

Quick and simple speciation analysis of chromium in cements

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Abstract: The extraction of total Cr(VI) from commercially available cements, based on DTPA + 0.2 mol dm⁻³ (NH₄)₂SO₄/NH₄OH mixture solution and subsequent selective determination of Cr(VI) has been proposed. The determination was carried out using the adsorptive voltammetric stripping method. The study was conducted using three different commercially available cement samples. It has been checked that the proposed extraction procedure guaranteed no changes of chromium speciation during cement analysis. For comparison extraction was also carried out with the use of recommended by United States Environmental Protection Agency (EPA) Method 3060A, based on 0.28 mol dm⁻³ Na₂CO₃ + 0.5 mol dm⁻³ NaOH). Additionally, the extraction process was carried out using only distilled water as an extraction mixture which allows to evaluate concentration of only soluble Cr(VI) forms contained in cement. In all three cements, the content of soluble Cr(VI) was below 2 ppm, i.e. the limit value by European Union Directive 2003/53/EC.

Keywords: cement, extraction, chromium speciation, voltammetric determination

1. Introduction

Chromium occurs in the nature both as a natural ingredient in rocks, minerals, soils and waters, as well as it gets into the environment as a result of anthropogenic activity. Chromium can occur in various chemical forms with valences varying from -2 to +6. However, only two of them, Cr(III) and Cr(VI) are stable enough to exist in the environment. Chromium at IV and V oxidation state can only form unstable compounds formed indirectly in Cr(III) and Cr(VI) reactions with oxidizing or reducing agents, respectively. It is very important that both forms occurring in the environment, i.e. Cr(III) and Cr(VI) drastically differ in their properties, chemical and biological reactivity, and thus have extremely different effects on humans. While Cr(III) is a trace element necessary for living organisms, Cr(VI) has harmful and toxic effects (Cheung and Gu, 2007; Cost, 2003; Dengwei and Kingston, 2000; Kocberber and Dönmez, 2007; White and Claxton, 2004). It has been confirmed that long-term exposure to even low doses of Cr(VI) compounds leads to many clinical problems. In this case occur circulatory disorders, liver diseases and respiratory system disorders e.g. asthma, bronchitis, pneumonia, laryngitis. To make things worse, hexavalent chromium can cause cancer, and in 1991 Cr(VI) was classified by the International Agency for Research on Cancer as being carcinogenic to humans. Another very common problem associated with the presence of Cr(VI) compounds are skin allergies, which can lead to severe inflammation, ulcers and even skin necrosis (Kumar et al., 2007; Wang et al., 2007). Professions particularly exposed to contact with chromium are construction workers, galvanists, locksmiths, printers, tanners, varnishers, painters. These professions are more frequently chosen by the males, hence chromium allergies in women are very rare. Sensitization occurs due to the presence of chromium mainly in cement and in industrial paints and oils (Lee et al., 1989; Gad, 1989; Katz and Salem, 1994). The source of chromium in cement are natural raw materials used to make clinker, which is the main component of cement. The chromium content in the clinker is estimated to be between 20 and 30 ppm. An additional source of chromium is hard coal used as a fuel, it contains on average 25 ppm of chromium. Magnesium-chromite refractory products used in kilns for burning clinker are another source of chromium in cement. The clinker production process takes place at high temperatures, up to 1450 °C, and in an oxidizing atmosphere. Such conditions favor the oxidation of Cr(III) contained in

raw materials, fuel and refractory linings of the furnace to Cr(VI). Oxidation of Cr(III) to Cr(VI) also occurs to a small extent during grinding in mills containing steel with a high content of chromium (Sinyounga et al., 2011; Frias and Sanchez de Rojas, 2002; Laforest and Duchesne, 2005; Macias et al., 1997; Tantawy et al., 2012; Frías and Sánchez de Rojas, 1995; Estokova, 2012).

In the mid-twentieth of the 20th century, attention was drawn to the fact that the hexavalent chromium contained in cement was largely washed away when preparing mortars and concretes. As it is known, contact with them is very harmful to health due to both carcinogenicity and allergenicity. For many years, various legislative and technological proposals have been introduced to minimize this threat. Consequently, Directive 2003/53/EC has been in force in the European Union since 2003, according to which the permissible Cr(VI) content in the effluent is 2 ppm. In Poland, this standard was established by the Regulation of the Minister of Economy and Labor in the Journal of Laws No. 2004/68/762 of July 5, 2004 and it concerns bagged cement. This restriction does not apply to loose cement that is used in mechanized and automated concrete plants or for the manufacture of other cement-containing products. In the case of bagged cement, the maintenance of low chromium content (below 2 ppm in leakage) should be ensured for a period of two months from the purchase of cement, ensuring proper storage of packaging.

