

FACTORS DECREASING THE CONTENT OF WATER-SOLUBLE CHROMATE IN CEMENT

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Abstract. The water-soluble chromate in Portland cement, i.e. the sensitizing chromium, can theoretically be eliminated or reduced in several ways: by changing the composition of the raw materials, by changing the manufacturing process, by dilution with chromate-free material, by precipitation, or by reduction combined with precipitation. Reduction with ferrous sulphate seems to be the only worthwhile possibility. All water-soluble chromate is reduced and precipitated by addition of 0.2% ferrous sulphate when the water-soluble chromate content reaches 15 $\mu\text{g Cr/g}$. Studies are now in progress to elaborate a practical application.

It is probable that only the water-soluble chromium compounds in cement are capable of inducing chromium allergy or eliciting dermatitis in chromium-sensitized persons. Due to the alkalinity of cement, only hexa-valent chromium (chromate) is soluble. However, tri-valent chromium is also an allergen (5) and it is uncertain if the skin, under normal conditions, can neutralize enough cement to allow tri-valent chromium to become soluble.

In order to eliminate or reduce the amount of soluble chromate in cement, the following methods can theoretically be considered.

Minimization or elimination of chromate supplied via raw material, kilnbricks or in grinding. The amount of chromium, always in a tri-valent form, in the raw material can vary. From the practical point of view it is difficult to choose material with a low chromium content, especially as large amounts are involved.

Two types of brick are used for kilns, the magnesite type with large amounts of added tri-valent chromium and the dolomite type with little or no chromium. Rotary kiln bricks should not, however, give off any amount worth mentioning except perhaps in a newly lined furnace (9, 10,

12, 14). Later, a relatively stable layer of clinker is built up.

It is probable that a small amount of chromium may be added to the slurry when grinding with nickel-chromium balls in the ball mill (9). This chromium can later be oxidized during the heating process, in contrast to the chromium which is added when clinker is ground (9, 10, 12).

In some factories, used kiln bricks are ground and mixed with the raw material, whereby a relatively large amount of chromium can accidentally be added to the cement. Such ingrounding should, of course, be avoided.

Diminished oxidation. Portland cement was previously produced in vertical kilns without a surplus of air. Little chromium or none at all was oxidized by this process (3, 4), which is still used for calcium aluminate cement in which no oxidation of the chromium occurs (6, 12). For technical reasons a surplus of air must be used in a modern rotary kiln for Portland cement.

Prolonged heating. Calcium chromate is not stable at high temperatures and the heating of clinker to 1400°C for 3 hours has been reported to diminish the chromate content from 10 to 1 $\mu\text{g/g}$ (12). From a technical point of view such heating is not possible in routine processing because of other changes in the clinker.

Low content of water-soluble sulphate. The amount of water-soluble sulphate in the clinker (i.e. cement without gypsum) can be reduced and thereby also the amount of water-soluble chromate, by using raw material that gives a relatively low alkali content (7). This would, however, give rise to practical and economic difficulties.

Gypsum, calcium sulphate, must for technical reasons always be added to the clinker, thus

Table I. Amount of iron sulphate necessary for complete reduction of Cr⁶ in cement

Cement sample	Original water-soluble Cr ⁶ ($\mu\text{g/g}$)	FeSO ₄ ·7H ₂ O (% added)	Fe(NH ₄) ₂ (SO ₄) ₂ ·6H ₂ O (% added)
1	2	0.10	0.25
2	15	0.20	0.50
3	13	0.20	0.50
4	40	0.25	

soluble sulphate is always present in Portland cement (6, 7). If the cement contains only the soluble sulphate released by action of gypsum, the chromium content is usually less than 5 $\mu\text{g Cr/g}$ (7).

Dilution by addition of material. Blast furnace slag and Pozzolan material, which do not contain hexa-valent chromium, are added for technical reasons (6, 11, 13). Their effect on the chromate content is studied in the present investigation.

Precipitation. Precipitation of the chromate with barium and lead has been reported (8, 15, 16, 24, 25, 26). This method is also investigated in the present study.

Reduction. Reduction with ascorbic acid and sulphur compounds has been reported (8, 19, 20, 21, 22). Generally speaking, the reducing agents have been incorporated in barrier creams to be used in cement work (19, 20, 25).

The reducing capacity of iron sulphate (Fe^{II}SO₄) has previously been studied for both dermatological (1, 12, 27) and technical reasons (28).

Binding. It has been suggested that an ion exchanger resin which can bind chromate should be incorporated in barrier creams (23). EDTA has also been used in the same way (8, 18).

