Determination of soluble hexavalent chromium in samples of Portland cement from Brazilian cement manufacturers

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ABSTRACT: Urbanization growing is nowadays highlighted in the big cities. Therefore, it is necessary to increase the production of cement, which is used in several areas of civil construction, to meet the growing demand. Thus, the objective of this study was to determine the content of hexavalent soluble chromium in Portland cement samples from different cement industries in São Paulo state, Brazil, since this chemical species can cause adverse health effects as well as being a potential human carcinogenic for those who manipulate it. In Brazil, the emission of Cr⁶⁺ in the cement has no restrictions, since there is no current Brazilian law that determines the maximum concentration of it, whereas, in Europe, the current law 2003/53/EC establishes a maximum of 2 mg kg⁻¹. It was found by the analysis that among all types of cement produced in São Paulo, the only one that did not exceed the standard limit was the CP III from manufacturer E (with Cr⁶⁺ concentration of 1.22 mg kg⁻¹), probably because this kind of cement has a high concentration of additions in its composition, responsible for diluting thereby chromium content. The other types of cement exceeded the established limit. CP II-Z cement sample from A manufacturer, for example, presented Cr⁶⁺ concentration of 4.00 mg kg⁻¹ (double the established limit). In comparison, CP II-F from manufacturer A presented 16.16 mg kg⁻¹ of Cr⁶⁺ concentration (8 times higher than the limit). It was concluded that Brazil urgently needs a law to regulate the hexavalent soluble chromium emission present in Portland cement to minimize the environmental and health effects that the cement out of specification may cause.

Key words: Health effects of Cr⁶⁺; Hexavalent chromium; Portland cement.

1. INTRODUCTION

The growing urbanization and the need for new bridges, airports, highways, and sanitation networks are currently evident in large cities. Therefore, it is necessary to increase the productivity of cement, the base material for obtaining the concrete used in various areas of civil construction, to meet the growing demand.

The manufacture of clinker, an intermediate material in the cement production process, requires the use of several raw materials, which have small amounts of elements that can interfere with and change the properties of the final product.

The cement manufacturing process needs limestone, clay, and gypsum (gypsum) as raw materials, which are considered mineral resources abundant in the earth’s crust. Small amounts of iron ore, bauxite, clay, or sand may be needed as a source of iron oxide (Fe₂O₃), aluminum oxide (Al₂O₃), and silica (SiO₂) to supply the chemical composition of the cement to the requirements process [1,2].

The cement industry in Brazil also uses co-processing as an alternative to save raw materials or replace additives to adjust cement’s final composition. In this kind of process, any solid waste, from any industry can be incorporated into the production process. Co-processing is economically viable for the industry, however, there is no control over the concentration of the elements which will be present in the final product.

Elements such as titanium (Ti), manganese (Mn), chromium (Cr), zinc (Zn), vanadium (V), and nickel (Ni), among others, play a fundamental role in the formation of clinker crystals, but in high percentages become harmful to the process, the environment, and human beings.

One of the elements that have a strong action on the properties of cement is chromium, which dermatologists attribute as a component that causes contact eczema, arousing the interest of scholars in the medical and occupational safety areas [3].

Chromium, like other elements, comes from the use of alternative fuels, industrial waste, and urban waste in the processing of cement, which together with the raw materials undergoes oxidation and can be found in valences +3, +5, +6, and rarely, +2. Cr⁶⁺ is normally formed in the clinker furnace due to a highly oxidizing atmosphere and the presence of ions that facilitate the conversion of trivalent chromium (Cr³⁺) to hexavalent chromium.
In general, hexavalent chromium has greater toxicity when compared to trivalent chromium, due to its greater ease of penetrating cells by crossing the cell membrane and binding to proteins. Adverse health effects related to Cr⁶⁺ exposure are gastrointestinal, immunological, reproductive, respiratory tract irritation, contact dermatoses, and skin ulcers, in addition to being a possible human carcinogen [4-6].

Chromium is present in food, water, and industrial products, either as an input or as a contaminant. According to Cheis (2013), this element is included in the list of the United States Environmental Protection Agency (Environmental Protection Agency) as one of the 129 most critical pollutants for the environment, so its disposal must follow strict requirements based on its toxicity.

The concern with this element is because cement handling is carried out together with water which solubilizes it, and in contact with the skin, it can cause contact dermatitis [3, 7, 8].

The cases of contact dermatitis caused by cement contact are well known in Europe. Cases in France, for example, were reported when the Paris subway was built, between 1900 and 1905. In Sweden, cases of contact dermatitis caused by cement have been known since 1943. These cases led to the implementation of legislation to control hexavalent chromium in Portland cement, limited to 2mg.kg⁻¹, as established by 2003/S3/EC [9].