Currently, various methods are used to minimize the amount of Cr(VI) leached from the cement. The most popular and bringing the best results ones are associated with the chromium immobilization in the cement paste by reducing Cr(VI) to Cr(III).

The following reducers are added to the cement (in amounts 0.3 - 0.7%):

- iron(II) sulfate - most often;
- tin(II) sulfate;
- antimony compounds.

Their action begins immediately following adding of water to the cement, then the transition of ions to solution occurs, including chromates(VI) and added salt, e.g. iron(II). As a result of hydrolysis of silicate cement components, the pH of the liquid phase increases simultaneously, and in the alkaline environment Fe(II) ions are strong Cr(VI) reducers. The impact of moisture and elevated temperature during cement storage causes the weaker performance of the reducers, which in turn increases the amount of leached Cr(VI) (Laforest and Duchesne, 2005; Macias et al., 1997).

Because the content of both total and soluble form of Cr(VI) is strategic and requires control, there is a continuing need for procedures to enable such monitoring. For determinations of solid samples it is necessary to carry out Cr(VI) into the solution first. The literature describes several Cr(VI) extraction methods that are evaluated in terms of ensuring that all forms of chromium are introduced into the solution while guaranteeing changes in the degree of chromium oxidation. In this work, we proposed using for the first time an extraction of Cr(VI) from cement by mixture 0.01 mol dm^{-3} DTPA + 0.2 mol dm^{-3} $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{OH}$ (pH= 8). To this time, this mixture has been successfully used for quantitative transfer of Cr(VI) to a solution from soil samples, ash and paint chips (Grabarczyk et al., 2006; Grabarczyk, 2008a). The purpose of this work was to prove that the proposed procedure can also be successfully used for quantitative extraction of Cr(VI) from cement samples with simultaneous assurance that no changes take place in the original oxidation state of chromium. The great advantage of this procedure is the short time necessary to perform it (10 minutes) and the use of a relatively low temperature (40 °C). For comparison, extraction was also carried out with the use of Method 3060A: Alkaline Digestion for Hexavalent Chromium recommended by United States Environmental Protection Agency (EPA) (Method 3060A). This method uses an alkaline solution (0.28 mol dm^{-3} Na_2CO_3 + 0.5 mol dm^{-3} NaOH) to extract Cr(VI). This method effectively dissolves both water-soluble and water-insoluble Cr(VI) compounds and prevents the reduction of Cr(VI) (Method 3060A). However, this procedure is time consuming (it takes about 1 hour) and requires the use of high temperature equal to 95 °C. This procedure is more inconvenient to carry out because it requires the simultaneous use of NaOH and high temperature. The procedure, which we propose has a number of advantages over this procedure. It requires much less time, the use of a safe temperature for the person performing the extraction and, above all, the reagents used are also friendlier for those carrying out the extraction process. Also, as it has been proved experimentally, the extraction procedure proposed by us ensures both the quantitative extraction of Cr(VI) from cement and preservation of the original of chromium oxidation state.

2. Materials and methods

2.1. Apparatus

The temperature of extraction was controlled using a thermostat PolyScience, USA. After extraction a centrifuge type 310, Poland, was used. Voltammetric measurements were carried out using Autolab PGSTAT10 analyser (Netherlands) and a controlled growth static mercury electrode in the HMDE mode, made by MTM Cracow, Poland. Voltammetric measurements were performed employing a three-electrode voltammetric cell of volume 10 cm³ consisting of an hanging mercury drop electrode (HMDE) as a working electrode, a Pt as an auxiliary electrode, and an Ag/AgCl as a reference electrode.

