# THE CHROMIUM CONTENT OF CEMENT AND ITS SIGNIFICANCE IN CEMENT DERMATITIS\*

# CLEVELAND R. DENTON, M.D.,<sup>†</sup> ROBERT G. KEENAN, M.S.,<sup>‡</sup> and DONALD J. BIRMINGHAM, M.D.§

Cement dermatitis has been generally regarded as resulting from primary irritation due to the alkaline, abrasive, and hygroscopic properties of cement (1-3). In the past few years, however, there have been several reports in the foreign literature indicating that dermatitis experienced by cement finishers, fabricators and masons may be due to a specifically acquired hypersensitivity to water-soluble chromate compounds present in cement (4-13). This interesting observation has only recently received attention in this country (14-16).

Preliminary fact finding for a study of cement dermatitis from the viewpoint of chromate allergic hypersensitivity revealed that while chromium had been detected in American cement in trace amounts, its actual concentration had never been determined by precise analytical methods (17, 18). Moreover, there was no available information regarding the chemical nature or water solubility of the chromium compounds present in American cement. Accordingly, several samples of cement produced in various parts of the United States were analyzed.<sup>1</sup>

It is proposed in this report to give the concentrations and water solubility of chromium compounds found in the cements examined, and to show that a patient with an allergic contact-type dermatitis due to potassium dichromate reacted to hexavalent chromium as found in aqueous washings of cement powder.

### ANALYTICAL PROCEDURE

Chemical analyses were performed on seven samples of type 1 portland cement (19) to determine the concentrations of hexavalent and total chromium in cement washings, and the total chromium present in the water-insoluble residues and in the original cement powder.

Single 50-gram samples of each cement sample were shaken with two successive 100 ml. portions of double distilled water for 30 minutes each at 25°C. The two suspensions obtained were each filtered and washed through four layers of Whatman No. 42 paper on a Buchner funnel. Each of the two resulting filtrates was analyzed directly for hexavalent chromium and again following the oxidative conversion of all other chromium present to the hexavalent state.

One-gram portions of the dried residue from the two washings and one-gram portions of the original cement sample were analyzed for total chromium. All chromium values were

\* From the U. S. Department of Health, Education, and Welfare, Public Health Service, Bureau of State Services, Division of Special Health Services, Occupational Health Field Headquarters, 1014 Broadway, Cincinnati, Ohio.

‡ Sanitarian (R), Chief, Physical Analytic Unit.

§ Senior Surgeon, Chief, Clinical Section, Dermatologist.

Received for publication June 11, 1954.

<sup>1</sup> Acknowledgment is given to the member companies of the Portland Cement Association who generously supplied cement samples.

<sup>†</sup> Senior Assistant Surgeon (R), Dermatologist.

# TABLE I

Sample No.	Wash No.	Cr <sup>+e</sup> in Washing µg/g	Total Cr in Washing µg/g	Total Cr in Residue µg/g	Total Cr in Unwashed Cement µg/g	Per Cent Cr Accounted for in Washings and Residue
1	1	1.26	3.00	26.0	28.0	104.6
	2	0.003	0.28			
2	1	2.95	3.52	43.0	52.0	90.9
	2	0.78	0.81			
3	1	0.03	1.58	30.9	35.2	92.3
	2	0.003	0.03			
4	1	1.46	1.59	30.0	31.8	101.5
	2	0.56	0.70			
5	1	3.15	5.16	36.0	38.9	106.6
	2	0.27	0.40			
6	1	3.01	3.30	26.9	29.3	105.1
	2	0.55	0.64			
7	1	6.9	7.0	57.5	60.0	100.3
	2	0.3	0.4			

Concentration of hexavalent chromium in two 100 ml. washings of 50-gram type 1 Portland Cement samples and total chromium in washings, residues and unwashed samples

determined by a diphenylcarbazide method for hexavalent chromium (20). Known amounts of trivalent chromium were carried through the same oxidative and color development steps as the cement samples in the preparation of hexavalent chromium analytical standards. Details of the methods used will be described in a subsequent report.

#### RESULTS

The chromium values obtained are shown in Table I. It may be noted that nearly all of the water-soluble chromium present is leached out in the first 30 minutes of washing. However, it is apparent that water-soluble chromium represents only a small portion of the total chromium in the original cement powder. With the exception of samples 1 and 3, hexavalent chromium accounts for over one-half of the water-soluble chromium.

The hexavalent chromium  $(Cr^{+6})$  values in the first filtrates vary from 0.03 to 6.9 micrograms per gram of original cement powder, or expressed as potassium dichromate the percentage range is 0.000008 to 0.002. If total water-soluble chromium is expressed as potassium dichromate, the percentage range is 0.00004 to 0.002. This latter range is given for comparison with the values cited below from the foreign literature which are, with one exception, for total water-soluble chromium present in cement washings.

German cements are reported to contain up to 0.0025 per cent water-soluble chromium expressed as potassium dichromate (7, 9). Norwegian cements have 0.002 to 0.02 per cent chromium in terms of water-soluble chromium compounds determined colorimetrically (8). The percentage range of water-soluble chromium in Swedish cements is given as 0.00002 to 0.002 without further qualifications (11). A chemical analysis of one Finnish cement showed about 0.0001 per cent water-soluble hexavalent chromium (13). It is apparent that the soluble chromium content of cement samples varies widely; however, the percentage range of soluble chromium in cement is of the same order for all countries.