In addition to skin effects, chromium can also cause respiratory problems due to particles emitted during the cement process, as well as contamination in soil and water. Recent studies show that soil and water were contaminated due to incorrect disposal of waste from Portland cement [10]. Lung cancer can also be related to the inhalation of chromium and volatile compounds emitted during the alkaline evaporation that occurs inside the industrial oven used in the cement production process [11].

Given the facts listed above, the cement industries must begin to emit the least possible amount of chromium, and for this, there must be effective legislation and better control of the type of additives that can be incorporated into cement production. In addition, awareness of all those involved in both the production and handling of cement is necessary as new diseases related to its chemical composition are being discovered. Individual and collective safety equipment can contribute to the reduction of toxic effects associated with cement.

The present work was to quantitatively determine the content of soluble hexavalent chromium present in samples of Portland cement from cement companies in the state of São Paulo, through chemical analysis, to obtain information regarding its toxicity and possible damage to health.

2. MATERIALS AND METHOD

2.1 Samples preparation and materials

Five cement samples collected from cement manufacturers located in São Paulo, Brazil, were analyzed regarding chromium concentration. The types of cement were CP II-F, CP II-E, CP II-Z, CP III, and CP V (which are the main cement types used in civil construction in Brazil).

Each type of cement was weighed (450 g) and mixed with 225 mL of deionized water. The mixture was put in a specific equipment to homogenize cement and mortar (EMIC NS027) and mixed at low velocity for 30 seconds. In the next 30 seconds, 1350 g of commercial sand was added to the mortar, and, after this time, the velocity was increased to high speed, for 30 seconds. After that, the rotation was stopped for 90 seconds (30 seconds was used to remove the material adhered to the equipment). After that, the equipment was turned on again, at a high velocity for 60 seconds. The final mixture was transferred to a vacuum filtration system, and it was filtrated until getting around 15 mL of filtrate. Samples preparation steps were done by using the procedures determined by European Standard EN196-10/2006.

General materials of chemistry laboratory such as mill (Herzog HSM 100), semi-analytical balance (Denver Instrument P-4002D), analytical balance (Sartorius BP221S), pH meter (Digimed DM-23), vacuum pump (Marconi MA-058), and automatic pipette (Thermo Electro – Finnipette), were used. Solutions of hydrochloric acid (37%), acetic (≥ 99.5%), diphenylcarbazide (≥ 98%), potassium dichromate (100%), and chromate standard solutions (5.0 mg.L⁻¹) were also used.

2.2 Quantification of chromium hexavalent

The standard curve was carried out by using a standard solution of chromate (5.0 mg.L⁻¹). Volumes of 1.0 mL, 2.0 mL, 5.0 mL e 10.0 mL were pipetted in volumetric flasks of 50 mL. An indicator (5 mL) was also added together with 5 mL of hydrochloric acid (0.04 mol.L⁻¹) and deionized water to complete the volume.

Samples were prepared as follows: 5 mL of each filtrate (obtained according to samples preparation step – item 2.1) was put in a becker (100 mL) with 5 mL of indicator, and 20 mL of deionized water. The solutions were homogenized. After that, the pH was immediately adjusted from 2.1 to 2.5 with hydrochloric acid (1.0 mol L⁻¹). The becker solution was transferred to a volumetric flask (100 mL), the volume was completed with deionized water and the solution was homogenized.

The quantification of chromium hexavalent was carried out by colorimetric technic (spectrophotometric). Metrohm UV-Vis Spectrophotometer - 662 photometer was used to determine the chromium final concentrations, which were expressed in mg kg⁻¹. All tests were done by using the procedures determined by European Standard EN196-10/2006 and performed in triplicate. The summary of the experimental procedure is shown in Figure 1.

The determination of the concentration of soluble hexavalent chromium in the samples, performed by the spectrophotometry technique, consisted of measuring the light absorption capacity of the sample in the visible region of the electromagnetic spectrum. This type of method is based on measuring the amount of radiation produced or absorbed by molecules or atomic species of interest [14]. When there is an incidence of a beam of light in a solution, part of the light is absorbed by this solution and the rest is transmitted, so the absorption of light basically depends on
optical path it travels [12-14]. The relationship of these factors is described by the Lambert-Beer law and expressed mathematically by equation (1).

\[ I = I_0 \times 10^{-\varepsilon \times C \times b} \]  

(1)