2.2. Reagents

Ammonium sulphate/ammonium hydroxide buffers were prepared from reagent grade H₂SO₄ and ammonium hydroxide obtained from POCh Gliwice, Poland. DTPA was obtained from Sigma-Aldrich, USA. KNO₃, Na₂CO₃ and reagents for preparation of acetate buffer (CH₃COOH, NaOH) used for voltammetric measurements were obtained from Merck, Germany. KNO₃ was additionally purified by three times recrystallization. Standard solutions of Cr(VI) and Cr(III) at a concentration of 1 g dm⁻³ were obtained from Fluka, Switzerland.

2.3. Cements

Three commercially available portland cements from different producers were used for the research: "Universal cement" from Ruben (CEM II / A-V 32,5 R named as CEMENT a), "Portland cement" from Warta (CEM II/B-M (V-LL) 32,5 R named as CEMENT b), "White cement" from Cemex (CEM I 52,5 R named as CEMENT c). The tested cements differed in their composition and compressive strength class. Cement c consists of at least 95% clinker and other components, max. 5% including whitening ingredients. It is characterized by the highest compressive strength of min 52.4 MPa. Cement a contains 80-94% clinker, 6-20% silica fly ash and other ingredients max 5%. The most diverse composition is cement b, which consists of clinker (65-79%), silica fly ash and limestone (21-35%) and other ingredients 0-5%. Both cements a and b are characterized by a similar compressive strength of min 32.5 MPa.

2.4. Extraction procedures

For voltammetric determinations of Cr(VI) in solid samples it is necessary to carry out Cr(VI) into the solution. The literature describes several methods of Cr(VI) extraction among which the following extraction mixtures should be mentioned: DTPA + (NH₄)₂SO₄/NH₄OH (Grabarczyk et al., 2006; Grabarczyk, 2008a), (NH₄)₂SO₄/NH₄OH (Séby et al., 2003), Na₂CO₃ + NaOH (Method 3060A), NaOH, K₂HPO₄ + KH₂PO₄ (Vitale et al., 1997), CO₂, Na₂CO₃ (Panichev et al., 2003). Two extraction procedures using different extraction mixtures were selected in this work for analysis of cement samples: DTPA + (NH₄)₂SO₄/NH₄OH and Na₂CO₃ + NaOH, and they were designated as procedures A and B, respectively. Procedure A proposed in this work was used for the first time for the extraction of Cr(VI) from cements. Procedure B is the recommended by United States Environmental Protection Agency (EPA) Method 3060A allowing quantitative extraction of all forms (soluble and insoluble) of Cr(VI) into solution.

Additionally, the extraction process was carried out using only distilled water which allows to pass to the solution only soluble Cr(VI) forms and this procedure is designated C. This procedure was carried out in order to check whether the tested cements meet the dedicated directive. This directive says that cement and cement-containing preparations may not be used or placed on the market if they contain, in the hydrated state, more than 0,0002% of soluble chromium VI in relation to the total dry weight of the cement.

2.4.1. Extraction procedure A

The composition of the extraction mixture: 0.01 mol dm⁻³ DTPA + 0.2 mol dm⁻³ (NH₄)₂SO₄/NH₄OH (pH = 8). Course of the procedure: a sample of cement (100 ± 5 mg) was added to 10 cm³ of extraction mixture and placed in a thermostat at 40 °C for 10 min. At this time, the sample was mixed using a magnetic

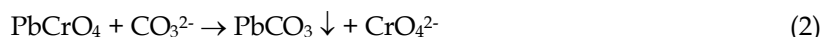
stirrer. The sample was then centrifuged for 5 min. In this procedure, metal ions from insoluble chromates are complexed by the complexing agent DTPA added and the freed chromate ion passes into the solution. This process can be represented by the following reaction using as an example the insoluble chromium compound PbCrO_4 .



2.4.2. Extraction procedure B

The composition of the extraction mixture: $0.28 \text{ mol dm}^{-3} \text{Na}_2\text{CO}_3 + 0.5 \text{ mol dm}^{-3} \text{NaOH}$.

Course of the procedure: a sample of cement ($100 \pm 5 \text{ mg}$) was added to 10 cm^3 of extraction mixture and placed in an oven at $95 \text{ }^\circ\text{C}$ for 1 h. Then the sample was centrifuged for 5 min. In this procedure, metal ions from insoluble chromates is precipitated as hydroxide or carbonate and the freed chromate ion goes into solution according to the exemplary reactions below recorded for the insoluble chromium compound PbCrO_4 .



