Are changing technologies in the manufacture of cement impacting on the incidences of chromate dermatitis amongst construction workers in Australia?

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Are changing technologies in the manufacture of cement impacting on the incidences of chromate dermatitis amongst construction workers in Australia?

The null hypothesis
The level of chromate dermatitis in the Australian Construction Industry remains constant.

The alternative hypothesis
There is a reduction in the incidences of chromate dermatitis in the Australian construction industry and its causes will be identified.

INTRODUCTION
- Literature Review
- Cobalt and Nickel Review
- Hazardous Substances
- Workers Compensation data
- Epidemiological data analysis

TECHNOLOGY
- Cement Processing
- Chemical composition
- Chromium Oxidative and Reductive states
- Replacement of compounds
- Change as expressed by the industry

DERMAL HYGIENE
- Causes of dermal toxicity Cr Co Ni
- Acute and Chronic effects
- Priming of the immune system
- Observation Survey PPE and Dermal Protection
- Education Campaigns

RISK MANAGEMENT
- Changes to OHS legislation
- Risk Reduction International Australian
- Substitution
- Engineering
- PPE
- Potential Risk Transfer
Chromium Valencies - Oxidative and Reductive States

Chromium Valencies and States

- **valency: Cr(0)** The metal occurs as plating, although toxic does not release allergenic chromium.

- **valency: Cr(III)** Chromium oxide \( \text{Cr}_2\text{O}_3 \) is not soluble enough to elicit chromium dermatitis and is partially soluble in an acid environment. However, trivalent chromium is the most common found in nature and biological materials.

- **valency: Cr(VI)** The hexavalent form of chromium is the most powerfully sensitising, both because of its solubility and its capacity to penetrate into skin. The preferred uptake of hexavalent chromium by cells and its reduction intracellularly to the trivalent form that is metabolically active and binds with nucleic acids within the cell has been suggested as the mechanism of mutagenesis from chromium.

- **reduction only occurs in selective body fluids** epithelial-lining fluid, blood plasma, saliva, gastric juices, erythrocytes, sweeping cells, as well as in several tissues of the organism, which appears to play a crucial role in affecting the bioavailability of hexavalent chromium to target cells, thereby limiting its potential carcinogenicity.
Route of entry for dermal absorption

- Follicular penetration
- Transcorneal penetration

Layers:
- Horny layer
- Epidermis
- Dermis
- Blood vessel
- Sebaceous gland
- Follicle
- Hair
Priming of the immune system
Chromate (Cement) Dermatitis
Are changing technologies in the manufacture of cement impacting on the incidences of chromate dermatitis amongst construction workers in Australia?

Biological Impacts - Findings

- cement has pH of 12-13 and lime is hygroscopic

- valencies:
  - Cr VI penetrates skin and freely crosses cell membrane and reduces intracellularly to trivalent state with a half life of 2 – 4 hours
  - Cr III hapten forms covalent bonds with skin protein a precursor to immunogenicity

- cobalt and nickel cement sensitisier only in the presence of chromium

- managing cement dermatitis through PPE and improved hygiene

- role of barrier creams in skin protection

- sunscreen – zinc as a potential barrier since 1982 (slip, slop, slap)
  - potentially act as a protective barrier against chromates
  - assist in healing chromium exposed and traumatised skin
  - maintain skin health and prevent hexavalent chromium breaking thru stratum corneum

- industry awareness and education campaigns
Risk Management

Findings

• Changes in WHS legislation
  – Occupational medicine
  – hazardous chemicals, SDS and labelling
  – hazardous chemicals regulation

• International risk reduction
  – Danish/European legislation of 2ppm
  – ground blast furnace slag
  – addition of ferrous sulphate
  – ascorbic acid
  – sodium thiosulphate
  – iron ammonium sulphate

• Australian risk reduction
  – changes to technology – replacement of compounds to be determined
  – automation
  – PPE, barriers, education, improved hygiene

• Risk Transfer
  – substitution of conventional construction methods for precast concrete products
What is Portland Cement

- Portland cement is created from heating crushed materials high in calcium carbonate, usually limestone, and clays or shales as a source of alumino-silicates.
- Raw materials are fed into a kiln, typically a revolving sloped cylinder, which progressively heats the material to about 1450 °C.
- Complex chemical reactions occur within the kiln, large quantities of CO₂ are released from the mix, the heating is also usually from fossil fuel sources, with associated high CO₂ emissions.
- The resulting material is known as clinker, which is then ground with some other materials, such as, Gypsum to create Ordinary Portland Cement.