# PATCH TESTING WITH CEMENT WASHINGS

The usual concentration of potassium dichromate solution employed for patch testing purposes is 0.5 per cent; however, percentages of 0.1 to 0.05 have been suggested recently (16).

A patient with a strong specific hypersensitivity to potassium dichromate was patch tested on three occasions with 0.005 per cent potassium dichromate solution and the first filtrate of cement samples No. 4 and No. 7 which were adjusted to pH 5.5. The concentration of hexavalent chromium in each filtrate in terms of potassium dichromate was 0.0001 and 0.0004 per cent respectively. The patient repeatedly showed a positive erythematous, edematous, papulovesicular patch test reaction to each of the test solutions. Patch tests with distilled water were negative. Control subjects did not react to any of the test solutions. It is probable that the average soluble hexavalent chromium content of cement would be sufficient to cause and maintain an allergic contact-type dermatitis in this patient.

#### DISCUSSION

Moistened cement undoubtedly exerts a primary irritant action on the skin; however, the recent findings of positive patch tests to hexavalent chromium in cement users indicates that allergic chromate hypersensitivity may initiate and maintain cement dermatitis. Soluble hexavalent chromium is apparently present in all cements to a varying degree. Cement artisans are exposed to higher hexavalent chromium levels than is indicated by analysis of cement washings, for as moisture evaporates from cement slurries in contact with the skin, the percentage of hexavalent chromium rises.

# CONCLUSION

Data cited and shown in this report indicate that allergic hypersensitivity to hexavalent chromium may be a contributing factor in certain cases of cement dermatitis.

# REFERENCES

- 1. KEIL, H.: The patch test with building materials, with special reference to hydraulic cement and lime. Urol. & Cutan. Rev. 47: 223-234, 1943.
- PECK, S. M.: A discussion of the commoner industrial dermatoses. Ind. Med. 14: 960-964, 1945.
- SCHWARTZ, L., TULIPAN, L. AND PECK, S. M.: Occupational Diseases of the Skin. Lea and Febiger, Inc., Philadelphia, 1947, Hydraulic Cement, pp. 171-173.
- PIRILÄ, V. AND KILPIÖ, O.: On dermatoses caused by bichromates. Acta dermat.venerol. 29: 550-563, 1949.
- 5. JAEGER, H. AND PELLONI, E.: Tests épicutanés aux bichromates, positifs dans l'eczéma au ciment. Dermatologica 100: 207-216, 1950.

- FREY, V. E.: Beitrag zur Bewertung der Jaeger' schen Kalibichromatoprobe auf Zement. Dermatologica 105: 244-250, 1952.
- 7. SPIER, H. W. AND NATZEL, R.: Zur pathogenes des zementekzems. 1. Zementekzem und chromatallergie. Arch. Dermat. u. Syph., 193: 537-550, 1952.
- 8. ENGEBRIGTSEN, J. K.: Some investigations on hypersensitiveness to bichromate in cement workers. Acta dermat.-venerol. 32: 462-468, 1952.
- 9. ENGELBRECHT, H.: Maurerekzem und Chromgehalt des Zements. Hautarzt 3: 542-546, 1952.
- PONTES DE CARVALHO, L. AND BRUM NEGREIROS, E.: Occupational dermatitis in cement workers. Hospital (Rio de Janeiro) 41: 495-501, 1952. (Abst., Excerpta Medica. Dermatology and Venereology 7: 101, 1953).
- 11. SKOG, E. AND THYRESSON, N.: The occupational significance of some common contact allergens. Acta dermat.-venerol. 33: 65-74, 1953.
- SIDI, E. AND LONGUEVILLE, R.: Dermites au ciment. Rôles des sels de chrome. Arch. mal. profess. 14: 41-44, 1953.
- PIRILÄ, V.: On the rôle of chrome and other trace elements in cement eczema. Acta dermat.-venerol. 34: 136-143, 1954.
- 14. Lead, cadmium and chromium poisoning. Foreign Letters, J.A.M.A. 151: 938, 1953.
- 15. WALSH, E. N.: Chromate hazards in industry. J.A.M.A. 153: 1305-1308, 1953.
- GAUL, L. E.: Metal sensitivity in eczema of the hands. Degree and range of sensitivity to chromium and its compounds. Ann. Allergy 11: 758-762, 1953.
- HELZ, A. W. AND SCRIBNER, B. F.: Spectrographic determination of minor elements in portland cement. J. Res. Nat. Bur. Standards 38: 439-447, 1947.
- 18. Personal communication to the authors from R. H. Bogue, Director, Portland Cement Association Fellowship at National Bureau of Standards, Washington, D. C.; F. J. Anderson, Dragon Cement Company, Inc., Northampton, Pennsylvania; and H. F. Vanderwerp, Technical Director, Peerless Cement Corporation, Detroit, Michigan.
- 19. Standard Specifications for Portland Cement (C 150-52). American Society for Testing Materials, Philadelphia, Pennsylvania.
- SALTZMAN, B. E.: Microdetermination of chromium with diphenylcarbazide by permanganate oxidation. Anal. Chem. 24: 1016-1020, 1952.