

Change in cement manufacturing process, a cause for decline in chromate allergy?

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Hexavalent chromate in cement is the commonest cause of allergic contact dermatitis, especially among construction workers. Over the past decades, there has been a general decline in the prevalence of chromate allergy among construction workers. We suspect that a change in the constituents of cement, resulting in the lowering of hexavalent chromate, contributed to the decline. Slag (free from hexavalent chromate) from the iron-quenched, blast furnace process has been used as a substitute for clinker (which contains high hexavalent chromate) in manufacturing cement. As a result, the slag has diluted the hexavalent chromate content of cement. Our analytical study showed that slag is free from hexavalent chromate and that the hexavalent chromate of clinker ranged from 6-17 µg/g. Substituting slag for clinker resulted in dilution of hexavalent chromate in the cement. The hexavalent chromate content of cement declines proportionately with increasing proportion of slag, e.g., a cement containing 5% slag has a total hexavalent chromate concentration of 17.5 µg/g, whereas increasing the proportion of slag to 60% reduced the hexavalent chromate content to 7.1 µg/gm in the same cement.

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Chromate, which is present as impurities in cement, has been the commonest cause of occupational allergic contact dermatitis in construction workers over the last 3 decades (1-6). Several preventive measures have been introduced to control chromate dermatitis among construction workers (7-9). These have included the addition of a reducing agent, e.g., ferrous sulfate, to cement to reduce sensitizing water-soluble hexavalent chromates (CrVI) to insoluble non-sensitizing trivalent chromium compounds. This preventive measures was introduced in Denmark in the early 1980s and subsequently in Sweden. Over the last decade, the prevalence of chromate allergy appears to have declined in most countries. The incidence of chromate dermatitis among construction workers has also declined, not only in countries that have introduced measures to add ferrous sulfate to their cement, but also in those where no such measures were taken. The reasons given for the decline have included automation and a reduction of hexavalent chromate concentration in cement. In contrast, in other countries the prevalence of chromate allergy has remained high. In the UK, 65% of 86 grouters working in the Channel Tunnel who had

occupational dermatitis had a positive patch test to chromate. This represented about 17% of the total grouters assessed (10).

In Singapore, the frequency of chromate allergy in our Contact and Occupational Dermatoses Clinic appeared to have declined significantly (5, 6, 10, 11). In 1986, the frequency in our Contact and Occupational Dermatoses Clinic was 6.8% and in 1992 2.7%. One cause was attributable to the decline in the number of construction projects in the country and another to the automation of construction processes and the introduction of the prefabrication construction process.

In addition, there have been some changes in the cement manufacturing process over the last decade. As clinker (which is a major constituent of cement) becomes scarce and more expensive, cement manufacturers have over the years found substitutes for clinker. Slag from iron blast furnace processing, a relatively cheap by-product of iron ore processing, is now used as a substitute for clinker (which contains CrVI).

We suspect that this change in the constituents of cement has led to a reduction in CrVI concentration in some cement. In this paper, we present

the findings of a study on the CrVI concentrations of 4 brands of cement, one of which had slag as one of its constituents. We also analysed the CrVI concentration of all the constituents of these 4 different brands. The effect of substituting different concentrations of slag for clinker was also studied by analysing the total CrVI concentration.

Materials and Methods

The study was carried out in 2 stages, viz, (i) determination of the CrVI concentration of the constituents (including clinker, gypsum and slag) and manufactured cement samples of 4 brands of cement manufactured in Singapore, (ii) effect of different concentrations of slag on the total CrVI concentration of a brand of cement.

The CrVI contents of the constituents (including clinker, gypsum and slag) of cement and manufactured cement were analysed in the following way (4, 13, 14).

A 10-g sample of the constituents or manufactured cement samples was mixed with 50 ml of water and left to stand for 30 min at room temperature with occasional stirring. The mixture was then filtered. A 5 ml aliquot of the filtrate was taken for colorimetric determination of CrVI concentration.

The reagents used were diphenylcarbazide and CrVI. Diphenylcarbazide was made by dissolving 0.5 g diphenylcarbazide in 100 ml of acetone and then mixing this solution with 100 ml of water. The CrVI standard (100 ppm) was made by dissolving 0.283 g of potassium dichromate ($K_2Cr_2O_7$) in 1 l of water. The samples were measured in a Phillips UV/VIS spectrophotometer (Model Pye Unicam PU 8600) with a 1 cm cell.

