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DETERMINATION AND QUANTIFICATION OF TOTAL CHROMIUM AND WATER SOLUBLE CHROMIUM CONTENTS IN COMMERCIAL CEMENTS

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ABSTRACT

It is common knowledge that the compounds of chromium VI can cause allergies, nasal lesions, bronchitis and especially dermatitis in professionals who work in the construction sector.
This paper deals with the quantification of total chromium and hexavalent chromium contents in different types of national cements (Types I and II) as well as with a comparative study of various imported cements (Type I), in order to know the contents of water soluble chromium in the cements made today.
These studies are a continuation of earlier research by the same authors and represent a contribution to the establishing of possible limitations of these compounds in future standards.

Introduction

The importance of environmental preservation was clearly demonstrated in an earlier work (1). The cement industry has long been striving to mitigate the possible contaminating effects of gaseous and solid emissions in factories.

Nevertheless, the current tendencies, stricter still in environment preservation, recommend the control of heavy elements, especially those that may be health damaging, as is the case of hexavalent chromium (2).

To this effect, the European Union of National Water Distributing Associations (EUREAU) and the Technical Committee for Cement and Lime Standardization TC-51 have expressed their concern over the deleterious effect caused by the presence of heavy elements (chromium, lead, cobalt, zinc, etc...) in the cements which are to be included in the works for storing, transportation and supplying of drinking water, considering the possible leaching effects, etc. Nonetheless, the Spanish Standard (3) and the European Experimental Standard (4) on cements do not yet include specifications concerning the contents of total or hexavalent chromium.

The Directive for the quality of waters for human consumption (5) as well as the Royal Decree on the quality of drinking waters in Spain (6), include specifications on maximum acceptable contents of chromium and other heavy elements for which reason these values must be observed in the future in the use of materials in contact with the water.

The contents of chromium VI in different raw materials, clinkers and additions used in the manufacturing of commercial cements were the object of analysis in the earlier researches. To this end, it was necessary to adjust a test methodology based on the existing related standard (7) (8) using the Inductively Coupled Plasma Emission Spectrometry Technique (ICP) as a means to carry out the quantification of chromium in the studied specimens.

The results obtained pointed out the importance of the factors related to the leaching tests, shaking time, the fineness of the specimens, etc. as well as the technical suitability of ICP for the determination of chromium contents.

The study presented in this paper is based on the quantification of total chromium and water soluble chromium contents in different cements manufactured in Spain and in imported cements, whose contents can serve as orientation in establishing limitations in future standards

Experimental

Materials

20 specimens of Portland cement manufactured by the Spanish Industry were selected for this study. According to the Standard UNE 80 301 (3) they were cements Type I and Type II, with different resistance categories: 35 MPa, 45 MPa and 55 MPa (Table I). These cement Types are similar to those included in the European Experimental Standard ENV 197-1 (4).

This research also includes the results corresponding to 10 cements imported from different countries, also listed in Table I.

Tests Methodology

The earlier studies (1) have proved the importance of the fineness of the materials in the leaching process. For this reason, the specimens were granulometrically characterized using the laser diffraction technique (9) thus obtaining distribution curves of the particle size as well as the specific surface of these specimens.

In order to determine the contents of total chromium in the specimens an acid disgregation with HF and HCl was carried out which enabled the dissolution of the specimen. The dissolution of Chromium VI is carried out according to the methodology described in one earlier work (1), which mainly consists of keeping the specimen in contact with water and shaking it during a period of time previously fixed.

The quantification of the total chromium and water soluble chromium is carried out by means of the Plasma Emission Spectrometry (ICP) technique.

Results and Discussion

The fineness is a physical parameter which plays an important role in the leaching of the water soluble chromium. In the research that was carried out, the minimum recommended specific surface was about 2500 cm^2/g in order to obtain representative values of water soluble chrome (1).

Figures 1a, 1b and 1c present the granulometric distribution ranges of different cements. As can be seen, national cements of Type 1 have an average particle size of between 9 and 16 microns, those of Type II have the average particle size of 10 to 18 microns and the imported cements´ average particle size is of 15 to 18 microns. All analyzed cements have particle sizes below 100 microns.

