Acta Dermatovener (Stockholm) 53: 225–228, 1973

CORRELATION BETWEEN ALKALI SULPHATE AND WATER-SOLUBLE CHROMATE IN CEMENT

S. Fregert and B. Gruvberger

From the Department of Dermatology, University of Lund, Sweden

Abstract. Since far more chromate can be extracted from cement with sodium sulphate than with water, the hypothesis was adopted that the amount of chromate which is extracted with water (i.e. the eczematogenous chromate) is dependent on the alkali sulphate originally found in the cement. A number of experiments have been performed which support this hypothesis. It is technically feasible to regulate the raw material so that no alkalisulphate forms in the clinker and thereby no water-soluble chromate. The content of such chromate in cement is thus relatively low and dependent only on the sligthly soluble gypsum (calcium sulphate) which is added to the clinker. However, from a financial point of view it is difficult to alter the composition of the raw material.

Brun (2, 3) found that when cement was extracted with sodium sulphate, 2–20 times more hexavalent chromium (chromate) was obtained than by extraction with water only. He presumed that only a part of the chromate in cement was "free" and that the rest was "adsorbed" but that a part could be "liberated" by sodium sulphate. He found that even the amount of chromate that could be extracted with water diminished with time. Thus, after 24 hours extraction very little or no chromate was obtained. If sodium sulphate was added after 24 hours of water-extraction, the chromate was recovered. Thus, the original "free" chromate also had been adsorbed after 24 hours, but could be "liberated" again.

It is known that cement normally contains alkali sulphate and we have therefore assumed that the chromate which was extracted by addition of water only was in reality "sulphate-extracted".

To test this hypothesis, several experiments were carried out.

MATERIAL AND METHODS

The cement samples were the same as those previously analysed (5). Samples of clinker were obtained from two Swedish cement factories.

The water-soluble chromate was determined by atomic absorption spectrophotometry as described previously (5). The determination of chromate extractable with sodium sulphate (20%) was carried out according to Petruzzellis et al. (5, 7). The sodium sulphate was free from chromium (4). The chromate values are expressed in μg/g.

Determination of water-soluble sulphate in cement

50 g of cement was shaken with 25 ml of water for 20 min. To the supernatant, 10 ml of $BaCl_2$ (10%) was added and the supernatant checked by adding more $BaCl_2$. Warm nitric acid (2.5 M) was added to the precipitate to disolve precipitates other than $BaSO_4$, e.g. $BaCrO_4$. The precipitate was washed three times with water, dried overnight at 105°C and finally weighed. Sulphate values are expressed in mg SO_4^{-2} per gram cement.

All determinations were made in duplicate.

INVESTIGATIONS

(*a*) The presence of water-soluble sulphate and water-soluble chromate was determined in cement samples from eight different factories (5). The results (Fig. 1) indicate that there is a correlation between the amount of water-soluble sulphate and water-soluble chromate.

(*b*) Because gypsum, calcium sulphate, is partly soluble in the alkaline environment, water-soluble sulphate will always be present in cement. Therefore the content of water-soluble sulphate and water-soluble chromate was determined in clinker, i.e. cement without gypsum. Since it seemed likely that the content of water-soluble sulphate might be lower or even absent in at least some clinker samples, the presence of sulphate and chromate was determined in seven samples of clinker from the same factory, obtained on different occasions. It was found, as seen in Fig. 2, that water-soluble chromate was present only in the three clinkers which contained soluble sulphate.

(*c*) Four different clinkers free from soluble

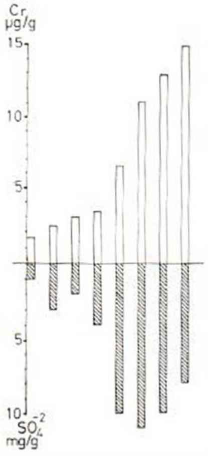

Fig. 1. Water-soluble chromate and water-soluble sulphate in 8 samples of cement.

sulphate and soluble chromate were extracted with sodium sulphate (20%), resulting in 26, 28, 28, and 38 µg Cr/g, which is about the same as was obtained when a similar cement was extracted in the same way (5). This shows that chromate is soluble only when sulphate is present.

