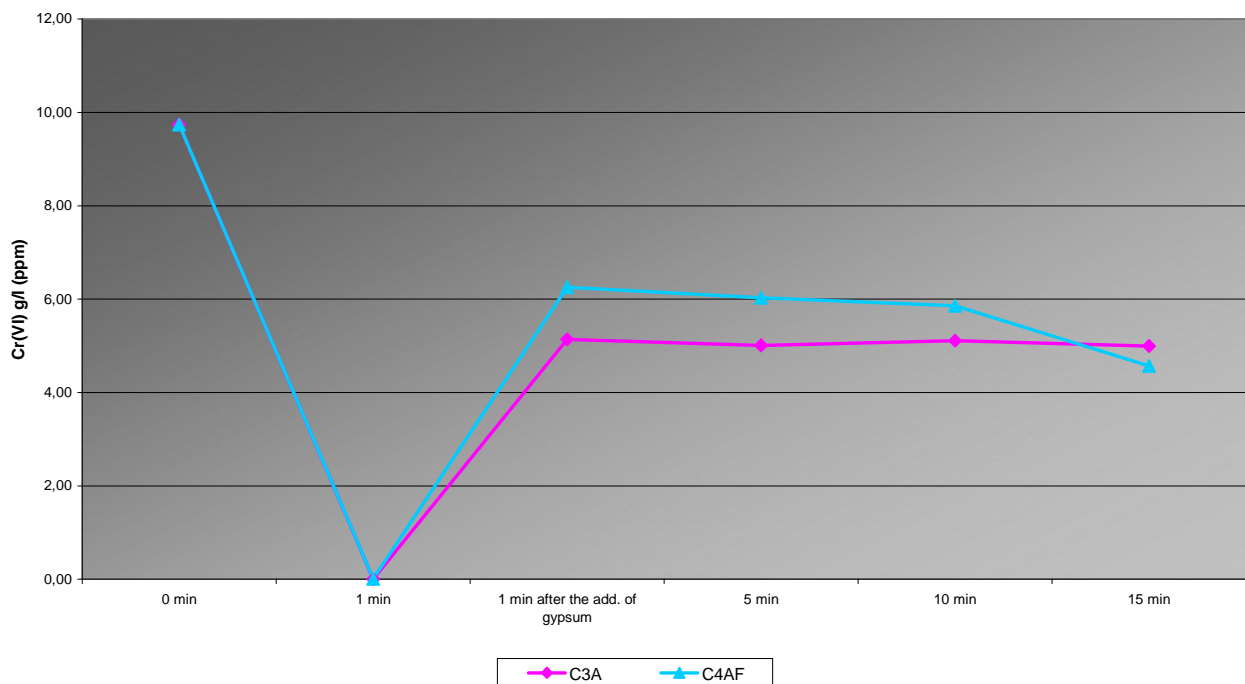
We decided to verify whether the immobilization of chromates by hydration products is reversible or not. We performed the following experiment:

- a sample of C₃A (50 g) was added to water (250 g) containing chromates (about 10 ppm) under continuous magnetic stirring;
- after 1 min the suspension was sampled using a syringe and filtered;
- after 1 min from the first sampling gypsum (25 g) was added to the suspension still under continuous magnetic stirring;
- in the same way several samples (after 5, 10 and 15 minutes) were taken and filtered and then all the filtered solutions were analyzed by ionic chromatography.

The results are summarized in table 3 and represented in graph 2 below.

TABLE 3	C ₃ A	C ₄ AF
Time	Cr(VI) – mg/l (ppm)	Cr(VI) – mg/l (ppm)
0 min	9,74	9,74
1 min	0,00	0,01
3 min – 1 min after gypsum added	5,14	6,26
5 min after gypsum added	5,01	6,03
10 min after gypsum added	5,11	5,86
15 min after gypsum added	5,00	4,57

GRAPH 2 - Immobilisation of Cr(VI) by systems C3A/C4AF/Gypsum - Effect of the post-addition of gypsum



It is clear that the chromates immobilized by the hydration of C_3A and C_4AF may be released if the concentration of sulphate in solution increases.

In order to go into greater detail and clarify the real mechanism of immobilization of chromates, we should consider what happens during the first minutes after the mixing of a Portland cement with water (9, 10). Because the release of chromium is practically instantaneous, we can avoid taking into account the silicate phases (whose hydration begins later) and focus our attention on the more reactive phases: aluminates and aluminoferrite. As soon as they enter into contact with water a gel is formed (5) on the surface of the clinker grain. This gel can be described as a colloidal solution of hydrated products in water over saturated with several types of ions (Ca^{2+} , Al^{3+} , OH^- , ...). The reactivity of the gel (the type and the morphology of the products obtained after the structurization of the gel itself) depends on several phenomena (e.g. the diffusion of ions through the gel, the electrical charges on the surface of the particles, the presence of additives, ...). In the presence of sulphate, the "final destiny" of the gel is the growth of the well known ettringite crystals, $Ca_6[Al(OH)_6]_2(SO_4^{2-})_3 \cdot 26H_2O$, that arise from the reaction of the first hydrated products and the calcium sulphate. These first hydrated products are responsible for the immobilization of chromates which are then released into solution when the ettringite is formed.

