HEXAVALENT CHROMIUM
IN THE CEMENT INDUSTRY
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THE QUESTION OF HEXAVALENT CHROMIUM PRESENCE IN PORTLAND CEMENT IS ALREADY A CURRENT ISSUE IN THE FICEM AREA

Marca de cemento sobrepasaría niveles de cromo

Denuncia Consumidores de Costa Rica

EUROPEAN UNION TERRITORIES IN THE REGION

Spain & Portugal are EU and FICEM members

THIS TOPIC IS LIKELY TO BECOME A GROWING CONCERN IN OTHER FICEM COUNTRIES
The Costa Rican Government (Ministerio de la Economía, Industria y Comercio) has issued a regulation following recommendations promoted by the World Health Organization (Cr VI content < 5.1 mg / kg)

The US Occupational Safety & Health Administration (OSHA) has in 2006 exempted Portland cement from its standard for occupational exposure to hexavalent chromium.

However:
On February 2, 2010, OSHA issued a Standard Letter of Interpretation which states “…work with cement is regarded as the most common cause of (hexavalent chromium) induced dermatitis”. The clean-up of any dusts that may contain hexavalent chromium should be performed using a HEPA filtered vacuum and appropriate PPE to prevent employee contact. The hexavalent chromium in the cement comes primarily from the grinding media (high chromium steel) used to reduce the “clinkers” to a fine powder during the production process.

Fortunately:
Risks for cement plant employees and construction workers are gradually being reduced.
Automation of cement technology
• – automation in manufacturing requires less workforce and occupational health and safety in general is a major concern within industry players
• – placement technology significantly decreased direct contact with wet cement for construction workers
1b - Definitions - What is Cr (VI)?
Difference between Cr (III) and Cr (VI)

Chromium is a metallic element of Worldwide distribution naturally found in its oxidative state
Resistant to corrosion and hard.
Trivalent – Cr (III) and Hexavalent – Cr (VI) forms are the most common forms found in cement.
Chromium (VI) compounds are most often products of industrial processes.

Cr (III): stable – Low solubility – Low reactivity  ➡️  Considered harmless
Cr (VI): unstable – Strong oxidizer – Soluble in water - ➡️  Considered a hazard

Airborne – Dissolved ingress of – Dermal exposure to Cr (VI) compounds are threats to human beings

Leads to: Recommended Exposure Limits – Maximum Content/Contaminant Level

Content of Cr (VI) is regulated in some industries:
Chromium metal – alloy production and use, steel mills - Welding  - Leather tanning industries, textile dyeing industries - Catalysts, pigments, paints and coatings production, printing ink production - Wood preservation industries

Cement manufacturing industry, construction industry due to working with Portland Cement
Cr (VI) is also highly regulated in drinking water
2 – Health hazards generated by presence of Cr (VI) in Portland cement

2.1 – Behaviors and situations leading to risks for humans (employees, clients, end users)

**Risks:** Inhalation, ingress, contact with skin in soluble form

Manufacturing, bagging, storage
Transportation

Usage (concrete, mortar)
2.2 – Occupational diseases

Acute inhalation exposure to hexavalent chromium may cause irritation and damage to the nose, throat and lungs. Dermal exposure to Cr (VI) may also cause allergic contact dermatitis and skin sensitization.

Leachate of hydrated cement is a major cause of occupational diseases in the construction industries.

Hexavalent chromium has been classified by International Agency for Research on Cancer (IARC) as Group 1, *carcinogenic to humans*

Well established link to lung cancer.

Several epidemiological studies have also found increased risks of cancer in the nasal cavity and paranasal sinuses in workers exposed to Cr (VI).

**CONSEQUENCES:**

- Allergies / dermatosis affecting the skin
- Carcinogenicity: lung cancer
- Acute affects (ingestion): gastrointestinal disorders, hemorrhagic diathesis,…
- Mutagenicity: chromosomal aberrations,…
Skin burns 1st and 2nd degree

Hand & foot eczema

Lung cancer

Trachea
Bronchi
Cancer
Lung cancer
3 – Potential sources of Chromium in the cement manufacturing process

Where is Chromium found?