Diagram of a typical cement kiln arrangement
## Chemical Composition of Cement – Pre Technology Change

(Starting Materials)

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Formula</th>
<th>Percent</th>
<th>HC (GHS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium Oxide (lime)</td>
<td>CaO</td>
<td>64%</td>
<td>✓</td>
</tr>
<tr>
<td>Silicon dioxide (silica)</td>
<td>SiO2</td>
<td>21%</td>
<td>✓</td>
</tr>
<tr>
<td>Aluminium oxide</td>
<td>Al2O3</td>
<td>5.8%</td>
<td>✓</td>
</tr>
<tr>
<td>Iron oxide</td>
<td>FeO3</td>
<td>2.9%</td>
<td></td>
</tr>
<tr>
<td>Magnesium oxide</td>
<td>MgO</td>
<td>2.5%</td>
<td>✓</td>
</tr>
<tr>
<td>Sulphur dioxide</td>
<td>SO3</td>
<td>1.7%</td>
<td>✓</td>
</tr>
<tr>
<td>Hexavalent Chromium</td>
<td>Cr[VI]</td>
<td>0.002%</td>
<td>✓</td>
</tr>
<tr>
<td>Alkali oxides</td>
<td></td>
<td>1.4%</td>
<td>✓</td>
</tr>
</tbody>
</table>
Chemical and mechanical contributions

Limestone is mined and transported to the cement plant where it is stored with other raw materials.

After grinding and blending, the raw materials are heated to around 1450°C in the suspension pre-heater tower (PH).

The heated raw material passes through the rotary kiln.

High temperature unit of the residual heat electricity generating unit is attached to the PH.

The cooled clinker is stored.

The hot clinker that emerges from the rotary kiln is passed through the cooling system (AQC).

Low temperature unit of the residual heat electricity generating unit is attached to the AQC.

Clinker and small amounts of other raw materials are finely ground into cement by ball milling.

Cement product storage and dispatch.
Sequence of reactions during the formation of cement
Changes in cement + concrete technology

Key Changes (The Big Hitters)

Mineral Admixtures - additions

- **SILICA FUME** is a by-product of induction arc furnaces in the silicon metal and ferrosilicon alloy industries
- **METAKAOLIN** high-reactivity metakaolin (MK) is one of the most recently developed supplementary cementing materials for high-performance concrete
- **FLY ASH** (pulverised fuel ash) is a by-product of an electricity-generating plant using coal as fuel,
- **SLAG** is a by-product of iron or steel production and the slag used in the concrete industry is mainly the slag from iron production and its full name is ‘ground, granulated blast furnace slag’ or GGBS
- **The changing technologies in concrete manufacture** significantly reduce the quantities of cement by volume, such as: new admixtures; Green concrete; Eco- cement: Magnesium carbonate crystals
- **KILN LINING** substitution of Spinel Bricks for Chromate Bricks in the melt zone
# Changes in cement technology

## Blended Cements

<table>
<thead>
<tr>
<th>Type</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portland blast-furnace slag cement (IS)</td>
<td>Contains 25-70% GGBFS</td>
</tr>
<tr>
<td>Portland-pozzolan cement (IP and P)</td>
<td>Contains a base of Portland and/or IS cement and 15-40% pozzolans.</td>
</tr>
<tr>
<td>Pozzolan-modified Portland cement (I(PM))</td>
<td>The base is Portland and/or Type IS cement with a pozzolan addition of less than 15%</td>
</tr>
<tr>
<td>Slag modified Portland cement (I(SM))</td>
<td>Contains less than 25% GGBFS</td>
</tr>
<tr>
<td>Slag cement (S)</td>
<td>GGBFS content of 70% or more. Type S can be blended with Portland cement to make concrete of with lime for motors; the latter combination would make the final cement a pozzolan-lime cement</td>
</tr>
</tbody>
</table>
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Technology – Findings

• investigation of cement manufacturing processes: wet – v- dry

• effects of processing cement to concrete on Cr IV levels
  – Australia showed the second highest hexavalent chromium levels of 5 countries across Asia, Europe and North America
  – levels of 20 – 38ppm have been recorded (levels of 10ppm will induce sensitisation)

• chemical and mechanical contributions –
  – raw materials; kiln linings – Spinel Brick Linings; grinding mills;

• chromium in the melt zone – oxidative and reductive states

• changes in cement technology:
  – substitution of slag for clinker – chemical immobilisation of chromium
  – chrome free kilns – spinel brick linings – reduction of chrome alloy steels
  – choice materials; additives

• automation of cement technology
  – automation in manufacturing less than 10 % of 1970’s workforce
  – placement technology significantly decreased direct contact with wet cement
Automation technology in cement

Production of Cement by the Dry Process

- Quarry (ies)
- Crushing Plant (s)
- Raw Materials Storage
- Corrective Materials
- Feed Bins
- Cooler Dedusting
- Coal Mill
- Hot Gas Generator
- Rotary Kiln
- Clinker Cooler
- Clinker Storage
- Mineral Gypsum Component
- Filter
- Cement Mill
- Cement Silo
- Bulk Dispatch
- Packing Machine
- Bag Palletization

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Changes driven changing raw materials

- Cement is the most widely used material, 1 tonne consumed for every living human
- As much as 5% of global CO$_2$ emissions are associated with cement production, with typically 1 tonne of cement produced responsible for 1 tonne of CO$_2$ emissions
- Raw materials such as limestone are becoming more difficult to locate and extract
- Motivation to use cheaper industrial waste as cementitious materials
- The changing technologies in concrete manufacture significantly reduce the quantities of cement by volume, such as:
  - New admixtures
  - “Green concrete”
  - Eco-cement: Magnesium carbonate crystals
QUESTIONS