A 5-ml aliquot of the water extract of each cement constituent and cement sample was diluted to 25 ml with deionized water, after the addition of 1.9 ml of 6N sulphuric acid. Then 0.5 ml of diphenylcarbazide solution was added and thoroughly mixed. The intensity of the resulting purple colour was measured by the UV/VIS spectrophotometer at 540 nm against a reagent blank and compared with a calibration curve.

The calibration curve was obtained by diluting 20, 40, 60, 80 and 100 μ l of CrVI standard solution to 25 ml with 0.2N sulphuric acid (equivalent to 2, 4, 6, 8 and 10 μ g CrVI) and adding 0.5 ml diphenylcarbazide. The absorbance of the standard versus the μ g CrVI content in μ g/25 ml was plotted. The minimum detection limit of CrVI was 0.5 μ g/g.

The concentrations of CrVI in the clinker, gypsum and cement samples were determined.

Results

The major constituents of most cement include gypsum (5%) and clinker (95%). Slag (20–60%) is added as a substitute for clinker in some cement.

Table 1 shows the hexavalent chromate concentration of the cement constituents and cement samples of 4 brands of cement in Singapore. Clinker contains the highest concentration of CrVI in all brands. The total CrVI of cement comes mainly from clinker. The 4 brands of Singapore cement contain concentrations of CrVI of 16 μ g/g.

Table 2 shows the effects of adding different concentrations of slag on the total CrVI concentrations of a brand (Brand D) of cement. The total CrVI concentration in the cement was inversely proportional to the concentration of slag (over clinker). The reduction of total CrVI concentration appears to result from the dilutional effects of slag over clinker, rather than to a chemical effect of the slag on CrVI.

Discussion

Jaegar & Pelloni in 1950 (1) were the first to identify the rôle of chromate as a cause of cement dermatitis. Unlike the insoluble trivalent chromium salts, the water-soluble CrVI sensitizes and causes

Table 1. Hexavalent chromate concentration constituents of 4 brands of cement that contain slag in Singapore

Cement	Cr(VI) μ g/g					
	constituents			finished products		
	clinker	gypsum	slag	OPC	PBFC	LHPBFC
brand A	12.9	1.1	—	6.0	—	—
brand B	13.8	1.4	—	8.1	—	—
brand C	6.0	0.8	—	5.2	—	—
brand D	17.0	1.0	0	15.8	11.2	2.3

OPC: ordinary Portland cement. PBFC: Portland blast furnace cement (with 20% slag). LHPBFC: low heat Portland blast furnace cement (with 60% slag).

Table 2. The effects of adding varying concentrations of slag on hexavalent chromate concentrations in a brand of cement (brand D)

Slag concentration (%)	wt (g)	Gypsum (g)	Clinker (g)	Cr(VI) (μ g/gm)
5	0.5	0.5	9.0	17.5
10	1.0	0.5	8.5	17.1
15	1.5	0.5	8.0	14.7
20	2.0	0.5	7.5	14.5
30	3.0	0.5	6.5	12.3
40	4.0	0.5	5.5	10.2
50	5.0	0.5	5.0	8.5
60	6.0	0.5	3.5	7.1

Gypsum maintained at 5% w/w. Total weight 10 g.

allergic contact dermatitis. Previous reports have shown that CrVI in cement is present in adequate concentrations to cause allergic contact dermatitis in man; the concentration of CrVI in cement has been reported to range from 10 to 30 $\mu\text{g/g}$ in the UK and 1 to 40 $\mu\text{g/g}$ in Sweden (2).

Irvine et al. (10) reported a high prevalence (17%) of chromate allergy among underground workers during the construction of the channel tunnel. 65% of grouters patch tested had positive reaction to chromate. They supported legislation to make cement less hazardous by the addition of ferrous sulfate in Europe.

This measure may not be necessary if the hexavalent chromate concentration of cement is reduced by changes in the cement manufacturing process.

In our study in 1985, we reported that the total CrVI concentration of 6 brands of Singapore cement ranged from 3.6 to 17.7 $\mu\text{g/g}$ (4). The prevalence of chromate allergy among patients attending our Contact and Occupational Dermatoses Clinic was 6.3% in 1984 (6). Chromate accounted for 52% of all occupational allergens in Singapore in 1984 (5). The prevalence of chromate allergy among construction workers (15%) was then also high (15).