3.1 - Raw materials
Limestone, shale, Clay, iron ore contain small quantities of chromium, mainly in Cr(III) form

3.2 – Fuels
A wide diversity of fuels are used in the cement industry, coal, petcock, natural gas, waste type fuels....
The end-contribution of total chromium in the clinker coming from fuel is minimal.
Solid waste, liquid waste, shredded tires fuels must be evaluated for hexavalent chromium content.

3.3 - Refractory bricks
Cement and lime kilns are the second largest user of magnesia-chromium refractories. Advantages of these bricks in cement kilns include excellent thermal shock resistance, good corrosion resistance and high hot strength
The use of mag-chrome bricks has virtually disappeared in cement kilns in Europe and North America due to the regulations and costs of disposal of the used bricks which may contain hexavalent chromium.
Mag-chrome bricks are still used in other parts of the World..
3.4 – Grinding media, equipment and devices

Chromium comes from wear metal from raw mill grinding process, if chromium alloys are used.

In Ball Mills: Inner structure (liners and wear plates) and grinding balls themselves
Information on alloy used is generally not available unless specifically requested

For Vertical Roller Mills: there is an option to use high Chromium content alloy for table and rollers against wear. However, high Cr alloy is more brittle and therefore is difficult to re-weld. Cement manufacturers can use both options, Ni-hard and high Cr depending on their re-welding philosophy. Ni-Hard is easy to re-weld several times. High Cr allow lasts longer, however it is difficult to re-weld.

Loss of material per ton of cement produced is however minimal.

3.5 – Additions in cement mills

Gypsum, pozzolans, GBFS, other mineral additions can be source of Chromium but generally in its trivalent form
Fly Ash should be evaluated (see chapter 6)
Chromium rich Kaolin must be evaluated after calcination.
4 – Formation of Cr (VI) during the manufacturing process

The input is the form of Cr (III) that can be transformed into Cr (VI) during the manufacturing process under favorable conditions. The quantity of Cr (VI) formed during the process will mainly depend on:

**Conditions in the cement mill**
- Wear metal from chrome alloy grinding media
- Air dynamics
- Moisture from gypsum dehydration
- Injection of cooling water
- Use of grinding aid and type of grinding aid

**Conditions in the kiln**
- Quantity of oxygen in the burning zone
- Alkalis concentration
What happens during the calcination and clinkerisation process?

The Chromium is fixed as alkaline or calcium chromate (Na₂CrO₄, K₂CrO₄, CaCrO₄). As a result, Portland clinkers and cements contain soluble chromates (usually in the range of 5 – 20 ppm or mg/kg, - 0.0005 to 0.002% - while the total chromium may reach 200 ppm - 0.02%)

Two prevailing conditions:

High temperature & high level of oxygen

The formation of hexavalent Chromium happens in a narrow zone of the kiln.
5 – Use of additives to reduce the level of Cr (VI) formed in hydrated cement

5.1 - Type of additives available on the market

Powder or liquid form

**Ferrous sulfate** - Fe SO$_4$ 7 H$_2$O – Heptahydrate ferrous sulfate – Fe SO$_4$ H$_2$O Monohydrate ferrous sulfate

Commercial form: powder

Soluble in water

Oxidizes slowly by air in cold air but more rapidly in hot conditions.

Alkaline conditions increase the oxidation rate

Typical addition rate: 0.5% by weight

**Stannous (tin) sulfate** - SnSO$_4$

Less sensitive than ferrous sulfate – Efficient at lower dosage

**Manganese sulfate** - MnSO$_4$.H$_2$O

Very efficient in reducing Cr (VI) content in cement
Stannous Chloride - \( S_nCl_2 \)
Zinc salts - \( ZnCl_2 \)
Antimony - Sb (III) – Works in alkaline conditions – Does not interact with free lime

5.2 Feed points
Feeding directly in the cement mill can lead to generation of heat and then could reduce the effectiveness of the reducing agent
5.3 Cost consideration

CAPEX
Storage and metering systems

Operations
Cost of reducing agents – Risk of loss
Ferrous sulfate: cheap but may require high dosage – Sensitive to storage conditions
Stannous sulfate and manganese sulfate: more expensive

5.4 Observations

Adding reducing agents partly solves the problems: it does not prevent the irritant dermatitis linked to the inevitable alkaline nature of cement.

Reducing agents will deteriorate quicker in warm and moist climates and have not specifically been developed for tropical climates – Expiry dates might have to be re-assessed when cement is stored in some peculiar conditions.

