

CONTACT POINTS

Release of hexavalent chromium from cement collected in Honduras and Sweden

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The association between cement and allergic contact dermatitis (ACD) to chromium is well-known around the globe.¹⁻⁷ Studies and reports from Latin America are rare, but indicate relatively high incidence rates of ACD to chromium,⁸ (eg. 11.8% in a study on occupational dermatoses [$n = 4710$] in Brazil 2007–2014)⁹ and that training of workers and increase of personal protective equipment is needed.¹⁰ We did not find previous studies from Central America. Compulsory measures to reduce hexavalent chromium [Cr (VI)] in dry cement, first implemented in Denmark in 1983¹¹ and later in the European Union in 2005,¹² resulted in a lower number of new cases of ACD to chromium in construction workers in several countries.^{11,13-15} In Taiwan, Cr (VI) in cement was actively reduced in 2004. A significantly decreased amount of chromium in urine, especially in workers with severe and continuous hand dermatitis, was noticed after the chromium reduction.¹⁶ Still, concerns have been raised regarding the most common chemical method of Cr (VI) reduction in cement, the addition of iron (II) sulfate.¹⁷ This can result in a relatively short period of effective chromium reduction, in increased corrosion problems,¹⁸ and has been criticized for not being the most optimal chemical method.¹⁹⁻²¹ Here, we analyzed cement samples of different ages from a country without cement regulation in Central America (Honduras) and with cement regulation (Sweden, included in the European Union) and compared them with published literature values.

METHODS

The water-soluble amount of Cr (VI) was measured after 1 hour extraction in ultrapure water (18.2 M Ω cm resistivity) at room temperature, according to the standard method EN196-10.²² After solid-liquid separation, the particle-free water solution was directly analyzed by means of the diphenylcarbazide method and spectrophotometry at 540 nm. All samples had concentrations above the limit of detection and all background control samples had concentrations below the limit of detection, which was determined to be 20 μ g/L, corresponding to 1 mg/kg Cr (VI) in dry cement. Independent triplicate samples were measured in parallel for each type of cement. Five different types of Honduran, and two different types of Swedish cements (all Portland cements) were tested. The Honduran cements were collected from ARGOS, CENOSA (Holcim Alliance, Jona, Switzerland). HOLCIM is a multinational enterprise and responsible for most cement manufacture in Central America (El Salvador, Honduras, Nicaragua, and Costa Rica). The two Swedish cements were from Cementa and intended for different purposes. Available details about the seven cement types are provided in Table S1, online supporting information). All of them were at least 1 year old and stored dry prior to the testing. In the case of the Swedish cements, the age of the cement meant that the manufacturer did not anymore guarantee a Cr (VI) content below 2 mg/kg.

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TABLE 1 Water-soluble hexavalent chromium in dry cement in this study (independent triplicate samples) compared with literature values

Country of sample origin	Publication year	Cement regulation for hexavalent chromium	Cement age when tested	Sample ID	Hexavalent chromium in mg/kg, mean \pm SD	Reference
Honduras	This study	No	≥ 1 year	A	6.0 \pm 0.74	This study
				B	5.9 \pm 0.27	
				C	5.9 \pm 0.38	
				D	8.2 \pm 0.52	
				E	5.3 \pm 0.29	
Sweden	2014	Yes	in use	F	0.38 \pm 0.067	27
				G	4.7 \pm 0.17	
Slovakia	2018		Fresh	L1	2.7 ^a	28
Singapore	1996	No	unclear	L2	2.1 \pm 0.87	23
Spain	1995			L3	5.2-15.8	29
India	1995			L4	5.8-24.2	29
India	2018			L5	1-5	30
Japan	2005			L6	9.3	31
Australia	1993			L7	0.2-8.1	32
USA	1976			L8	1.0 \pm 1.7 (<0.01 - 5.2)	33

^aExtraction temperature of 30°C, sample collected from a concrete element factory.

RESULTS AND DISCUSSION

Table 1 shows the amount of water-soluble Cr (VI) in the different cement samples, compared to literature values. The Honduran cement samples contained a slightly higher water-soluble content as compared to the Swedish samples of similar age. The variability in water-soluble Cr (VI) in cement is rather high, ranging from <0.01 to 24.2 mg/kg in the different studies. Studies suggest differences in raw materials are the main cause of variability, and that Cr (VI) in cement mainly derives from the clinker,²³⁻²⁵ which is a raw material that has been oxidized at high temperatures. Also, the water-extractable amount of Cr (VI) could be influenced by the sulfate content in cement.²⁶ Hence, the substitution of clinker, for instance by slags, and of chromium-containing grinding media in the finish mill, have also been suggested as possible measures to reduce Cr (VI) in cement.^{20,23}

Amounts of Cr (VI) in cement as detected here, and reported in the literature, still pose a risk for the development and elicitation of ACD. This might be even a greater problem in regions like Central America that lack comprehensive occupational health care systems and the possibility to conduct chemical analyses. There are still many countries that do not have a compulsory reduction of Cr (VI) in cement. The most commonly used iron (II) sulfate reduction method is causing some technical problems and may not last more than 6 months, but chemical alternatives can be developed.

CONFLICTS OF INTEREST

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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