Where \( I \) is the transmitted light intensity, \( I_0 \) is the incident intensity, \( C \) is the sample concentration (mol L\(^{-1}\)), \( b \) is the optical path (cm), and \( \varepsilon \) is the molar absorption coefficient, which is a parameter characteristic of each molecular species in a given solvent and a specific wavelength [17-19]. The \( I/I_0 \) ratio is the fraction of incident light that is transmitted and is known as transmittance (\( T \)). The absorbance (\( A \)) is given by equation (2). Equation 3 is the combination of equations 1 and 2.

\[ A = \log \left( \frac{I_0}{I} \right) = -\log T \]  

(2)

\[ A = \varepsilon \times C \times b \]  

(3)

Adequate treatment of the UV-Vis data requires a standard curve that graphically corresponds to the absorbance values with the concentrations of the pre-defined solutions at a fixed wavelength. This standard curve is used to quantitatively determine a property of an unknown sample from samples with known properties [15]. The line equation is then determined through the linearity obtained from the standard solutions, making it possible to determine unknown concentrations through the read absorbances [12-15]. Thus, with the data obtained, the amount of hexavalent chromium in the filtered solutions (in mg kg\(^{-1}\)) was calculated, by using equation (4).

\[ \text{Cr}^{6+} = C \times \left( \frac{V_3}{V_2} \right) \times \left( \frac{V_1}{m} \right) \]  

(4)

Where, \( \text{Cr}^{6+} \) is the amount of soluble hexavalent chromium in mg kg\(^{-1}\); \( C \) is the hexavalent chromium concentration obtained from the calibration curve versus concentration in mg kg\(^{-1}\); \( V_1 \) is the volume of water (mL); \( V_2 \) is the aliquot volume (mL); \( V_3 \) is the volume of the volumetric flask (mL), and \( m \) is the mass of cement (g).

3. RESULTS

Standard curve data such as the absorbances measurements and their respective concentrations are shown in Table 1. The standard curve is shown in Figure 2. Equation 5 shows the equation of the line obtained by the linearity of the standard curve.

\[ y = 1.0008 \times x - 0.0097 \]  

(5)

<table>
<thead>
<tr>
<th>Absorbance</th>
<th>Concentration (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.095</td>
<td>0.10</td>
</tr>
<tr>
<td>0.183</td>
<td>0.20</td>
</tr>
<tr>
<td>0.475</td>
<td>0.50</td>
</tr>
<tr>
<td>1.000</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 1 Standard curve data for hexavalent chromium.

After the determination of the standard curve, different cement samples, from different manufacturers were analyzed under the same conditions (Table 3). Equation (5) was used to determine the concentration of hexavalent chromium in all samples from absorbances read by the equipment.
According to European standard 2003/53/EC, the maximum limit of Cr\textsuperscript{6+} established for cement samples is 2 mg kg\textsuperscript{-1}. Table 2 shows that among all types of cement produced in São Paulo, Brazil, the only one that did not exceed the allowed limit was the CP III cement sample, from the E manufacturer. CP III cement usually has a high concentration of additions in its production, what can contribute to dilute hexavalent chromium in the product, resulting in low content when compared to the other types (1.22 mg kg\textsuperscript{-1}).

The addition of solid waste from the iron ore production in the CP III cement can reach up to 70% by weight. This type of residue mostly contains calcium silicates and aluminosilicates, and less trace elements. However, the chromium concentration determined is close to the European limit, being subject to extrapolation if the manufacturer changes its production. A possible cause for the difference between the results obtained between factories E and A in CP III cement is the range of steel slag (from iron production) that can be added in this process. According to the manufacturers, the addition of that residue usually varies from 35% to 70%. Thus, it is possible that factory A added less amount of steel slag when compared to factory E, so, in factory E the chromium was more diluted than in factory A. All the other types of cement exceeded the established limit, in different proportions (Table 2).

As shown in Table 2, the CP II-F sample, from factory A, was the one with the highest concentration of soluble hexavalent chromium. One of the possible causes is the proportion of raw material and the corrections used to add value to the cement, not considering the high incorporation of chromium in the process. Factory B, in turn, produces cement with a lower concentration of chromium than factory A, but it is still above the limit.

It is also possible to observe from Table 2 that CP II-F, CP II-E, and CP V cement samples, from the same manufacturer (B) present similar hexavalent chromium contents, which means that chromium content is related to the production process, the raw materials, and to the co-processing (incorporation of by-products from other industries).

The difference observed in the same cement type, but from different manufacturers, can be related to the localization of their mineral deposits and the concentration of trivalent chromium present in them, which is converted into hexavalent after the clinker formation step.

