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A Discussion of the Paper "DETERMINATION AND QUANTIFICATION OF TOTAL CHROMIUM AND WATER SOLUBLE CHROMIUM CONTENTS IN COMMERCIAL CEMENTS" by M. Fŕias and M. I. Sánchez Rojas*

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Drs Fŕias and Sánchez Rojas have performed a valuable study in determining the total chromium and hexavalent water soluble chromium contents for a range of different production cements (1). They have established that there is no direct relationship between the total chromium and hexavalent water soluble chromium contents for the different series of cements examined. In these, the total chromium lies between 20 mg and 106.7 mg per kg, and the water soluble chromium between 0.9 mg and 24.2 mg per kg. Also, they make the important deduction that although controls of chromium in cement are necesssary, because of the toxicity of water soluble chromium, merely limiting the total chromium content would not be enough, because of the low correlation coefficient between total and water soluble chromium.

Chromium exists as a trace element in cement in the hexavalent and trivalent forms (and occasionally in the divalent state as well), and arises primarily from the raw materials utilised in cement manufacture. It is generally assumed that all hexavalent chromium present as chromate (CrO_4^{2-} ions) is likely to be water soluble. This may not necessarily be the case always. Where pure gypsums are employed in cement manufacture any residual chromate in the gypsum is normally negligible. With impure gypsums the situation is not known for certain.

Sulphate (SO_4^{2-}) and chromate (CrO_4^{2-}) ions are commonly isomorphous in many salts and minerals (2). Indeed, the AFt phase (ettringite) formed during hydration $C_3A.3CaSO_4.32H_2O$ has a bright yellow chromate analogue $C_3A.3CaCrO_4.32H_2O$, which is isostructural and readily enters into solid solution with it (3). Thus, should there be any traces of chromate in the raw gypsum, for instance, or any free chromate ions exsolved from the clinker phases, upon hydration the CrO_4^{2-} ions could readily enter the AFt phase in solid solution and not be readily water soluble as a result. Also, trivalent chromium can substitute for aluminium in the AFt phase. The turquoise coloured chromium (III) ettringite $3C_3A.Cr_2O_3.3CaSO_4.32H_2O$ has a similar structure and also enters into extensive solid solution with ettringite (4). Clearly, the distribution of Cr (III) and Cr (VI) in cements and their hydration products is an area that requires some more experimental investigations.

In the Scandinavian countries attempts are made to limit Cr (VI) by grinding in ca. 0.5-0.6% ferrous sulphate $FeSO_4.7H_2O$ during clinker-gypsum grinding. Whilst ferrous ions as they oxidise

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to ferric ions can reduce chromium (VI) to chromium (III): $3Fe^{2+} + Cr^{6+} \dashrightarrow 3Fe^{3+} + Cr^{3+}$ in the cement environment with other reducible species present amongst the tract elements, it is still not completely clear just how efficiently ferrous sulphate functions in respect of total reduction of Cr (VI) to Cr (III). There is certainly qualitative evidence of reduction in terms of chromate colour removal by visual inspection.

It is of interest to note that for white Portland cements, where the yellow chromate even at trace levels can interfere with the desired whiteness, it is common practice during manufacture to quench the clinker formed in a reducing atmosphere after leaving the kiln burning zone. Under these conditions Cr (VI) is reduced to Cr (III), or better to Cr (II), iron (III) to iron (II) and Mn (III) to Mn (II), which result in producing a significant lowering of colour intensity and hence a better whiteness (5).

In conclusion, the work undertaken by the authors (1) represents a valuable contribution to the proposed basis for introducing possible limits on water soluble chromium contents of cements in the future, particularly for those cements used in the storage, transport and supply of drinking water.

References

1. M. Fŕias and M. I. Sânchez Rojas, Determination and quantification of total chromium and water soluble chromium contents in commercial cements. Cement and Concrete Research, 25(2), 433-439 (1995).

2. P. Ramdohr and H. Strunz, "Klockmanns Lehrbuch der Mineralogie", 15. Auflage, Ferdinand Enke-Verlag, Stuttgart (1967).

3. J. Bensted and S. P. Varma, Studies of ettringite and its derivatives. Part 2. Chromate substitution. Silicates Industriels, 37(12), 315-318 (1972).

4. J. Bensted and S. P. Varma, Studies of ettringite and its derivatives. Cement Technology, 2(3), 73-76, 100 (1971).

5. J. Bensted, White and coloured Portland cements. World Cement, 24(2), 13-19 (1993).