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Evaluation of Total, Water-soluble and Hexavalent Chromium Contents in Construction Materials(Concretes, Cements)

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Abstract: The objective of the study is to determine the contents of total chromium, water-soluble chromium and hexavalent chromium in cements and concretes specimens taken from manufacturing or construction sites. Chromate is an allergen that is widespread in the environment and is richly contained in cements. Metals were extracted with microwave oven and analyzed by atomic absorption spectrometer. Hexavalent chromium was analysed by ion chromatography. The concentrations of total chromium, water-soluble chromium and hexavalent chromium in cements were 36.02~108.01, 15.95~89.01 and 26.77~89.61 mg/kg, respectively. The concentrations of hexavalent chromium in cements were higher than 2 mg/kg, a maximum value recommended in Northern European Countries. The concentrations of total chromium, water-soluble chromium and hexavalent chromium in concretes were 17.44~76.25, 0.98~17.71 and ND~24.13 mg/kg, respectively. Especially Hexavalent chromium was detected only from concrete specimens from construction sites. It is oxidized or reduced status by environmental condition or surrounding materials.

Keywords: total, water-soluble and hexavalent chromium, dermatitis, cement, concrete

Introduction

Nowadays, large buildings generally have reinforced concrete structures or steel frame structures. Concrete operation account for a large part of the construction of such buildings. Concrete refers to a hardened mixture of cements, gravels, water, sand, and other additives. Recently, concrete exposure of workers in such construction sites and cement manufacturing industry is gaining higher attention, as it was found out that dermatitis can develop when skin is exposed to cements.[1)]

Cement dermatitis is known to be caused due to alkaline, water-absorbing and irritating property of cements. In the late 1950s, experts discovered that water-soluble chromium was the element that causes cement allergy. The source of total chromium in cements is lime and clay mineral, raw material of cements. Trivalent chromium is oxidized to hexavalent chromium (Cr(VI)) while being crushed with a clinker, and the latter is water-soluble and acts as an allergen.[2)] In addition, heat-resistant bricks within the kiln and mineral additives and grinding media used in cement manufacturing are also known as the source of chromium in cements.[3)]

Previous studies report that part of trace amounts of heavy metals in Portland cements can cause allergic contact dermatitis, suggesting that Ni and Co can also cause this problem as well as chromium already identified as a causal agent.[4)]

According to the US Bureau of Labor Statistics's data, the incidence of occupational skin disease stood at 1.2 persons for every 10,000 workers for the overall industries, while the number was 1.6 for the construction industry. In particular, concrete workers had to spend 13 days off from work due to work-related skin problems, which was significantly higher than 2~5 days from other industries.[5)] In Denmark, it is reported that workers in fabricated concrete building manufacturing had the highest chrome sensitivity (10.5%) and hand eczema (11.9%). In addition, 5~15% of workers who get in touch with cements containing hexavalent chromium suffered allergic contact dermatitis, which is 25 times higher than that of general public.[6)] It was also reported that 20~40% of workers with allergic contact dermatitis after exposure to cement suffered sustained allergic dermatitis even without additional exposure.[7)]

In Northern European countries including Denmark,

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Finland and Sweden, hexavalent chromium content in cements are controlled not to exceed 2 mg/kg since 1981 after the skin disease issue due to hexavalent chromium in cements garnered a lot of attention[7]. While medical data is relatively lacking, Eugeniusz suggested the hexavalent chromium level in cements of 10 mg/kg as a concentration that can pose the risk of allergic response.[8]

Cements vary in types depending on raw material or manufacturing processes. Among them, the most widely used for concrete construction is Portland cement. Major elements of Portland cements include lime (CaO), silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3). Depending on contents and properties for each usage, Portland cements are classifies into 5 types (type 1~type 5). Among them, type 1 Portland cement account for more than 90% of total cement production and 97~98% of the entire Portland cements[9]. Portland cement is typically used in concrete floors, walls, pavement, buildings as well as mortar and grout mixtures.

Currently in Korea, workers in construction sites are routinely exposed to cements and concretes without specific warnings. In particular, workers handling wet cements are highly likely to develop irritant contact dermatitis and allergic contact dermatitis. However, there is no legal restriction on the heavy metals such as chromium while this issue is not gaining a lot of attention, resulting in excessive exposure to these elements in such workers. There is few investigation on such exposure. In particular, in Korea, hexavalent chromium is recognized as a carcinogen and studies were conducted mostly focusing on relevant processes,[10-12] while few studies were undertaken with regard to skin problems.

Against this backdrop, this study intends to identify the status of total chromium, water soluble chromium and hexavalent chromium contents in ordinary Portland cements produced in Korea that are being used or was used in construction industry.