(*d*) To the four clinkers (Fig. 2) which lacked soluble sulphate, 3.5% gypsum, calcium sulphate, was added, forming complete Portland cement. Some of the chromate then became water-soluble (Fig. 3). Thus, the water-soluble part of the gypsum has the capacity to render some chromate soluble.

(*e*) To clinker without water-soluble chromate but containing 33 µg Cr/g extractable with sodium sulphate (20%), various amounts of sodium sulphate were added. As can be seen in Fig. 4, the content of water-soluble chromate increases with the alkali sulphate added.

(*f*) To the three clinkers (Fig. 2) ocntaining water-soluble sulphate and chromate, 10% ammonium chloride (NH_4Cl) was added and heated at 1 200°C for 3 hours. The free alkali was evaporated by this procedure (6) and the water-soluble sulphate disappeared. Less than 1 µg Cr/g was then water-soluble.

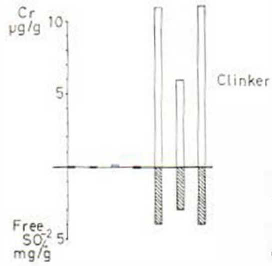

Fig. 2. Water-soluble chromate and water-soluble sulphate in 7 samples of clinker.

Fig. 3. Water-soluble chromate in clinker before and after adding of gypsum (cement = clinker + gypsum).

Cement containing 13 µg water-soluble chromium and 10 mg water-soluble SO_4^{-2} per gram was treated in the same way. Less than 1 µg Cr/g was then water-soluble. Thus, decrease of the alkali decreases the solubility of sulphate and thereby also the content of water-soluble chromate.

(*g*) Clinker always contains water-insoluble sulphate and this can be partly dissolved by alkali. To the four clinkers (Fig. 2) lacking both soluble sulphate and soluble chromate, 1 M NaOH was added (50 ml to 5 g of clinker). Soluble sulphate (2 mg SO_4^{-2}/g) was then found and the amount of soluble chromate increased to about 4 µg Cr/g. Thus, increase of alkali is held to increase the solubility of sulphate and thereby also the content of water-soluble chromate.

(*h*) Cement samples containing water-soluble sulphate (10 mg SO_4^{-2}/g) and water-soluble chromate (13 µg Cr/g) were extracted with water for 24 hours, after which time the SO_4^{-2} had decreased to 2.5 mg/g and the chromate to 5 µg Cr/g.

(*i*) From cement samples containing water-soluble sulphate, 28 µg Cr/g could originally be extracted with sodium sulphate. After 24 hours of water extraction, 25 µg Cr/g could be extracted with sodium sulphate.

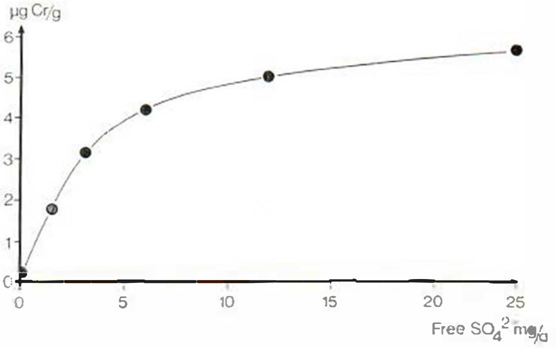

Fig. 4. Correlation between water-soluble chromate and added alkali-sulphate in clinker.

The findings in (*h*) and (*i*) may indicate that the solubility of chromate decreases when the sulphate is incorporated during the hydration process of cement manufacture, but can be "liberated" again with sodium sulphate.

(*j*) Two parts of cement (13 μg Cr/g) and 1 part of water were mixed and then dried as a thin layer under plastic occlusion for 2 months. The hardened concrete was then crushed in an agate mortar. The water-soluble chromate content was 4 μg/g cement.

The amount of sodium-extractable chromate was, in the original cement, 28 μg. In the hardened concrete the chromate content was 27 μg Cr/g of cement. Thus, the solubility of chromate decreases during the hardening process but remains extractable with sodium sulphate.

k) Pisters described (8) how 1 g of cement of known content of total chromium was extracted with 100 ml of sodium sulphate (20%) for 48 hours at 80°C under continuous stirring. All the extracted chromium was hexa-valent. In the present investigation the ratio of extractable chromate and total chromium for four cement samples from different factories was 36/66, 13/52, 17/43 and 50/173. Thus, only a part of the total chromium can be extracted with sodium sulphate.

