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The Chromium, Cobalt, and Nickel Contents of American Cement and Their Relationship to Cement Dermatitis

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Dermatitis due to handling cement continues to be an occupational problem. This paper describes laboratory and human studies undertaken to determine the content of chromium, cobalt, and nickel in American cement samples and their etiological roles in causing dermatitis observed in cement workers in the United States.

Introduction

CEMENT DERMATITIS has been a recognized problem for many years. It results from general irritation to the skin due to the alkaline, abrasive, and hygroscopic properties of cement.[1,2] Some individuals manifest sensitization reactions due to metals contained in cement. In studies[3,4] conducted and published in 1954 and in 1957, we were able to demonstrate that the chromium content of American Portland Cement was of sufficient concentration that allergic hypersensitivity to this metal could be implied as a contributing factor, in some instances, to the occurrence of cement dermatitis.

Pirila,[5] of Finland, reported that European cement contained nickel and cobalt, in addition to chromium, in quantities sufficient to produce cutaneous reactions in workmen allergic to these metals. In 1968 Geiser,[6] in Switzerland, studied nearly 600 workers with cement dermatitis and concluded that chromium and cobalt were the most important factors in producing sensitivities to cement. Huriez *et al.*[7] tabulated data from 1,822 cases of cement dermatitis seen in French, Belgian, Swiss, and Portuguese dermatology clinics, of which 76% elicited positive patch-test reactions to chromium.

The objectives of our present study were to analyze American cement for chromium, cobalt, and nickel and, by conducting patch-tests on cement workers, to determine the role of these metals in the etiology of cement dermatitis.

Materials and Methods

Laboratory Studies

Fifty cement samples were obtained through the cooperation of members of the American Portland Cement Association, and 42 were selected for analyses. Chemical analyses were performed on the cement samples to determine the concentrations of total and hexavalent chromium, total cobalt, and total nickel in the cement washings, and the total chromium present in the orig-

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inal (untreated) cement samples.

Separate 50-g portions of each cement sample were mechanically shaken with two successive 10-ml aliquots of double-distilled water. The two suspensions obtained were filtered and diluted to 250 ml with double-distilled water, as described previously.[3] Each of the resulting filtrates, F1 and F2, was analyzed directly for total chromium, total cobalt, and total nickel by atomic absorption spectrophotometry with a Perkin-Elmer Model 303 double beam atomic absorption spectrophotometer. Standard operating procedures were followed;[8] however, instrument parameters were optimized for maximum sensitivity. Standard curves were prepared for cobalt, chromium, and nickel, using known quantities of commercial standard solutions obtained from Aztec Instruments, Inc., Westport, Connecticut. Filtrates F1 and F2 were analyzed for hexavalent chromium by the diphenylcarbazide method of Keenan and Perone,[4] using a Bausch and Lomb Spectronic 20 spectrophotometer set at 540 nanometers.

Total chromium determinations were made on 0.1-g portions of the original cement samples by the diphenylcarbazide-permanganate oxidation method of Saltzman.[9] A series of trivalent chromium standard solutions were prepared and carried through the entire procedure, using the zero standard as the colorimetric blank. All chemicals used in the analyses were reagent grade and all water used was double-distilled.

Human Studies

In cooperation with Mr. Robert V. Beam, International Representative, Operative Plasterers' and Masons' International Association of the United States and Canada, arrangements were made to take pertinent medical histories and perform patch-tests on workers who handled cement. These studies were performed in the San Francisco Bay area of California during May 1970.

Ninety-five construction workers who regularly worked with cement were interviewed and examined for past history of skin diseases and present evidence of dermatitis. Each worker was patch-tested on separate skin sites of the back with aqueous solutions of the following materials:

potassium dichromate, 0.25%
cobalt nitrate, 2.0%
nickel sulfate, 5.0%
sodium arsenate, 10.0%
cement filtrate No. 37, containing 4.7 μg Cr^{+6}/g
cement filtrate No. 39, negative for Cr^{+6}
distilled water

The dichromate, cobalt, and nickel solutions were below the know irritancy level; therefore, any positive reactions obtained were interpreted as allergic hypersensitivity reactions to these metals. A commercial patch-test plaster, reinforced with occlusive tape, was applied to each skin test site for 48 hours. Readings were made once only within 30 minutes of patch removal. Test sites were graded by the method of Fisher,[10] using a scale from 0 to 4+.