Materials and Methods

Sample Collection

Concrete samples were taken in areas with ongoing or completed construction operation between October and November 2004. 4 out of total 7 samples were taken in the ongoing construction sites while remaining 3 were taken in already completed houses. Table 1 shows sampling sites.

As for cement, major ingredient for concrete mixtures, 5 cement products were randomly chosen among domestic products. All 5 products represented ordinary Portland cements and all were bought from commercially available stocks on a same day to be used as samples.

Preparation of Samples

Bulk concretes were finely ground with a mortar and was wind-dried in the ambient air for one day. Air-dried concrete particles were sieved and those with pore size less than 150 μm were used as a sample for analysis. Cement was analyzed in its intact status. Before analysis, both concrete and cement was dried in the oven at 105°C for 6 hours. The purpose of this treatment was to eliminate water contents within samples since final concentration is calculated based on a dry-weight.

Total Chromium

Pre-treatment of sample for total chromium analysis referred to a 'kiln dust method',[13] which is an ashing pre-treatment method using microwave

Table 1. Sample information for concrete

No.	Sampling site	Date	Construction
1	Bridge construction work, Injae-gun	2004. 10. 18	Working
2	Bridge construction work, concrete mixer, Injei-gun	2004. 10. 18	"
3	Middle-school new construction work, Gunpo-city	2004. 11. 05	"
4	Middle-school new construction work, after 3 months, Gunpo-city	2004. 11. 05	"
5	New APT which becomes 4 months, Ansan-city	2004. 11. 13	Finished
6	Reconstruction APT which passed 25 year, Seoul	2004. 10. 26	"
7	APT which passed 7 year, Muan-gun	2004. 10. 22	"

Table 2. Operating condition of microwave digestion system

Stage	Power (W)	Voltage (%)	Ramp time (min)	Pressure (psi)	Temperature (°C)
1	1200	100	20:00	90	210

oven. Approximately 0.3 g of oven-dried sample was placed on a Teflon vessel, followed by addition of high-purity nitric acid (redistilled 99.999%, Aldrich, USA) 10 m*l* and ashing with MARS (Microwave Accelerated Reaction System, CEM, USA). Ashing condition is summarized in Table 2. After ashing, the sample was diluted to 40 m*l* with distilled water. As this solution still included particulate matters mostly from concretes or cements, the solution was centrifuged for 15 minutes at 1800 rpm and the upper solution was removed and analyzed.

Chromium was analyzed with a flame atomic absorption spectrometer (SpectrAA 880, Varian, Australia) at 359.7 nm wavelength.

Water-soluble Chromium

For water-soluble chromium, ISO 15202-2 Annex B method[14] was used as a reference. Approximately 0.2~0.5 g of oven-dried sample was weighed, 5 m*l* distilled water was added, followed by shaking at 120 rpm for 60 minutes in 37±2°C shaking water-bath (NB-303, N-Biotech, Inc., Korea). Extracted solution was filtered with filtering extraction equipment with nitrocellulose filter paper (0.8 μm poresize, 47 mm diameter, AAWP04700, Millipore, USA) that allowed only water-soluble components to pass. High purity nitric acid (redistilled 99.999%, Aldrich, USA) was added to stabilize filtered extract until the analysis of target metal, and distilled water was added to make the final volume 25 m*l*. Atomic absorption spectrometer was used for the analysis. Analysis condition is the same as that of total chromium.

Hexavelant Chromium

For hexavalent analysis, NMAM (NIOSH Manual of Analytical Methods, US National Institute for Occupational Safety and Health) standard test method # 7604[15] and the approach of Chung Sik Yoon[16] were used as a reference. 0.3 g of oven-dried samples was taken, 5 m*l* of 2% sodium hydroxide + 3% sodium carbonate extract solution were added, followed by extraction for 45 minutes with sonicator (PowerSonic 420, Hwashin Tech, Korea). As the extracted solution still contained particulate matters from the sample, it was centrifuged for 15 minutes at 1800 rpm. supernatant was filtered with PVDF filter paper (0.45 μm poresize, 13 mm filtersize, 44513-PV, TITAN Filtration system, USA). Chromate ion (CrO_4^{2-}) was analyzed with ion chromatograph with conductivity detector attached (DX-120, Dionex, USA). Analysis condition is shown in Table 3.