INVESTIGATIONS

Determination of chromium in water extract. Five grams of cement was shaken mechanically with 50 ml distilled water for 15 min and then filtered and washed at 100 ml water. The water extract was sucked direct into an Atomic Absorption Spectrophotometer (Perkin-Elmer 303) for the determination of chromium (6).

In order to determine the tri- and hexa-valent

chromium separately, the hexa-valent was chelated by ammonium pyrrolidine-di-thiocarbamate at pH 8.0 and extracted from the water solution by methyl-*iso*-butylketone before determination in the atomic absorption spectrophotometer (6).

All determinations were made in duplicate. The amounts of metals are expressed in $\mu\text{g Cr}$ per gram of cement.

Dilution by addition of material. One part of either blast furnace slag or of Pozzolan material was mixed with two parts of Portland cement containing water-soluble chromate (15 $\mu\text{g Cr/g}$).

10 $\mu\text{g Cr/g}$ was found in both mixtures. Thus, there was no reduction, but the decrease corresponds only to the dilution of the material (17). Some samples of furnace slag contain sulphides which can reduce chromate in an acid environment which is why a false value can be obtained if a colorimetric method with diphenylcarbazide and sulphuric acid is used (6, 17). In the present investigation the chromate was determined in an alkaline environment.

Precipitation. Barium hydroxide (5%) was added to Portland cement containing water-soluble chromate (10 $\mu\text{g Cr/g}$). No water-soluble chromate was found in this mixture. Thus, the report on complete precipitation is confirmed.

Lead acetate (5%) was added to Portland cement containing water-soluble chromate (10 $\mu\text{g Cr/g}$). No water-soluble chromate was found in the mixture. Thus, the report on complete precipitation of lead is also confirmed.

Reduction

(a) *Ascorbic acid* (5%) was added to cement containing water-soluble chromate (13 $\mu\text{g Cr/g}$). The content of chromate decreased to 6 $\mu\text{g Cr/g}$.

(b) *Sodiumthiosulphate* (5%) (Na₂S₂O₃) was added to cement containing water-soluble chromate (13 $\mu\text{g Cr/g}$). The content of chromate decreased to 9 $\mu\text{g Cr/g}$.

(c) *Sodium metabisulphite* (5%) (Na₂S₂O₃) was added to cement containing water-soluble chromate (13 $\mu\text{g Cr/g}$). The content of chromate decreased to 9 $\mu\text{g Cr/g}$.

(d) *Sodium dithionite* (Na₂S₂O₄) in various concentrations was added to cement containing water-soluble chromate (10 $\mu\text{g Cr/g}$). When 0.2% was added, all the chromate was reduced and precipitated.

(e) Ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and ferrous ammonium sulphate (Mohr's salt) ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) in various concentrations were added to cement containing water-soluble chromate. All the chromate was reduced, as detailed in Table I. No chromium at all was present in the filtrate, since the reduced chromium, after reduction into tri-valent form, was precipitated in the alkaline environment.

DISCUSSION

It does not seem possible for technical or economic reasons to appreciably diminish the content of water-soluble chromate in Portland cement by changing the composition of the raw material, or by changing the construction of the kiln, or even the process itself. As described earlier, a low water-soluble sulphate content also results in a low water-soluble chromate content (7) and it is conceivable that this sulphate content can be minimized in certain factories by modification of the raw materials. However, as a generally applicable method, this is not feasible.

The addition of blast furnace slag or Pozzolanic material reduces the water-soluble chromate content and this fact should be exploited as much as possible, even though the chromium sensitization risk cannot be completely eliminated.

Precipitation with barium and lead is not really a practical proposition, since the amounts required (5% of the final cement product) would not be justifiable on economic grounds. A conclusive fact is that both lead and barium are poisons and their use should not be permitted, for ecological reasons.

It is uncertain whether creams with binding ion exchangers, reducing substances (e.g. ascorbic acid, sulphur compounds) or ferrous sulphate have any important clinical effect.

One must take into account the fact that the active substances are only present on the skin for a short time and therefore they need to be applied many times a day, which is no doubt a practical impossibility over a period of several years.

The addition of sodiumthiosulphate and sodiummetabisulphite in such a high concentration as 5% does not achieve complete reduction of the chromium. In contrast, sodiumdithionite does afford complete reduction with a concentration as

low as 0.2%. However, this substance loses its reduction properties considerably if stored, especially in a damp environment. Thus, it may well be of little practical use.

The best solution of the problem would no doubt be to add ferrous sulphate. The amount of ferrous sulphate required to achieve complete reduction is small, 0.1%–0.2%, and it is inexpensive. Amounts of up to 5% ferrous sulphate do not affect Portland cement technically (2).

At present, studies are in progress to determine if it is best to add FeSO_4 simultaneous with the grinding of gypsum to clinker, or when mixing cement with water for use.

