

Chromate Sensitization and Elicitation from Cement with Iron Sulfate

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For some years, iron sulfate has been added to cement manufactured in the Scandinavian countries to prevent sensitization to and elicitation from chromate in cement. Allergic contact dermatitis from chromate is reported here in 3 workers with hand dermatitis and exposure to cement containing iron sulfate. Although iron sulfate had been added to the cement, high chromate concentrations were found in many samples of cement to which these workers were exposed. Key words: Allergic contact dermatitis; Occupational; Prevention.

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For some years, iron sulfate has been added to cement manufactured in the Scandinavian countries to prevent sensitization to and elicitation from chromate in cement. A recent Danish study showed a decreased incidence of chromate hypersensitivity and hand dermatitis among construction workers exposed to cement containing iron sulfate (1). In the present study, sensitization to and elicitation from chromate in 3 workers with exposure to cement with iron sulfate are reported.

CASE REPORTS

Case 1

A 19-year-old man got hand dermatitis after working as a bricklayer for one year. The dermatitis developed 5 months after addition of iron sulfate to cement in Sweden had begun. Patch testing revealed hypersensitivity to potassium dichromate and thiuram-mix. Rubber gloves, which the patient had used occasionally, yielded a negative test result. Several cement samples from various batches and brands were analysed for the presence of chromate. Concentrations between 2.0 and 4.6 µg hexavalent chromium/g cement were found. The dermatitis disappeared when he was on sick leave but returned when he went back to work. Due to the cement dermatitis he had to change his job. Without exposure to cement he has stayed free of dermatitis.

Case 2

A previously healthy 18-year-old man developed a dorsal hand dermatitis 3 months after taking employment at a fac-

tory manufacturing drain pipes and water supply equipment as well as prefabricated building materials of concrete. The dermatitis improved during weekends and got worse during work. Patch testing revealed hypersensitivity only to potassium dichromate when the testing was performed with the standard series supplemented with his own working materials. When he developed the dermatitis, iron sulfate had been added to cement in Sweden for 5 years, so no obvious chromate source was found. Therefore, the plant was visited in an attempt to obtain information that might help explain the chromate hypersensitivity and the dermatitis.

Mainly bulk cement was used at the plant. It was shipped daily to the factory. This cement was never stored more than a few days. However, the manufactured products had occasionally to be repaired, for which purpose cement from sacks was used. Also this cement contained iron sulfate. The cement from one sack could be used for a period lasting up to some weeks. Samples for chromate determination were taken from bulk cement and cement from one unbroken and one previously opened sack. Hexavalent chromium was found in the bulk cement at 0.006 µg/g cement, in the unbroken sack at 0.3 and the previously opened sack at 7.3.

After these findings our patient was assigned other work with no exposure to cement, and subsequently the dermatitis disappeared.

Case 3

A 41-year-old man had worked as a bricklayer for 20 years when he got hand dermatitis. This happened before the introduction of iron sulfate-containing cement. The dermatitis was shown to be an allergic contact dermatitis from chromate in cement. For many years he had a mild hand dermatitis, which suddenly got worse. This deterioration occurred 5 years after the introduction of cement containing iron sulfate. Chromate analysis of the cement that he used showed a concentration at 3.0 µg hexavalent chromium/g cement.

Atomic absorption spectrophotometry

An atomic absorption spectrophotometer (Perkin-Elmer 2380) with a Graphite Furnace (Perkin-Elmer HGA 400) and an autosampler (Perkin-Elmer AS-1) was used for determination of water-soluble chromium in the various cement samples. 50.0 g of cement and 25.0 ml of water were stirred for 10 min and then filtered before analysis. For those samples in which water-soluble chromium was demonstrated, a colorimetric method was used to determine the amount of hexavalent chromium (2). All water-soluble chromium demonstrated in the various cement samples was in hexavalent form. The detection limit was 0.002 µg/g cement.

