

## SSDI 0008-8846(95)00206-5

## A Reply to the Discussion by Dr. Bensted of the paper "DETERMINATION AND QUANTIFICATION OF TOTAL CHROMIUM AND WATER SOLUBLE CHROMIUM CONTENT IN COMMERCIAL CEMENTS"

M. Frías and M.I. Sánchez de Rojas Instituto C. C. "Eduardo Torroja" (CSIC) Serrano Galvache, S/N. 28033 Madrid. Aptdo. 19002. 28020 Madrid. Spain.

The authors wish to thank Dr. Bensted for the interest he has shown in the work covered in the mentioned article. This study is a continuation of what has appeared in prior numbers of this journal (1).

The intention of this work is to underscore the presence of chromium in cements and offer a model for its detection and quantification. The authors are pleased to learn that the work may be a contribution to future research, and that colleagues with similar experiences may be able to discuss and expand on that already carried out. This will serve to mitigate environmental deterioration and improve health, since as is known the presence of chromium VI has important repercussions on these and is catalogued as a toxic and dangerous chemical element.

In the majority of cases when pioneering research is begun, one of the important difficulties is the lack of related bibliography, which makes such research more difficult, so that objectives previously set do not correspond to reality.

In the case of water soluble hexavalent chromium, no prior works existed for cement products and therefore an initial study was carried out which covered a wide range of cements from different factories, both in Spain and abroad, in order to be able to observe the influence of various factors such as the nature of the raw materials, clinkering and cooling, type of additions, etc., which play an important part in the formation of hexavalent chromium.

However, the authors are aware that the amount of water soluble hexavalent chromium analyzed in commercial cements, is lower than that which initially exists during the hydration process:

<sup>\*</sup>CCR <u>25(2)</u>, 433 (1995)

- \* As shown in the previous work (1), reducing agents may be present in these cements, such as: nitrites, sulphides, etc., which in the majority of cases are introduced through the incorporation of active additions when forming mixed cements. Even though these species have a negative effect, in this specific case they offer a beneficial effect by reducing the hexavalent chromium to a lesser state of oxidation (CrIII).
- \* According to the comments by Dr. Bensted, during the hydration process in cements the chromate ion can form part of the hydrated compounds, modifying their structures and causing a possible negative effect on the later behaviour of these cements, particularly of their rheological properties.

Furthermore, is known that the use of industrial byproducts in cement (fly ash, blast furnace slag, lead or copper slags, etc.) may result in the inclusion of minority elements (Zn, Pb, etc.) which in some cases can affect it by delaying setting times, due to alterations in the hydrated compounds (2, 3, 4).

In spite of these negative microstructural modifications, from the point of view of a reduction in the percentage of soluble chromium, as the presence of reducing agents as the reactions of chromium in the hydration processes, is a manner of mitigating the presence of hexavalent chromium in cements.

For this reason some Nordic countries, which are concerned by the toxicity of this element and aim to achieve lower hexavalent chromium contents, recommend the incorporation of reducers such as SO<sub>4</sub>Fe (5).

In Spain there is no type of recommendation or standard in this respect; however it is true that Spanish cements analyzed show low levels of soluble chromium when compared with imported cements.

The carrying out of studies that offer new data on the presence and control of chromium VI in cements, and discussions that serve to clarify work carried out, are contributions to the establishment of limitations and test methodology to determine this element, and may in future be included in international standards.

For this reason all the works arising from this objective, such as: the nature of raw materials, process conditions when producing portland clinkers, types and percentages of additions, reducing agents, combinations of hexavalent chromium in hydration processes, etc., must be studied in depth in order to discover in the greatest possible detail everything related to the presence and behaviour of chromium VI in cements.

## References

- 1. M. Frías, M.I. Sánchez de Rojas, N. García, M.P. Luxán, *Cement and Concrete Research*, 24, N.3, 533-541 (1994).
- 2. W. Lieber, Fifth Int. Sym. on the Chemistry of Cement. Tokyo, II, 444-454 (1968).

- 3. S. Asano, F. Toda, CAJ Review, 46-47 (1981).
- 4. H. Unchikawa, K. Tsukiyama, Y. Mihara, Zementa Kalk Gips, N. 4, 195-203 (1978).
- 5. National Board of Labour Protection, Chemical Unit. Finland (1992).