Storage conditions and packaging (bulk or bags) will impact shelf life of the cement.

Excess dosage will impact cement and concrete quality (lower strength – expansion – internal sulfate attack – increase of setting time – increase of water demand – coloration)
Granulated Blast Furnace Slag

Blast Furnace Slag is basically free from hexavalent chromium.

Good way to dilute the hexavalent chromate content of blended cement.

Coal Fly Ash

More attention should be placed on Fly Ash because of presence of Cr (III) in different quality of coals used by power companies

Cr (VI) / total Cr ratio in fly ash:
- About 10% burning bituminous coal
- Up to 30% when burning subbituminous and low-rank coal

Concentration of total Chromium in Fly Ash can reach 300 ppm

Higher concentration can be found at the bottom of stockpiles
7 – European Union regulations related to Cr(Vi) in cement

7.1 - Chemical content restriction / marking requirements

First regulation Implemented in 1999 by the EU - Directive 1999/45: labelling requirements

European Directive 2003/53/EC was implemented January 2005

17.7.2003 EN Official Journal of the European Union

Maximum Contaminant Level + Marking requirements

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<tr>
<th>47. Cement</th>
<th>(1) Cement and cement-containing preparations may not be used or placed on the market, if they contain, when hydrated, more than 0.0002 % soluble chromium VI of the total dry weight of the cement.</th>
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<td>(2) If reducing agents are used, then without prejudice to the application of other Community provisions on the classification, packaging and labelling of dangerous substances and preparations, the packaging of cement or cement-containing preparations shall be legibly and indelibly marked with information on the packing date, as well as on the storage conditions and the storage period appropriate to maintaining the activity of the reducing agent and to keeping the content of soluble chromium VI below the limit indicated in paragraph 1.</td>
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<td>(3) By way of derogation, paragraphs 1 and 2 shall not apply to the placing on the market for, and use in, controlled closed and totally automated processes in which cement and cement-containing preparations are handled solely by machines and in which there is no possibility of contact with the skin.’</td>
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7.2 – Testing procedure

Testing standard EN 196-10

A test portion of cement is used to make a standard mortar with CEN Standard sand and water in accordance with current standard BS EN 196-1. The mortar is mixed for a specified time and then filtered. An aliquot of filtrate is first treated with s-diphenylcarbazide reagent and then acidified within a narrow range of pH (2.1 to 2.5). In acid solution, chromium (VI) forms a red-violet complex with the reagent and its absorption/color is measured using a visible light spectrophotometer set at a wavelength of 540 nanometres although other instrumental/end-point procedures are permitted. The content of water-soluble chromium (VI) is determined from a calibration curve and is expressed to the nearest 0.0001%.
8 – Conclusions & recommendations to prepare for tighter regulations

Be aware of a concern that might hit our region sooner than later in new regulations for the industry.

There are scientific uncertainties about how hexavalent chromium is generated in cement manufacturing process but the matter is serious enough to be pro-active and prudent.

Know what Cr VI content is in your cements – Conduct Audit – Request chemical composition of grinding devices / wear plates from manufacturers

Audit areas in plants and storage sheds where airborne Cr(VI) can be found and compare it with international Permissible Exposure Level.
Develop awareness among employees and subcontractors working at the plants and develop a specific monitoring program.

Reducing agents do not make cement safe to handle without PPE (personal protective equipment). Cement, when wet, can cause two types of contact dermatitis, allergic dermatitis and irritant dermatitis. Reducing agents only protect against allergic dermatitis. The same PPE is required for handling wet cement since reducing agents were introduced as was previously required. Correct PPE would ensure users do not suffer allergic dermatitis, irritant dermatitis or burns.

Pay particular attention to welding works which can increase health risks linked to Cr (VI).
Work with chemical companies **to develop specific customized solutions for lowering Cr VI** content if needed ahead of implementation of new regulations. The use of reducing agents must be envisaged with extreme caution.

**Develop awareness** within clients, truckers, end users through education campaigns / Promote use of PPE and improved hygiene

Pay a particular attention to clients prefabricating concrete pipes for drinking water, civil work contractor using soil-cement techniques or roller compacted concrete.

In keeping with the FICEM philosophy, use experience of Spanish and Portuguese FICEM members to **spread knowledge and experiences** among Latin American and Caribbean FICEM members.
THANK YOU
GRACIAS