Hydrated aluminates by direct synthesis

Unfortunately, while ettringite has structure and characteristics that have already been studied and defined (6, 7, 8), the hydration of aluminates leads to a family of compounds that may be very different. A simpler model for the study of the first hydration products of a

Portland clinker is the hydration of pure tricalcium aluminate: the most stable hydrate is the C_3AH_6 ($Ca_3[Al(OH)_6]_2$) which may crystallize in various cubic forms, of which at ambient temperature the most stable is the icositetrahedra (9, 11). Figure 1 shows an image collected with the ESEM - FEG (Environmental Scanning Electron Microscope - Field Electron Gun) of a C_3AH_6 crystal obtained in our lab during an experiment of the hydration of pure C_3A . Even though the C_3AH_6 is, from a thermodynamic point of view, the most stable hydration product of pure tricalcium aluminate, several types of different hydrates can be formed, whose formation is faster (kinetic control) (11). The CAH_{10} , C_2AH_8 and C_4AH_{19} (which may crystallize in the form of hexagonal plates) belong to this family.

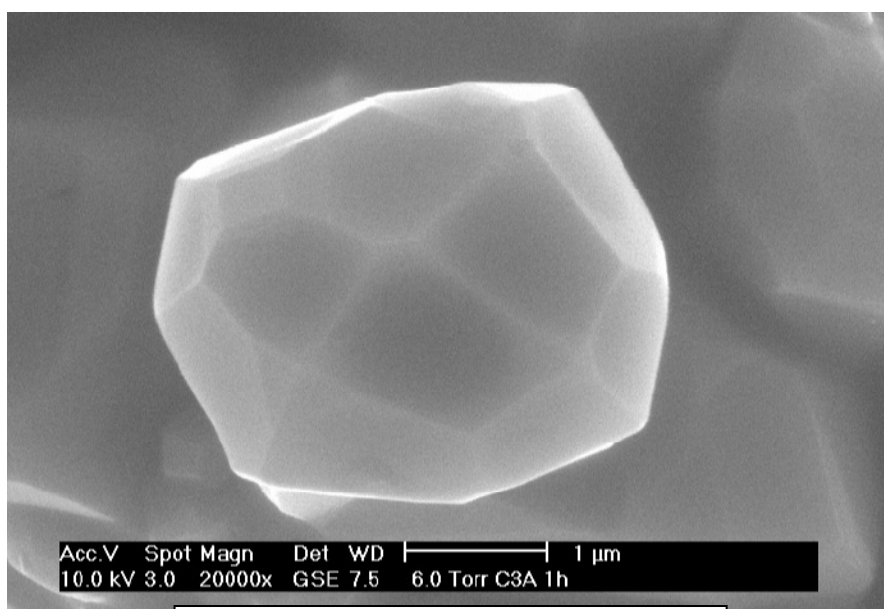
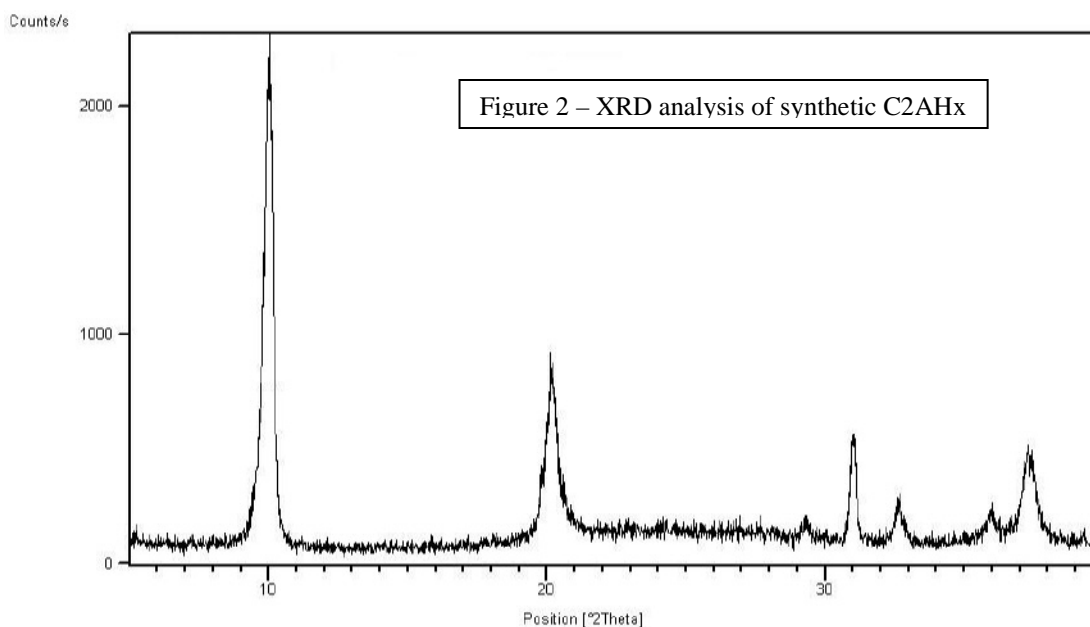