Our present study has shown a decline in the CrVI concentration of Singapore cement that contains slag. Brand D, OPC (Ordinary Portland Cement, which contains no slag), had a CrVI concentration of 15.8 $\mu\text{g/g}$, while PBFC (Portland Blast Furnace Cement), which contains 20% slag, and LHPBFC (Low Heat Portland Blast Furnace Cement), which contains 60% slag, had a lower concentration of CrVI, being 11.2 $\mu\text{g/g}$ and 2.3 $\mu\text{g/g}$, respectively. We suspect that the decline in CrVI content was due to a change in the constituents of cement and a result of a change in manufacturing process. The prevalence of chromate allergy in patients attending our clinic has also since declined (6.8% in 1986 and 2.7% in 1992) (11, 12).

In a recent report comparing the CrVI concentration of cement from different countries, a wide concentration range was found (16). In some countries, including Singapore, the concentration of CrVI in some cement was low. In Sweden and Denmark, the CrVI concentration in cement has been reduced by adding ferrous sulfate to cement (17). This was adduced as a possible cause of the decline in the prevalence of chromate dermatitis among construction workers in Denmark (17). Chromate dermatitis from cement was never reported to be a major problem in the US and Canada. One reason could be the low concentration of CrVI in cement in these countries, due to differences in the constituents of cement.

Cement does not have a constant composition. It is made from clinker (chalk or limestone), clay (or shale) and gypsum (calcium sulfate). The source of chromates in cement remains controversial. It was believed to come from chrome steel grinders and ash. Johnston & Calnan (2) found chromate in clay, coal ash and chalk (clinker). Most of these chromates exist as insoluble trivalent chromium compounds, but are converted into water-soluble CrVI in the kiln (18).

Over the last 2 decades, the manufacturing process and constituents of cement have changed. This could have resulted in lowering the concentration of CrVI in some cement. Of probable significance is the more widespread use of quenched-iron, blast-furnace slag as a substitute for clinker in cement in the mid-1980s.

Quenched-iron, blast-furnace slag is a by-product of the iron ore extraction process. Iron ore, containing iron oxides, silica, alumina, etc. (70% of total weight), is mixed with fluxing stone (containing limestone and/or dolomite, equivalent to 5% of total weight) and fuel (coal, forming 25% of total weight) in the iron blast-furnace operation. The blended raw materials (burden) and coal are introduced at the top of furnaces. As the materials move down through the furnace, the ignited coal eventually supplies enough heat to melt the burden. The slag results from fusion of the fluxing stone (limestone/dolomite) with the gangue (siliceous and aluminous residues from the iron ore) and coal ash in the blast furnace. The molten slag floats on top of the molten iron and below the unmelted burden. Both molten materials are continually drawn off at regular intervals from the furnace. Slag is tapped from modern blast furnaces using high quality ore burden.

Over the last decade, an improved slagging process was introduced in the US and Canada in iron blast-furnace processes. These slags are more widely used as cementous materials. Slag has been used in cement in the US and Canada since the 80s. The main constituents of slag include calcium oxide (40%), silicate (38%), magnesium oxide (10%) and aluminium oxide (8%). It contains small quantities of total iron, manganese and sulfur, etc. (19). This might have explained the lower concentration of CrVI in North American cement, and the relatively lower prevalence of chromate dermatitis in the US and Canada compared to Europe. This might also explain the lower concentration of CrVI recently in Singapore cement.

Our study indicated that increasing the concentration of slag over clinker proportionally reduced the CrVI concentration of cement (Table 2). This is *not* similar to the effect of adding a reducing agent, e.g. ferrous sulfate. Previous studies have

shown that ferrous sulfate at a low concentration of 0.35%, was able to reduce almost all CrVI in cement (8, 9). It is therefore unlikely that the slag in cement reduces CrVI chemically, but the reduction in the CrVI concentration is probably due to the dilutinal effect of slag over clinker.

The substitution of slag for clinker in cement resulted in the dilution of CrVI concentration in cement. This could be one of the reasons for the observed decline in the prevalence of cement dermatitis among construction workers in recent years in Singapore.

We expect the prevalence of chromate dermatitis in other countries to decline as slag is more widely used to substitute for clinker in cement manufacturing in other countries. Our findings indicate the need for dermatologists to be familiar with changing manufacturing processes, in order to understand changes in disease trends.

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