DISCUSSION

Allergic contact dermatitis due to chromate (hexavalent chromium) in cement has been for a long time,

and in many countries still is, one of the commonest causes of occupational allergic contact dermatitis in men. Previously, it was demonstrated that iron sulfate has the capacity to reduce hexavalent chromium into a trivalent form (3). In a laboratory investigation, no demonstrable water-soluble chromium was found in cement when iron sulfate had been added (3). It is known that trivalent chromium will precipitate as chromic hydroxide in an alkaline solution.

As cement has a high alkalinity, this chemical process most probably explains why it was impossible to demonstrate water-soluble chromium in cement to which iron sulfate had been added. For this reason, iron sulfate has been added to all cement in connection with the manufacturing process in the Scandinavian countries for some years. In a recent study it was demonstrated by patch testing chromate-hypersensitive individuals that the eliciting capacity of cement disappeared when iron sulfate had been added (4). The result of the recent Danish study showing a decreased incidence of chromate hypersensitivity and of hand dermatitis in construction workers was therefore not surprising (1).

Usually, Scandinavian cement contains hexavalent chromium between 2 and 40 $\mu\text{g/g}$ cement before addition of iron sulfate. For some years a surplus of iron sulfate has been added to such cement, which means that no, or only traces of, water-soluble chromium is detected in freshly made cement. The laws in the Scandinavian countries require, or will require, hexavalent chromium concentrations below 2 $\mu\text{g/g}$ cement.

However, the results of the chromate analyses of the present patients' own cement samples showed a hexavalent chromium concentration exceeding 2 $\mu\text{g/g}$ cement in most samples, which all originated from Swedish cement.

The first patient was occupationally exposed to cement prior to the addition of iron sulfate, but the hand dermatitis developed 5 months after the introduction of iron sulfate-containing cement. The history and the results of patch testing and chemical analyses of various brands and batches of cement from his work strongly indicated that he was sensitized to chromate after the introduction of cement with iron sulfate. At first the presence of chromate in the cement samples was believed to be due either to introductory problems with the addition of iron sulfate to the cement, or to the use of old cement packages without iron sulfate. However, the chemical analyses of the cement samples to which cases 2 and 3 were

exposed indicated that the problem was not an introductory one. These samples originated from Swedish cement manufactured 5 years after the introduction of iron sulfate-containing cement.

The finding of hexavalent chromium above 2 $\mu\text{g/g}$ cement in many cement samples was surprising. All these samples with hexavalent chromium exceeding 2 $\mu\text{g/g}$ cement were taken from sacks which usually had been opened a few days to a few weeks before the sampling. Our chemical analyses indicate that the way of distributing and storing iron sulfate-containing cement is of importance for its chromate concentration. When cement is exposed to moisture during storage, the iron sulfate in it is likely to be changed in such a way that the hexavalent chromium will not be reduced when the cement is mixed with water. The ways of manufacturing iron sulfate-containing cement differ slightly in the Scandinavian countries. It is not known whether this is significant for the efficiency of iron sulfate in reducing hexavalent chromium in cement.

Usually, higher concentrations of an allergen are required for induction of sensitization as compared with elicitation of dermatitis in an already sensitized individual. The addition of iron sulfate to cement has never been believed to entirely eliminate chromate in cement. Thus, the sensitization—and particularly the elicitation—reported in this study was not surprising, but remarkable, since the 3 workers reported were exposed to cement with 'unreduced' levels of chromate despite the addition of iron sulfate.

The preventive effect of iron sulfate in cement with respect to chromate hypersensitivity and allergic contact dermatitis from chromate in cement is not in doubt. However, this study shows that there are still technical problems to be solved as far as the use of iron sulfate is concerned. Also, there are certain medical and/or legal implications in connection with knowledge of possible exposure to high concentrations of chromate in cement despite the addition of iron sulfate. This is of importance to some individuals both as regards the explanation of their chromate hypersensitivity and dermatitis, and possible claims on workers' compensation.

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