Results

Laboratory Studies

Forty-two samples of Portland cement

TABLE I
Geographic Source of Cement Samples

Source	Sample No(s)
Arkansas	1
California	7, 25
Georgia	11
Illinois	22
Iowa	9, 41
Kansas	30
Maryland	40
Michigan	13
Mississippi	24
Missouri	26, 28, 29
Ohio	12, 18, 20, 34, 36, 42
Pennsylvania	4, 5, 6, 8, 10, 14, 17, 23, 31, 32
Tennessee	3, 27
Texas	2, 15, 19, 21
West Virgina	38, 39
Wisconsin	16
Wyoming	33, 35, 37

manufactured in the United States were analyzed for their chromium, cobalt, and nickel content. Table I lists the geographical distribution of the cement samples. Table II shows the total chromium in the raw (untreated) samples, the total and hexavalent chromium, and the total cobalt and total nickel in the filtrates. All quantities are expressed as micrograms of element per gram of cement.

TABLE II
The Chromium, Cobalt[a], and Nickel[a] Content of American Cement Samples
(Micrograms of element per gram cement)

Sample No.	Total Chromium Raw Cement	Total Chromium F1 and F2 Filtrates[a]	Hexavalent Chromium (Cr^{+6})
1	45.0	0.5	<0.1
2	30.0	<0.5	<0.1
3	40.0	<0.5	<0.1
4	25.0	1.0	<0.1
5	17.5	<0.5	<0.1
6	124.0	2.0	<0.1
7	25.0	0.9	<0.1
8	25.0	2.6	<0.1
9	40.0	4.6	0.8
10	32.5	5.6	<0.1
11	20.0	6.7	<0.1
12	30.0	9.1	4.2
13	32.5	6.4	0.9
14	13.0	1.3	<0.1
15	25.0	1.5	<0.1
16	20.0	5.1	2.3
17	15.0	7.4	0.4
18	22.5	6.0	1.8
19	25.0	5.5	2.2
20	20.0	1.3	<0.1
21	40.0	3.9	0.6
22	25.0	10.1	5.4
23	35.0	3.5	<0.1
24	45.0	3.0	0.8
25	42.5	3.7	<0.1
26	32.5	2.4	<0.1
27	20.0	<0.5	<0.1
28	20.0	5.6	1.9
29	32.5	<0.5	<0.1
30	25.0	3.4	0.1
31	25.0	7.5	<0.1
32	5.0	0.5	<0.1
33	32.5	4.6	3.9
34	25.0	4.7	0.8
35	20.0	3.4	2.1
36	20.0	6.4	5.1
37	30.0	6.4	5.2
38	20.0	4.9	3.8
39	20.0	2.5	<0.1
40	22.5	3.3	<0.1
41	35.0	2.4	<0.1
42	40.0	4.3	<0.1

[a]For these 42 samples, the analyses of the F1 and F2 filtrates showed the total Ni content and total Co content to be less than 0.5 μg/g in every instance.

All untreated cement samples contained chromium. The lowest concentration was 5.0 μg/g (No. 32 from Pennsylvania); the highest was 124.0 μg/g (No. 6 from Pennsylvania). The average chromium content of all raw cement samples was 29.5 μg/g of cement. Total chromium (water-soluble) was markedly diminished in the filtrates when compared with the original cement samples.

The total chromium content of the filtrates ranged from <0.5 μg/g (No. 2 from Texas, Nos. 3 and 27 from Tennessee, No. 5 from Pennsylvania, and No. 29 from Missouri) to 10.1 μg/g (No. 22 from Illinois). If the five filtrates containing less than 0.5 μg/g of total chromium are excluded, then the average total chromium of all cement filtrates is 3.7 μg/g of cement.

Only 18 of the 42 filtrates contained measurable quantities (0.1 μg/g or higher) of hexavalent chromium (Cr^{+6}); the highest concentration was 5.4 μg/g of cement. None of the filtrates contained measurable nickel or cobalt (0.5 μg/g or higher for each element).

Human Studies

Ninety-five male cement workers were examined in this investigation. Ages of workers in the study population ranged from 19 to 65 years. The workers were members of the following crafts: cement masons, plasterers, hod carriers, brick layers, and laborers. Table III shows the distribution of the number of years employed in cement work. More than 50% of the workers examined had worked with cement for 15 years or longer. Twenty-five workers had a history of cement dermatitis or cement burns. Nine workers described their erup-

tions as localized, while sixteen had a generalized eruption. This represents greater than 25% of the sample interviewed and examined. Thirteen workers had lost time from work due to cement dermatitis.