2.4.3. Extraction procedure C

The composition of the extraction mixture: H_2O . Course of the procedure: a sample of cement ($100 \pm 5 \text{ mg}$) was added to $10 \text{ cm}^3 \text{ H}_2\text{O}$ and stirred at room temperature for 15 min. The sample was then centrifuged for 5 min.

2.5. The method of Cr(VI) determination in extract

The adsorptive stripping voltammetry (AdSV) method was used to determine the Cr(VI) content in the extracts. The voltammetry method was chosen because of its high sensitivity, speed, simplicity and low cost of the apparatus. In the AdSV method, in order to obtain low detection limits, the determined ion is accumulated on the working electrode in the form of an electrochemically active complex. In the case of Cr(VI) various complexing agent were used, however, DTPA was the most commonly employed, and the signal was additionally amplified by using the catalytic effect occurring in the presence of KNO_3 (Grabarczyk and Korolczuk, 2003). The calibration graph for Cr(VI) in this method was linear in the range from 1×10^{-10} to $1 \times 10^{-8} \text{ mol dm}^{-3}$ and the detection limit was $2.5 \times 10^{-11} \text{ mol dm}^{-3}$ (1.2 ng dm^{-3}). In this procedure, in order to obtain high Cr(VI) selectivity against Cr(III), the fact is used that after introduction of DTPA into the solution, the formed Cr(III)-DTPA complexes pass with time into the electrochemically inactive form and thus they do not affect the signal obtained from Cr(VI). The transition time of Cr(III)-DTPA complexes into the electrochemical inactive form is drastically shortened if this process occurs at $40 \text{ }^\circ\text{C}$. It is assumed that as soon as 5 minutes after the introduction of DTPA into the solution of the Cr(III)-DTPA complex they pass into the electrochemically inactive form and the obtained voltammetric signal comes only from Cr(VI) (Grabarczyk, M., 2008b). The method allows for Cr(VI) determination in the presence of about 50–100 fold excess of Cr(III).

2.5.1. Voltammetric measurement

The standard measuring procedure was performed in the following way. To the voltammetric cell the following solutions were added: adequate volume of extract (in the range $0.005\text{-}0.05 \text{ cm}^3$), 2 cm^3 of 1 mol dm^{-3} acetate buffer ($\text{pH} = 6.1$), 0.5 cm^3 of 0.2 mol dm^{-3} DTPA and 2 cm^3 of 2.5 mol dm^{-3} KNO_3 were placed into the voltammetric cell. Next the solution was diluted to 10 cm^3 with triply distilled water and final concentrations were 0.2 mol dm^{-3} acetate buffer, 0.01 mol dm^{-3} DTPA, 0.5 mol dm^{-3} KNO_3 . In the case of analysis of the extract obtained as a result of extraction by procedure B and C, the sample prepared in this way was thermostated for 5 minutes at $40 \text{ }^\circ\text{C}$. In this time the Cr(III) ions present in the extract turned into an electrochemically inactive complex with DTPA and after that the voltammetric measurement was carried out. In the case of analysis of the extract obtained as a result of extraction by procedure A, the solution prepared in this way was directly subjected to voltammetric measurement.

This is due to the fact that already during the extraction DTPA was present in the solution and Cr(III) ions had already turned into the form of the electrochemically inactive complex with DTPA.

The voltammetric measurement consisted of the three main steps by changing the working electrode potential as follows:

- accumulation step -1.0 V for 30 s, during this time Cr(VI) contained in the solution in the electrode layer was reduced to Cr(III) and an electrochemical active Cr(III)-H₂DTPA complex was formed, which was adsorbed on the HMDE electrode;
- equilibration time 5 s;
- signal registration by the changing the potential from -1.0 V to -1.4 V, during this step Cr(III)-H₂DTPA was reduced to Cr(II)-H₂DTPA and the current associated with this process was recorded as a peak. To increase the sensitivity of the determinations, a catalytic effect associated with the presence of KNO₃ ions was used.

During the first steps the solution was stirred using a magnetic stirring bar, while the equilibration and the signal registration were carried out without mixing solution. The intensity of the obtained peak on the voltammogram was proportional to the concentration of Cr(VI) in the solution. The Cr(VI) content in the extract was calculated using the standard addition method.