REFERENCES

- Burckhardt, W., Frenk, E., de Sépibus, D., Paschoud, J. M., Szadurski, J. & Schwarz, K.: Abschwächung der ekzematogenen Wirkung des Zementes durch Ferrosulfat. *Dermatologica* 142: 271, 1971.
- Cementa AB, Sweden: Personal communication, 1972.
- Flatt, R. & Cusani, P.: Sur le dosage du chrome dans les produits de l'industrie du ciment. *Anal Chim Acta* 21: 181, 1959.
- Flatt, R.: Sur la teneur en chrome des ciments. *Chimia* 13: 80, 1959.
- Fregert, S. & Rorsman, H.: Allergy to trivalent chromium. *Arch Derm (Chicago)* 90: 4, 1964.
- Fregert, S. & Gruvberger, B.: Chemical properties of cement. *Berufsdermatosen* 20: 288, 1972.
- Correlation between alkali sulphate and water-soluble chromate in cement. *Acta Dermatovener (Stockholm)* 53: 225, 1973.
- Ippolito, F.: La chelazione dei cromati mezzo di prevenzione della dermatite allergica da cromo. *Dermatologia* 12: 137, 1961.
- Johnston, A. J. M. & Calnan, C. D.: Cement dermatitis. *Trans St. John's Hosp Derm Soc* 41: 11, 1958.
- Keiling, K.: Chromgehalt der Zemente. *Deutsch. Bauakademie, Baustoffe, Heft 19*. Verlag f. Bauwesen, Berlin, 1962.
- Kramer, W.: Blast-furnace slags and slag cements. IV Int Symp Chem Cement, Washington, D.C., 1960, p. 957.
- Kühnen, G.: Über den Chromgehalt von Zementen. *Berufsgenossenschaft/Betriebssicherheit* No. 40, 130, 1966.
- Malquori, G.: Portland-Pozzolan cement. IV Int Symp Chem Cement Washington, D.C. 1960, Paper VIII-3, p. 983.
- Matouschek, F.: Die Beeinflussung des Chromatgehaltes des Zementklinkers durch chromhaltige Magnesitsteine. *Zement-Kalk-Gips* 11: 496, 1962.
- Panconesi, E., Sertoli, A., Fabri, P. & Venturi, A.: New preventive measures against chromium-allergic eczema in masons. *Ital Gen Rev Derm* 10: 9, 1970.

16. Panconesi, E., Sertoli, A., Venturi, A. & Fabri, P.: La precipitazione del cromo mediante un sale di bario nella prevenzione dell'eczema allergico da cemento. *Folia Allerg* 27: 194, 1970.
17. Pisters, H.: Chrom im Zement und Chromatekzem. *Zement-Kalk-Gips* 19: 467, 1966.
18. Resl, V. & Sýkova, J.: Versuche in vitro mit Schutzsalben gegen Chrom- und Nickelschädigung der Haut, *Derm Wschr* 151: 1327, 1965.
19. Samitz, M. H., Epstein, E. & Katz, S.: Inactivation of hexavalent chromium. *Arch Derm (Chicago)* 85: 595, 1962.
20. Samitz, M. H.: Ascorbic acid in the prevention and treatment of toxic effects from chromates. *Acta Dermatovener (Stockholm)* 50: 59, 1970.
21. Samitz, M. H., Gross, S. & Katz, S.: Inactivation of chromium ion in allergic eczematous dermatitis. *J Invest Derm* 38: 5, 1962.
22. Samitz, M. H., Epstein, E. & Katz, S.: Inactivation of hexavalent chromium. *Arch Derm (Chicago)* 85: 77, 1962.
23. Schuppli, R.: Neue Möglichkeiten der Behandlung von Chromatekzemen. *Dermatologica* 134: 60, 1967.
24. Sertoli, A., Venturi, A. & Fabri, P.: Sull'inattivazione del potere eczematogeno del cemento con sali di bario. *Rassegna di Derm Sif* 21: 390, 1968.
25. Sertoli, A., Venturi, A. & Lo Brutto, M. E.: Tentativi di inattivazione del potere sensibilizzante del cemento. *Rassegna Derm Sif* 20: 415, 1967.
26. Scolari, E. G.: Directives et orientation actuelles de nos recherches concernant la pathogénie de l'eczéma de contact. *Dermatologica* 135: 408, 1967.
27. Tataru, C., Marinescu, A., Capusan, I., Ripan, R. & Liteanu, C.: Hautschädigungen bei der industriellen Gewinnung von Kaliumbichromat. *Berufsdermatosen* 5: 283, 1957.
28. Ulfstedt, L.: Intern. Siporex AB Labor. Report 32, reg. No. 2210, 1949.

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