At the time of patch-testing, the group was examined for dermatitis. Fifteen workers had a mild dermatitis of the hands, which consisted of xerosis with erythema and mild scaling of the skin. Twenty workers had a more active disease manifested by eczematous lesions with vesicles, erythema, and fissures in various stages. Some of the workers had occupational stigmata consisting of healed alkali burns and callosities on the hands and wrists. Thus, more than one-third of the workers had evidence of a mild to moderate dermatitis. None of the workers had a severe hand dermatitis at the time of examination.

Table IV summarizes the results of patch-testing. One worker ilicited a 1+ patch-test reaction to filtrate No. 37 containing 4.7 micrograms of hexavalent chromium per gram of cement. None of the workers had positive reactions to nickel, cobalt, distilled water, or cement filtrate No. 39, which was free of hexavalent chromium, nickel, and cobalt. Three workers had positive reactions to sodium arsenate, which appeared to be an expresison of irritancy. The patch-test results show a very low degree of latent contact sensitization to chromium and no evidence of cobalt and nickel sensitization among the group tested.

TABLE III
Number of Years in Cement Work—95 Workers

Years Employed	Number of Workers
1–5	12
6–10	20
11–15	20
16–20	17
Over 21	31

Discussion

All of the American cement samples analyzed in this study, which represented a wide geographic source, contained chromium. However, the presence of water-soluble chromium in cement filtrates represented only 10% of the total chromium present in the original sample. More importantly, the concentration of water-soluble hexavalent chromium known to produce cutaneous allergic effects, represented only 0.03% of the total chromium present in a sample. The lack of measurable cobalt and nickel in our samples suggested that contact dermatitis due to these two metals does not occur in American cement workers. Our findings with respect to the presence of chromium is consistent with most of the analyses of cement in Europe.[5,6,7] The number of cement workers who leave the industry appears to be small when compared with the number of workers in other construction crafts.[11] During the initial examination of cement workers, a request was made to have

TABLE IV
Results of Patch Tests on Ninety-Five Cement Workers

Material Tested	Number of Workers with Positive Reactions					
	0	Trace	1+	2+	3+	4+
0.25% Potassium dichromate	94	0	1*	0	0	0
2.0% Cobalt nitrate	95	0	0	0	0	0
5.0% Nickel sulfate	95	0	0	0	0	0
10.0% Sodium arsenate	92	0	1	2	0	0
Filtrate No. 37 containing 4.7 μg Cr^{+6}/gm of cement	94	0	1*	0	0	0
Filtrate No. 39 Negative for Cr^{+6}	95	0	0	0	0	0
Distilled water (control)	95	0	0	0	0	0

*The workers with positive reactions to potassium dichromate and filtrate No. 37 were different individuals.

all current and former union workers with severe and unconrtollable dematitis brought in for examination; however, there were only two men in this category and they were unavailable.

Many of the workers in this study have had dermatitis of a mild to moderate degree. The patch-tests performed failed to support an increased evidence of chromium sensitivity, or any evidence of cobalt and nickel sensitivities in this group. This was an unexpected finding. Other reports of chromate sensitivity as a causal factor of cement dermatitis have cited frequencies from 50% to 100% of affected workers.[12] In one recent epidemiologic study of 366 cement workers in Bergen, Norway, 6% (21) had eczema. Among these 21 men with eczema, 17 (81%) were allergic to dichromate.[13]

Only one worker in our study had a positive patch-test to potassium dichromate, which was interpreted as an allergic hypersensitivity reaction to chromium. One worker had a positive patch-test to cement filtrate No. 37 which contained 4.7 μg Cr^{+6}/g of cement, but failed to react to potassium dichromate. It is believed that the positive patch-tests to sodium arsenate were due to irritancy. The general lack of response to the two cement filtrates would also rule out some unknown sensitizer being present in cement. All patch-test readings were made at 48 hours. It has been suggested that if only one delayed reading could be made, it should be done at 72 hours.[14,15] Perhaps an additional 1% or 2% positive reactors would be identified at 72 hours that were not recognized at 48 hours. The results of this study suggest that chromium, cobalt, and nickel do not play an etiological role in the development of cement dermatitis in American workers. However, in order to more accurately estimate the incidence of chromium, cobalt, and nickel hypersensitivity in the cement industry, additional patch-testing of cement workers in other geographical areas of the United States is necessary.