TABLE I: Samples

SAMPLES	TYPE I	TYPE II	SC 35	SC 45	SC 55	SAMPLES	TYPE I	SC 35
1	X			X		21	X	X
2	X			X		22	X	X
3	X			X		23	X	X
4	X			X		24	X	X
5	X			X		25	X	X
6	X			X		26	X	X
7	X			X		27	X	X
8	X				X	28	X	X
9	X				X	29	X	X
10	X		X			30	X	X
11		X	X					
12		X	X					
13		X	X					
14		X	X					
15		X	X					
16		X	X					
17		X		X				
18		X	X					
19		X	X					
20		X	X					

National cements: Samples 1-20
Imported cements: Samples 21-30
SC: Strength Class

Figure 2 shows the maximum and minimum values of the specific surface, obtained by means of laser granulometry (9), corresponding to the granulometric curves previously presented. These ranges of specific surface are superior to the recommended value mentioned before. For this reason these cements did not require any previous grinding in order to carry out the leaching test.

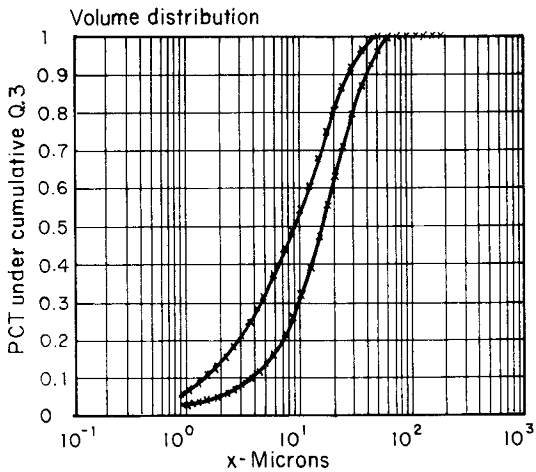
The contents of total chromium and hexavalent water soluble chromium expressed in mg/Kg, present in the 30 studied cements are shown in Figures 3a, 3b and 3c.

Figure 3a, corresponding to the Type I national cements, presents values of total chromium of between 20 mg/Kg and 100 mg/Kg, while the range of values for the water soluble chromium is between 2.7 mg/Kg and 10.8 mg/Kg.

In Type II national cements, Figure 3b, the total chromium content is between 34 mg/Kg and 106.7 mg/Kg and in the case of water soluble chromium it is between 0.9 mg/Kg and 7.8 mg/Kg.

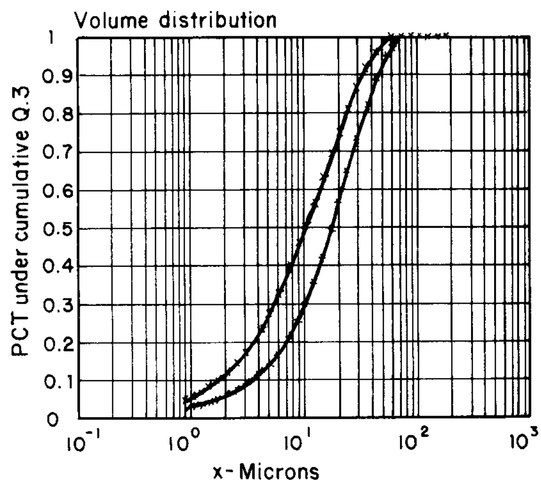
The values of total chromium content presented by the imported cements (Fig. 3c) are between 40.2 mg/Kg and 93.8 mg/Kg and those of water soluble chromium are between 5.8 mg/Kg and 24.2 mg/Kg.

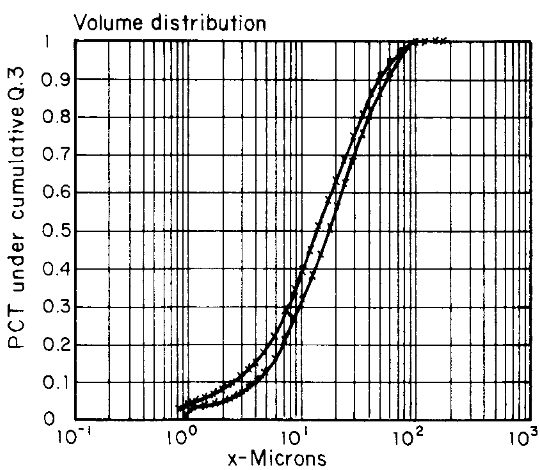
The analytic results reveal that total chromium content ranges are similar in all three groups of analyzed cements. Nevertheless, when leaching tests are carried out on these cements, the water soluble chromium content is higher in Type I cements, both national and imported ones, than in Type II cements. This is mainly due to the fact that Type II cements contain pozzolanic materials most of which do not provide



a: National Cement Type I

b: National Cement Type II





c: Imported Cements

Fig. 1.-Granulometric range.

