ATILH
ASSOCIATION TECHNIQUE DE L'INDUSTRIE DES LIANTS HYDRAULIQUES

DECRYPTAGE N°3

Cements: causticity and allergens

Causticity = basicity (= pH > 9)

Allergens: chemicals that cause allergic reactions

Key Points

- **Cements are known to cause both irritation, owing to their basicity, and skin allergies, triggered by allergens including hexavalent chromium.**
- **Since cement's causticity can neither be eliminated nor decreased by chemical means, it is crucial to protect oneself against it through collective preventive measures, by avoiding contact with cement and by wearing Personal Protective Equipment (PPE).**
- **In order to lessen their allergenic potency, cements have been subject to a regulatory limit on their (soluble) chromium VI content during hydration, at the European level, based on tests carried out by certain Nordic countries.**
- **Studies conducted in various European countries have shown this measure to be effective in mitigating skin allergy risks.**
- **Cements nevertheless remain potent irritants, with an ongoing incidence of skin allergies. Preventive measures to minimise possible contact between products containing cement and cement workers' skin remain necessary.**

INTRODUCTION

Cements are commonly used in the construction, public works and precast concrete sectors and are typically made up of Portland clinker and several other principal constituents (mainly granulated blast furnace slag (GBFS), fly ash from coal combustion and/or calcium carbonate), as well as small quantities of calcium sulphate (gypsum, anhydrite).

Cements are known to cause skin irritation and allergies among people who handle them.

In order to minimise harm to cement workers, cements have been subject to a regulatory limit on their (soluble) chromium VI content at the European level.

The present article takes stock of the main health risks faced by cement workers: the origin and effects of, and ways to, attenuate causticity, the effects of hexavalent chromium on health and the effects of placing a limit on (soluble) chromium VI content as well as said limit's consequences on prevention.

REGULATION, CLASSIFICATION AND LABELLING

There is no harmonised regulatory classification system for cement at the European level. Cement suppliers must classify and label cements according to known hazards, in accordance with the European CLP Regulation ((EC) n°1272/2008 of 16 December 2008 as amended). The labelling of cements marketed in Europe is liable to vary between suppliers. The diagram below shows the pictograms, warning statements and hazard statements used by most European suppliers (1) and in particular by cement manufacturers in France. Formulators must use cement classification and labelling and follow the rules of the CLP Regulation concerning mixtures for the products they place on the market.

Danger

H318: Causes serious eye damage
H315: Causes skin irritation
H317: May cause an allergic skin reaction
H335: May cause respiratory irritation

FIGURE 1 - Hazard pictograms and hazard statements applicable to cement

In addition, the CLP Regulation states that for fresh mortars and ready-mix concretes, label information is to be provided to non-professional customers in a separate document.

In light of the recognised cement-induced skin allergies to chromium VI, marketing and using cements containing more than 0.0002% (2 mg/kg or 2 ppm) soluble chromium VI when hydrated (in mixing water) was prohibited at the European level in January 2005 (Directive 2003/53/EC of 18 June 2003), except in special cases. This ban is now incorporated into the European REACH regulation. Water-soluble chromium VI contained in cement must be measured using the harmonised test method adopted by the European Committee for Standardisation (EU Regulation 126/2013 of 13 February 2013), transposed into standard NF EN 196-10.

The CLP Regulation stipulates that where chromium reducing agents are used, the cement's packaging (or that of mixtures containing cement) shall include information indicating date of packaging, storage conditions and the appropriate storage time, so that the reducing agent remains active and the soluble chromium VI content is kept below the set limit.

By way of derogation, the limitation of chromium VI content shall not apply to placing on the market and to using cements in controlled, closed and fully automated processes, in which cement and cement-containing mixtures are handled exclusively by machinery and there is no risk of skin contact. Under the CLP Regulation, labels on cements exceeding 2 ppm of chromium VI must bear either the hazard statement H317 or the EUH203 statement "Contains chromium (VI). May produce an allergic reaction."

Since cements are considered hazardous substances, they must be used in accordance with the general regulations on prevention concerning dangerous chemical agents laid down by the French Labour Code (articles R. 4412-1 to R. 4412-57).

Cement causes two major types of skin damage: irritation and allergy. Adverse effects to the skin and eyes caused by the use of cements have been public knowledge for a long time. These effects were first acknowledged in a French Table of occupational diseases in 1936. As things currently stand, cement-caused affections may be claimed as occupational diseases according to Table 8 of the French General social security scheme or Table 14 of the Agricultural social security scheme.