Table 3. Analytical conditions of ion chromatograph

Parameters	Conditions
Extraction solution	2% NaOH + 3% Na_2CO_3
Detector	Conductivity detector
Column	AS5(4 mm×250 mm) + AG5
Eluent	0.5 mM Na_2CO_3 + 7.0 mM NaOH
Flow rate	1.5 m*l*/min
Injection volume	25 μ*l*

Results

Total chromium, water-soluble chromium and hexavalent chromium in cements produced by 5 domestic manufacturers are summarized in Table 4. Average concentration of total chromium in cements was 73.53 mg/kg, ranging between 36.02 and 108.01 mg/kg. Average concentration of water-soluble chromium was 48.78 mg/kg, ranging between 15.95 and 89.01 mg/kg, and this type of chromium accounted for 44~82% of total chromium. Average concentration of hexavalent chromium, the causal material for allergic contact dermitis stood at 48.70 mg/kg, with a range of 26.77~89.61 mg/kg which represented 48~83% of total chromium. Such results were in line with the report by Potgieter *et al.*[3] who reported that hexavalent chromium was 30~80% of total chromium in cements and 8~26% of hexavalent chromium was water soluble in South Africa. Also Osama *et al.*[17] reported that 50~80% of total chromium is typically extracted as hexavalent chromium in Portland cements. In addition, Frias and Rojas[2] evaluated total chromium and hexavalent chromium in Portland cements in Spain and reported total chromium range of

Table 4. Chromium concentration of cements

Sample	Total Cr	Water-soluble Cr		Cr (VI)	
	mg/kg	mg/kg	% (in Total Cr)	mg/kg	% (in Total Cr)
S cement	86.95	45.42	52	58.00	67
D cement	67.47	50.39	75	36.07	54
H cement	108.01	89.01	82	89.61	83
A cement	69.20	43.13	62	33.06	48
C cement	36.02	15.95	44	26.77	74
Mean	73.53	48.78	63	48.70	65

20~110 mg/kg, and that of hexavalent chromium (water-soluble) at 0.9~25 mg/kg, showing similar total chromium level with the data from this study. As hexavalent chromium represents that of water-soluble chromium, a direct comparison is not available.

Currently in Korea, there is no regulation on hexavalent chromium in cements while Nothern European countries control hexavalent chromium concentration in cement to be lower than 2 mg/kg. This study shows that samples from all 5 cement manufacturers exceeded this level by 13~45 times. Furthermore, they also were significantly higher than the allergic response risk level of 10 mg/kg as suggested by Eugeniusz.[8] In particular, the product of "H" company turned out to have the highest total chromium of 108.01 mg/kg, as well as the highest water-soluble chromium and hexavalent chromium levels with 89.01 and 89.61 mg/kg, respectively.

Table 5 shows total chromium, water-soluble chromium and hexavalent chromium concentration in concretes. Total chromium, water-soluble chromium and hexavalent chromium level ranged 17.44~76.25, 0.98~17.71 and ND~24.13 mg/kg, respectively. Water-soluble chromium represented 6~30% of total chromium, which was lower than the level in cements. Total chromium concentrations from ongoing construction sites (samples 1~4) were significantly higher than those from already completed buildings (samples 5~7) ($P<0.05$). Such trend was particularly apparent for hexavalent chromium which was not detected in concretes from buildings older than 4 months. However, concretes from ongoing construction sites contained hexavalent chromium of 11.56~24.13 mg/kg. As the case with cements, this level was 5~12 times higher than Northern European standards. Hexavalent chromium is quite unstable in the environment, and can easily change its oxidized or reduced status by environmental condition or surrounding materials.[10,11] This suggests that the type of chromium might change in the environment as time passes.

Conclusions

Cements produced by 5 domestic manufacturers

Table 5. Chromium concentration of concretes

Sample No.	Total Cr	Water-soluble Cr		Cr (VI)		Construction
	mg/kg	mg/kg	% (in Total Cr)	mg/kg	% (in Total Cr)	
1	76.25	17.71	23	11.56	15	Working
2	61.01	14.79	24	16.32	27	"
3	42.62	5.13	12	24.13	57	"
4	39.67	11.57	29	13.80	35	"
5	26.95	7.94	30	ND*	-	Finished
6	17.71	1.62	9	ND	-	"
7	17.44	0.98	6	ND	-	"

*ND: Not detected.

were evaluated for total chromium, water-soluble chromium and hexavalent chromium contents, and the results ranged 36.02~108.01, 15.95~89.01 and 26.77~89.61 mg/kg, respectively. In particular, hexavalent chromium exceed Northern European standard of 2 mg/kg by maximum of 45 times. In concretes, the level of total chromium, water soluble chromium and hexavalent chromium was 17.44~76.25, 0.98~17.71 and ND~24.13 mg/kg, respectively. Hexavalent chromium was detected only in specimens from ongoing construction sites.

This study is the investigation of the status quo covering only some of cements or concretes. However, the data suggest that the level of hexavalent chromium was very high, exceeding Northern European standards. Due to the small number of samples, there is a certain limit this study. But the data of this study suggest that further investigation and exposure evaluation should be undertaken.

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