DISCUSSION

The present investigation shows that when clinker, i.e. cement without gypsum, does not contain water-soluble sulphate, it does not contain water-soluble chromate (*b*). If gypsum or sodium sulphate are added, the chromate becomes soluble (*c, d, e*). When sulphate solubility is decreased by the addition of ammonium chloride at a high temperature (*f*) the chromate content is also diminished. When sulphate solubility is increased by the addition of alkali, the chromate content is also increased (g). As sulphate becomes incorporated by the hydration of cement during 24 hours' extraction with water (*h*) or 2 months' hardening (*j*) the solubility of chromate decreases. When this cement is extracted with 20% sodium sulphate just as much is obtained as was obtained at the original cement extraction (*i, j*).

Even with prolonged extraction at higher temperatures plus sodium sulphate, only a part of the total chromium is obtained (*k*).

Brun's (2, 3) finding that little or none of the water-soluble chromate remains after 24 hours of extraction is explained by Pister's finding (8), that the amount of sulphate diminishes or disappears after 24 hours. These findings have been confirmed in the present study (*h*). However, this decrease was restored when 20% sodium sulphate was added (*i*).

The present findings verify our hypothesis that the amount of water-soluble chromate in Portland cement is dependent on the water-soluble sulphate. Since chromate is obtained by extraction with water alone, it implies that chromate has been extracted with the soluble sulphate already present in cement.

According to the findings that chromate and sulphate interact and that sulphate is known to be incorporated into the calcium aluminate to form calcium hydrosulpho-aluminate (1) it can be postulated that the chromate too is incorporated into this compound.

To reduce the content of water-soluble chromate and thus possibly the risk of sensitization, cement should contain as little water-soluble sulphate as possible.

Since all cement must, for technical reasons, contain gypsum (calcium sulphate) which is to a certain extent soluble, one must count on cement generally containing chromate in soluble form. This was the case in the 52 samples from different countries previously studied (5).

The amount of water-soluble sulphate in the actual clinker should be reduced by keeping the content of alkali at a low level. Since alkalinity is dependent on the nature of the raw material, and since factories use the local raw material, it would no doubt be not only a technical hut also a financial problem to alter the composition of the raw materials. The total content of chromium seems, on the other hand, to be of minor importance. As shown previously, the total content in two samples was considerably higher than in all others, but the values of water-soluble chromate were among the lowest (5).

From the practical point of view, it is therefore necessary to find other ways of completely eliminating the water-soluble hexa-valent chromate in cement.

REFERENCES

1. Bogue, R. H. & Lerch, W.: Hydration of Portland cement compounds. Ind Eng Chem *26:* 837, 1934.

2. Brun, R. M.: Contribution à l'analyse des chromates du ciment. Helv Chim Acta *46:* 2933, 1963.
3. Brun, R. M.: Contribution à l'étude des chromates du ciment. Nouvelle technique pour le test épicutané au ciment. Dermatologica *129:* 79, 1964.
4. Fregert, S., Gruvberger, B. & Heijer, A.: Sensitization to chromium and cobalt in processing of sulphate pulp. Acta Dermatovener (Stockholm) *52:* 221, 1972.
5. Fregert, S. & Gruvberger, B.: Chemical properties of cement. Berufsdermatosen *20:* 238, 1972.
6. McCoy, W. J. & Eshenour, O. L.: Significance of total water soluble alkali contents of cement. Proc. 5 Symp. Chem. Cement, Tokyo *2:* 437, 1968.
7. Petruzzellis, V., Rantuccio, F., Meneghini, C. L. & Bruno, P.: In tema di morbilità cutanea da cemento in cantieri edili e nelle cementerie. Giorn Ital Derm Minerva *44–110:* 485, 1969.
8. Pisters, H.: Chrom im Zement und Chromatekzem. Zement-Kalk-Gips *19:* 467, 1966.

Received August 25, 1972

S. Fregert, M.D.
Section of Occupational Dermatology
University Hospital
S-221 85 Lund
Sweden