HEALTH EFFECTS OF CEMENTS

Causticity and its effects on health

Causticity is created when cement is dissolved in water, even in very small quantities (perspiration can hydrate cement, causing serious injuries). During hydration, cement releases chemical substances such as calcium hydroxide (lime) and alkalis which cause hydration water to become extremely basic (pH = 14). This basicity (=causticity) is inherent to producing and using cement.

The most common effect of causticity is **irritation**, a mild form of burning, which occurs mainly on the hands and fingers when handling products containing cement. Certain working conditions can affect the knees of masons, kneeling unprotected in fresh concrete when laying and finishing. Due to the very high pH of the mixing water and despite cement's classification as a non-corrosive irritant, fairly severe **burns** may arise from prolonged contact. Burns can lead to lesions causing serious, sometimes irreversible, damage to the human body.

Hexavalent chromium and its effects on health

Chromium has its origins in the cementing process, more specifically in its contents in the raw materials, fuels and magnesium-chromium refractory bricks, as well as in the chromium steels of raw mills, mill liners and mill balls. Since the 2000s, balls and liners have been eliminated from cement plants, thus cutting down considerably the chromium content oxidised in the kiln atmosphere which subsequently finds its way into cement.

Cements can lead to **allergic dermatitis**. Chromium VI yields more positive reactions in patch tests on people with cement skin allergies than any other allergen. In some cases, patch tests may also give positive readings for other allergens such as chromium III or cobalt (2).

The occurrence of skin allergies is promoted by cements' irritant properties and the abrasive quality of cement-containing materials which deteriorates the skin.

Once developed, a skin allergy will reappear at the slightest contact with the allergen, whether present in cement or another product. These conditions can result in disability, forcing the allergic person to change jobs to avoid any contact with cement.

Health effects of cement inhalation

As regard the effects of cement dust inhalation on human health, existing studies tend to focus on the effects of exposure in the cement industry. A 2017 review, of available scientific literature on the associations between exposure in the cement industry and non-carcinogenic respiratory effects, reports recent studies showing a dose-response relationship between dust exposure and a decrease in lung function in cement workers. These effects are related to high dust exposures in some plants and could be due to the irritating nature of cement dust.

No link has been established between exposure to cement dust and other pathologies. A meta-analysis published in 2016 does not point to an increase in overall mortality, either by cancer, cardiovascular or respiratory diseases, in the cement industry.

Number of affections caused by cements recognized as occupational diseases

The number of cement-induced affections (recognized as occupational diseases according to Table 8 of the French General social security system), which peaked at over 2,000 cases per year in the 1960s, has gradually dropped to around 50 cases per year in 2015. Figure 2 shows the downward-trending number of cement-induced occupational diseases recognized and compensated each year according to r Table 8 since the early 2000s.

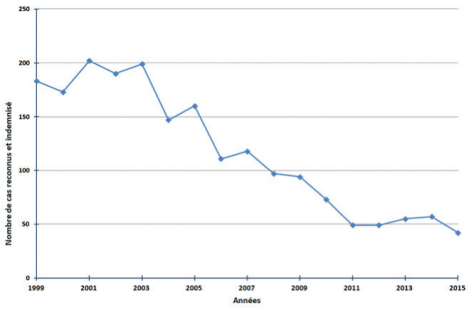

FIGURE 2 - Trend in the number of cement-induced occupational diseases since 1999

IMPACT OF LIMITING CHROMIUM VI CONCENTRATIONS AND OF CHANGES IN CEMENT COMPOSITION

The first measures limiting soluble chromium VI in cement were enacted in Denmark in 1983, followed by Finland in 1987, by making the addition of ferrous sulphate to cement mandatory. Ferrous sulphate lowers chromium VI content by reducing it to chromium III. A Danish study (3) showed a decrease in the prevalence of skin allergies to chromium VI, which were significantly higher than that of irritant dermatitis, among workers exposed daily to wet cement. The study concluded that the addition of ferrous sulphate had an influence on abating cement-induced skin allergies. In Finland, a study (4) compared incidence of skin allergies to chromium VI over two periods (1978-1987 and 1988-1992) among masons and precast industry operators. The Finnish study showed a one-third decrease in the incidence of skin allergies to chromium VI, whereas irritant dermatitis cases remained practically constant. The study also underscored the usefulness of iron sulphate.