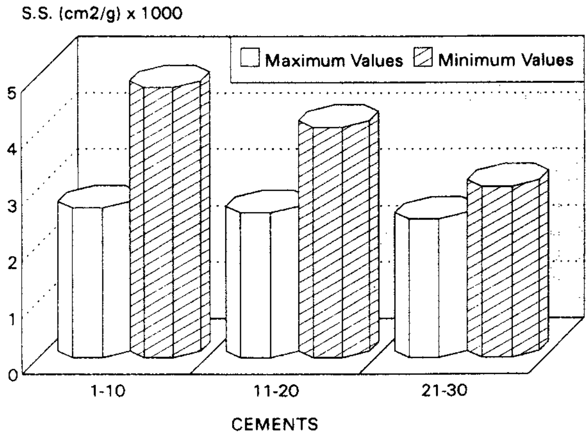


Fig. 2.- Specific Surface. Range of values.

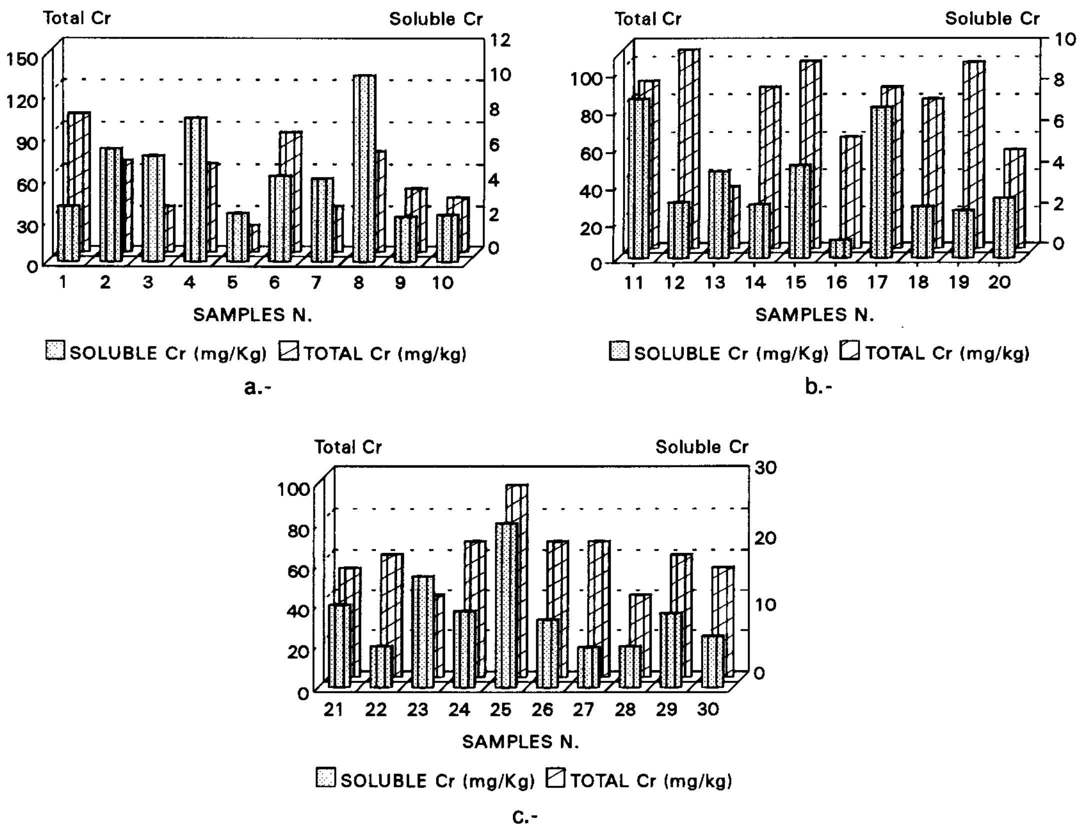


Fig. 3.- Chromium Contents. a.- Type I, b.- Type II, c.- Imported Cements

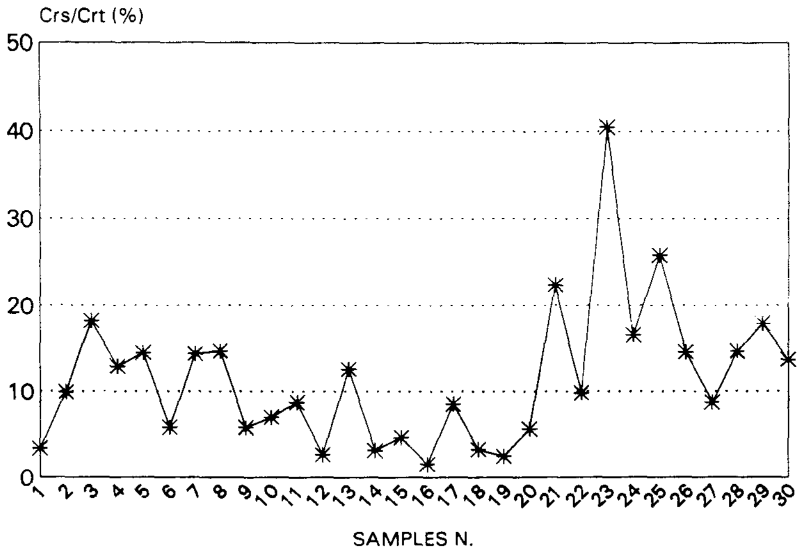


Fig. 4.- Relation between total Cr and soluble Cr.

hexavalent chromium, while Type I cements with a clinker content superior to 95%, according to the existing standard (3,4) present a higher content of water soluble chromium. This is due to the fact that clinker is the component which provides the highest content of water soluble chromium to the cements, as was pointed out in the previous work (1), since the processes of clinkerization are those in which the oxidation of chromium III into chromium VI, regarded as a toxic element for human health.

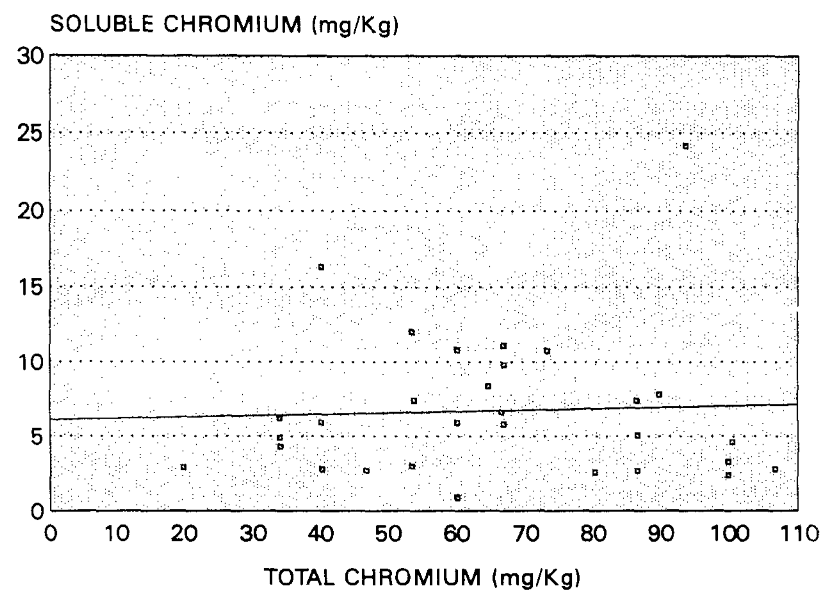


Fig. 5.- Correlation Coefficient.

In the previous Figures, it can also be seen that the imported Type I cements generally present higher content of chromium VI than the national Type I ones. This fact is prominent in Figure 5 which offers percentages of water soluble chromium in relation to total chromium. Thus, it can be observed that in all studied cases national cements of Type I have a soluble Cr/total Cr ratio of less than 20%, while the imported cements have percentages between 10% and 40%. In Type II cements there is only one specimen in which the percentage of the soluble chromium/total chromium relation exceeds 10%.

There is no direct relation between the total chromium content and the hexavalent chromium content. Figure 4 presents values of water soluble chromium in relation to total chromium with a very low correlation coefficient (0,05), which proves the previously stated conclusions.

These analytical results underline the wide margin of water soluble chromium, classified as toxic, present in commercial cements. For this reason, a control of content of this element in cements is necessary. Nonetheless, a mere limitation of the total chromium content would not be enough because of the low correlation coefficient between the two.

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