Figure 1 – ESEM image of a C_3AH_6 crystal

In this scenario, it is difficult to identify the type of hydrate that may immobilize the hexavalent chromium in its structure. Beside the hydration of portland clinker or pure tricalcium aluminate, it is possible to obtain hydrates aluminates (or ettringite) by direct synthesis in aqueous solution of calcium salts (CaO , $\text{Ca}(\text{NO}_3)_2$) and sodium aluminate ($\text{Na}_2\text{OAl}_2\text{O}_3$) (or aluminium sulphate $\text{Al}_2(\text{SO}_4)_3$). This method allows us to obtain, by controlling the conditions of synthesis (e.g. temperature, concentration of reagents, time of reactions, ...), single types of hydrated aluminates and to verify their ability to immobilise hexavalent chromium simply by conducting the synthesis in water containing chromates.

An example of this synthesis, performed in our lab, is reported here: 5 g of calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) was dissolved in 100 ml of water containing 50 ppm of Cr^{6+} (the 50 ppm Cr^{6+} solution were prepared by dissolving 0,1414 g of $\text{K}_2\text{Cr}_2\text{O}_7$ dried at 120°C for 2 hours, in 1 litre of distilled water). The solution was then poured in a two-necked, round bottomed flask. The pH was adjusted to 12 with CaO , then a solution of sodium aluminate ($\text{Na}_2\text{OAl}_2\text{O}_3$, 2,5 g in 100 ml of distilled water) was added, under magnetic stirring, with a dropping funnel. The pH was kept between 11,5 and 12,5 by adding a suspension of 40 g/l of CaO and the velocity of adding of sodium aluminate was controlled at about 0,1 ml/min. The precipitate was filtered and characterized by X-ray diffraction and ESEM-FEG, and the amount of hexavalent chromium in the filtered solution were determined by ionic chromatography.

The results of the XRD analysis on the precipitate (figure 2) demonstrate that we obtained an hydrated aluminate of general formula C_2AH_x .



The images collected with the ESEM-FEG (figure 3) show hexagonal plates which are the typical shape of the crystals of these hydrated aluminates.

The results of the analysis of hexavalent chromium (corrected taking into account the effect of the dilution of the solution during the synthesis) show that, of the initial 50 ppm of Cr⁶⁺, only 3,4 ppm remained in solution: this means that a great part of the chromates has been captured by the C₂AH_x and immobilized in its structure.

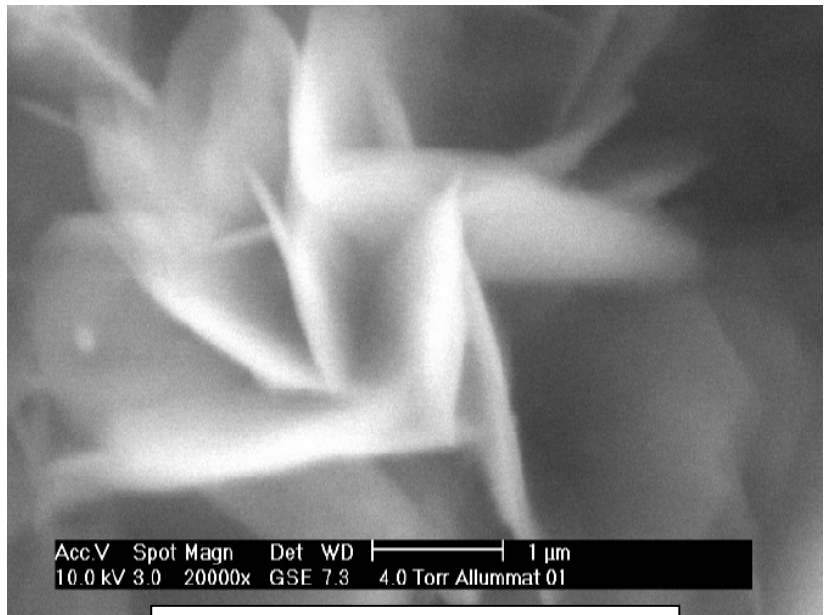


Figure 3 – ESEM image of synthetic C₂AH_x

Conclusions

- both tricalcium aluminate (C₃A) and tetracalcium aluminoferrite (C₄AF) which are the most reactive phases of Portland clinker are able to immobilize chromates in their structure. In the presence of gypsum, the ettringite that is formed has a lower tendency to capture the chromate ion.
- The immobilization of chromates by the C₃A and C₄AF is reversible: if the concentration of sulphate in solution increases, the equilibrium shifts to the formation of ettringite and the chromium captured can be released into solution.
- *The hydration of C₃A in the absence of gypsum can form several types of products. Using a direct synthesis in aqueous solution it has been demonstrated that the C₂AH_x type of hydrated product can immobilize hexavalent chromium; we may suppose a similar behaviour for the other forms.*

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