Summary and Conclusions

Chromium was present in all cement samples analyzed; however, the concentrations of water-soluble hexavalent chromium represented only 0.03% of the total chromium present. Only one of the ninety-five cement workers patch-tested with chromium was considered as having an allergic hypersensitivity to chromium. None of the cement samples contained measurable cobalt and nickel. None of the workers tested elicited positive reactions to cobalt and nickel.

On the basis of our laboratory and human studies, there is little evidence of a high degree of chromium hypersensitivity and no evidence of cobalt and nickel hypersensitivities in American cement workers. Cement dermatitis in the United States, in our judgment, continues to be a problem associated with the irritant nature of cement. The three factors which are responsible are the alkalinity, abrasiveness, and hygroscopicity of wet cement.

References

1. Possick, P. A.: Cement Dermatitis. *Cutis 5:* 167 (1970).
2. Schwarz L., L. Tulipan, and D. J. Birmingham: *Occupational Diseases of the Skin,* 3rd Ed., p. 258, Lea & Febiger, Philadelphia, Pa. (1957).
3. Denon, C. R., R. G. Keenan, and D. J. Birmingham: The Chromium Content of Cement and Its Significance in Cement Dermatitis. *J. Invest. Dermatol. 23:*189 (1954).
4. Keenan, R. G., and V. B. Perone: The Determination of Hexavalent Chromium in Portland Cement Washings and Total Chromium in Washings, Residues and Unwashed Samples. *Am. Ind. Hyg. Assoc. Quart. 18:*231 (Sept. 1957).
5. Pirila, V.: On the Role of Chrome and Other Trace Elements in Cement Eczema. *Acta Dermato-Venereol. 34:*136 (1954).
6. Geiser, J. D.: Les facteurs de sensebilisation dans l'eczema an cimet. *Schweiz. Med. Wochschr. 98:*1193 (1968).
7. Huriez, C., P. Marten, and F. Planque: Dermites des cimenties. Synthese des donnees recueillies apres ordination electronic de I. 904 observations reunies dans 30 Services de

Dematologic. *Ann. Dermatol. Syphilig. 96:* 375 (1969).
8. .....: *Analytical Methods for Atomic Absorption Spectrophotometry.* Perkin-Elmer Corp., Norwalk, Conn. (May 1966).
9. Saltzman, B. E.: Microdetermination of Chromium with Diphenylcarbazide by Permanganate Oxidation. *Anal. Chem. 24:*1016 (1952).
10. Fisher, A. A.: *Contact Dermatitis,* p. 27, Lea & Febiger, Philadelphia, Pa. (1967).
11. Personal communication to one of the authors (P.A.P.) from a union representative (May 1970).
12. Wilkinson, D. S., and E. Cronin: Contact Dermatitis XIX Sensitivity to Chromium in Cement Dermatitis. *Brit. J. Dermatol. 87:*400 (1972).
13. Hovking, G.: *Cement Eczema and Chromium Allergy: an Epidemiological Investigation.* (Thesis), The University of Bergen, School of Medicine, Bergen, Norway (1970).
14. Epstein, E., W. J. Rees and H. I. Maibach: Recent experience with patch test screening. *Arch. Dermatol. 98:*18 (1968).
15. Malten, K. E., S. Fregert and H. J. Bandmann: Occupational Dermatitis in Five European Dermatological Departments. *Berufsdermotosen 19:*1 (1970).

Wayne State University Institutes

Three institutes for civil engineers working with water pollution will be sponsored by Wayne State University and held in the McGregor Memorial Conference Center on the campus in Detroit during July. Each conference runs five days, Monday through Friday.

The first of the institutes, studying water supply and treatment, will be held July 15-19 and examines areas including filtration, flocculation and water reclamation and reuse.

The second, on water pollution control, runs July 22-26 and includes studies of primary, secondary and tertiary treatments, sludge and chlorination.

Industrial waste treatment will be studied in the final institute, July 29-August 2, which uses specific cases to illustrate treatment methods in dealing with problems such as thermal discharge and pH adjustment.

Tuition is $275 for one institute, although those electing more than one will be charged $250 for each. The fee includes all tuition and course notes, an evening reception and an awards banquet. Hotel accommodations can be arranged near the conference center.

These annual pollution institutes are cosponsored by the Department of Civil Engineering of Wayne State University's College of Engineering and the Department of Conferences and Institutes of the College of Lifelong Learning. For information, telephone (313) 577-2406.