A study conducted in the United Kingdom attempted to assess the effectiveness of the reduction in chromium VI concentration in cement imposed by European regulations (5). It showed a significant decrease in the incidence of dermatitis among construction workers exposed to cement over the periods spanning 2002-2004 and 2005-2009. The decrease is more significant for allergic dermatitis caused by chromium VI than for those with another origin. The decrease is particularly marked for chromium VI-related dermatitis in 2004-2005, when the limit set on chromium VI concentration went into effect (see Figure 3). The study concluded that European regulations curbing the use of chromium VI in cements had proven effective in scaling down the incidence of cement-caused chromium VI allergic dermatitis.

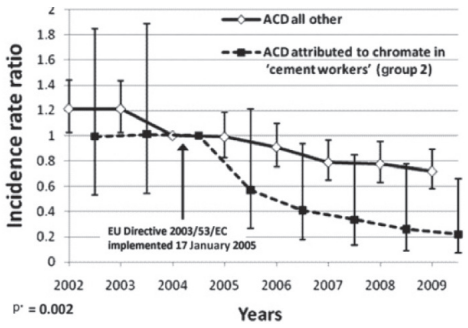

FIGURE 3 - Estimated annual evolution in the number of contact allergy cases attributed to chromates between the group of cement workers exposed to cement (Group 2) and all other allergy cases.

ACD = Allergic Contact Dermatitis

Other studies, conducted in Germany (6) and France (7) in particular, also show a decrease in the incidence of cement-induced chromium VI allergic dermatitis, but fail to establish a clear link with decreased chromium VI concentration in cement.

Taken together, these studies support the conclusion that at least part of the decrease in the incidence of chromium VI skin allergies among cement users stems from a lowering of chromium VI content. The reduction in the incidence of irritation dermatitis, and certainly part of the decrease in cases of allergic origin comes from improved prevention on construction sites and in the precast industry. Cement-related skin diseases have however not disappeared, and cement may yet still trigger severe chromium VI allergies in young people after limited exposure periods (8).

In order to keep levels of chromium VI in cements low, reducing agents have come into use. Ferrous sulphate was the first such agent, though others, based on tin compounds or antimony trioxide, have more recently been placed on the market. It should be noted that antimony trioxide is dangerous for people's health, classified as a category 2 carcinogen at the European level. The risk linked to antimony appears very limited, given the dosage of the admixture, around 15 g/tonne of cement per ppm of chromium VI to be reduced.

During the last 15 years, irrespective of the limitation placed on chromium VI concentrations, cement composition has evolved in tandem with increased usage of industrial by-products such as granulated blast furnace slag (GBFS) and fly ash (FA). These additions reduce cement basicity, to a small extent, and therefore also tend to reduce their irritancy potential. Though slags, which are generally the major addition, may not contribute significant chromium VI quantities, they can nevertheless, along with fly ash, introduce various potentially allergenic metals, depending on their origin.

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CONSEQUENCES OF THESE DEVELOPMENTS ON PREVENTION

Despite the risks associated with cement having been moderated, skin allergies have not been eradicated, with cases of irritant dermatitis continuing to occur. The limitation of (soluble) chromium VI has no impact on attenuating its irritant quality.

Therefore, cement workers are still advised to avoid coming into contact with cement or the products containing it, especially when mixed with water. The technical precautions most commonly taken are:

- Automated operations;
- Avoiding contact with wet cement: no handling with bare hands (smoothing with fingers,...) or picking up tools covered in cement without gloves, ...;
- Avoiding exposure to dry cement: using low-dust processes, isolating cement dust producing machines, …;
- Wearing suitable gloves and safety glasses;
- Implementing hygiene measures: regularly changing work clothes, washing hands with neutral soap after handling cement;
- Informing both regular and occasional workers of the risks involved.

The prevention of cement-related risks also requires placing the safest possible cements on the market. In particular, given the incorporation into cements of industrial by-products such as blast furnace slag or fly ash, cement producers need to be particularly vigilant in the selection and control of these by-products to ensure that allergy-causing metals such a nickel, cobalt, beryllium, etc. are used as sparingly as possible.

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Conclusion

- **Cement hazard = irritating (pH related) + allergenic (Cr^{6+} related).**
- **The restriction placed on Cr^{6+} in cements has effectively reduced allergy risks but does not affect its status as an irritant.**
- **Other elements such as nickel or cobalt, derived from cement constituents other than clinker, may be allergenic.**

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