Another discrepancy in the results can be related to the co-processing activity, when each manufacturer uses different fuel in the cement furnace, which does not have adequate attention regarding the chromium content, and is responsible for the incorporation of some elements, such as chromium, in the final product.

It should be noted that some cement industries use furnaces and mills with chromium in the composition of the materials, which can detach and/or contaminate the process, however, more detailed studies must be carried out to confirm this hypothesis. Another alternative is to add some chemicals to turn soluble chromium into insoluble [16].

After the produced cement is commercialized, construction workers can have several health problems due to contact with cement containing soluble hexavalent chromium, such as contact dermatitis, irritation of the

### Table 2 Hexavalent chromium concentration from different Brazilian cement samples.

<table>
<thead>
<tr>
<th>Cement types</th>
<th>Manufacturer</th>
<th>1\textsuperscript{st} reading (mg kg\textsuperscript{-1})</th>
<th>2\textsuperscript{nd} reading (mg kg\textsuperscript{-1})</th>
<th>3\textsuperscript{rd} reading (mg kg\textsuperscript{-1})</th>
<th>[Cr\textsuperscript{6+}] average ± standard deviation of 1\textsuperscript{st} to 3\textsuperscript{rd} reading (mg kg\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP II-F</td>
<td>A</td>
<td>16.50</td>
<td>15.90</td>
<td>16.08</td>
<td>(16.16 ± 0.01)</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>8.92</td>
<td>8.75</td>
<td>8.81</td>
<td>(8.83 ± 0.01)</td>
</tr>
<tr>
<td>CP II-E</td>
<td>B</td>
<td>7.43</td>
<td>7.86</td>
<td>7.93</td>
<td>(7.74 ± 0.01)</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>12.62</td>
<td>12.32</td>
<td>12.49</td>
<td>(12.48 ± 0.01)</td>
</tr>
<tr>
<td>CP II-Z</td>
<td>A</td>
<td>3.72</td>
<td>4.18</td>
<td>4.11</td>
<td>(4.00 ± 0.01)</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>4.22</td>
<td>4.19</td>
<td>3.97</td>
<td>(4.13 ± 0.01)</td>
</tr>
<tr>
<td>CP III</td>
<td>E</td>
<td>0.98</td>
<td>1.26</td>
<td>1.42</td>
<td>(1.22 ± 0.01)</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>5.86</td>
<td>6.65</td>
<td>6.77</td>
<td>(6.43 ± 0.01)</td>
</tr>
<tr>
<td>CP V</td>
<td>B</td>
<td>7.32</td>
<td>6.54</td>
<td>6.63</td>
<td>(6.83 ± 0.01)</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>13.25</td>
<td>13.11</td>
<td>13.47</td>
<td>(13.28 ± 0.01)</td>
</tr>
</tbody>
</table>
Regarding environmental effects, chromium is listed by the US Environmental Agency (EPA) as one of the 129 most critical pollutants, so its disposal must follow stringent requirements based on its toxicity. Another concern of environmental contamination comes from cement particles that can spread with the wind and rain, polluting the air and water, and accumulating in plants, animals, and the soil, but there are not enough studies regarding the concentration and the harmful effects caused by this type of contamination.

Part of the contamination can also come from the use of cement to build structures that will be used as a water reservoir, which may contain leachate soluble hexavalent chromium [17]. The public health problem can be aggravated by the contamination of water by hexavalent chromium because this species can be dissolved in water at unknown concentrations.

4. CONCLUSIONS

The hexavalent chromium concentration was determined for ten samples of Portland cement from cement manufacturers from São Paulo, the biggest city in Brazil. It was found by the spectrophotometry technique that among all types of cement produced in São Paulo, the only one that did not exceed the standard limit, established by the European standard, was the CP III. All the other types of cement exceeded the established limit.

It was concluded that Brazil urgently needs a law to regulate the hexavalent soluble chromium emission present in Portland cement, as well as an awareness for the construction workers regarding the possible health damages that hexavalent chromium can cause.

Since the cement industries of São Paulo state are producing cement with high content of chromium hexavalent, without considering the high toxicity, the right use of personal protective equipment (PPE) as well as the propagation of the information about the health damages that chromium can cause, can soften this problem provisionally.

Another way to minimize the problem shown in this study is to add ferrous sulfate during cement production to reduce the content of soluble hexavalent chromium in the product. According to some studies, ferrous sulfate can turn soluble hexavalent chromium into insoluble, thus minimizing the contamination of construction workers. However, it is necessary to verify if the addition of that chemical will not influence the properties of cement and concrete.

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