3. Results and discussion

3.1. Cr(VI) determined in extract obtained by procedure A

For the first time it was proposed to use DTPA + (NH₄)₂SO₄/NH₄OH as an extraction mixture for the determination of Cr(VI) in cements. Three cements marked as CEMENT a, CEMENT b and CEMENT c were used in the study. Six extractions were carried out for each of them and the results obtained are presented in Table 1.

3.2. Cr(VI) determined in extract obtained by procedure B

Analogously to the above experiments, measurements using Method 3060A recommended by EPA (Method 3060A), which was called in our paper as procedure B were performed. The experiments were carried out using the same cements that were used when applying extraction procedure A, i.e. CEMENT a, CEMENT b and CEMENT c and obtained results are presented in Table 2. As can be seen, the results obtained using the extraction procedure A and B are very similar for each cement, which can confirm that both procedures allow quantitative extraction of both soluble and insoluble Cr (VI) forms from cement.

3.3. Cr(VI) determined in extract obtained by procedure C

Cr(VI) determined in extract obtained by procedure C responds to water soluble content of chromium. This designation is particularly important considering that this value is the basis for whether a given cement can be sold. The results obtained for the cements tested in this work are presented in Table 3. It can be seen for all three analysed cements that the satisfactory results were obtained, because in no case the value of the water-soluble concentration Cr (VI) exceed the permissible norm of 2 ppm. Cement and cement-containing preparations may not be used or placed on the market if they contain, in the hydrated state, more than 0,0002% soluble chromium VI in relation to the total dry weight of the cement.

Table. 1. The results obtained for Cr(VI) determination in cements using extraction procedure A. In brackets the relative standard deviations in % are given (n=5)

Type of cements	Cr(VI) concentration in cement obtained for individual samples (µg/g)						Average Cr(VI) content in cement (µg/g)
	sample I	sample II	sample III	sample IV	sample V	sample VI	
CEMENT a	33.2 (4.7)	36.2 (3.8)	35.3 (2.6)	36.1 (3.5)	34.7 (5.1)	33.8 (4.3)	34.9 ± 1.7
CEMENT b	28.8 (5.2)	27.5 (4.6)	26.7 (3.7)	29.1 (3.3)	29.0 (4.8)	27.7 (5.2)	28.1 ± 1.4
CEMENT c	41.7 (4.4)	40.8 (4.1)	40.1 (3.2)	40.3 (2.8)	39.5 (3.9)	38.8 (4.4)	40.4 ± 1.5

Table 2. The results obtained for Cr(VI) determination in cements using extraction procedure B. In brackets the relative standard deviations in % are given (n=5)

Type of cements	Cr(VI) concentration in cement obtained for individual samples ($\mu\text{g/g}$)						Average Cr(VI) content in cement ($\mu\text{g/g}$)
	sample I	sample II	sample III	sample IV	sample V	sample VI	
CEMENT a	33.5 (3.8)	35.5 (3.7)	35.8 (4.2)	35.2 (2.9)	34.0 (5.0)	33.4 (4.4)	34.6 ± 1.2
CEMENT b	30.6 (3.3)	31.3 (4.1)	28.4 (3.9)	30.1 (4.6)	32.0 (4.0)	29.3 (5.0)	30.3 ± 1.9
CEMENT c	40.1 (4.5)	38.5 (4.8)	39.2 (4.7)	38.1 (3.8)	38.7 (4.6)	39.9 (2.9)	39.1 ± 1.0

Table 3. The results obtained for Cr(VI) determination in cements using extraction procedure C. In brackets the relative standard deviations in % are given (n=5)

Type of cements	Cr(VI) concentration in cement obtained for individual samples ($\mu\text{g/g}$)						Average Cr(VI) content in cement ($\mu\text{g/g}$)
	sample I	sample II	sample III	sample IV	sample V	sample VI	
CEMENT a	1.55 (5.2)	1.72 (4.6)	1.63 (4.9)	1.70 (5.3)	1.67 (3.5)	1.61 (4.8)	1.65 ± 0.10
CEMENT b	1.04 (5.1)	1.22 (4.3)	1.20 (4.9)	1.17 (5.7)	1.15 (4.9)	1.10 (5.2)	1.15 ± 0.11
CEMENT c	1.77 (6.0)	1.82 (4.4)	1.75 (5.8)	1.88 (5.5)	1.92 (4.3)	1.85 (5.7)	1.83 ± 0.09

3.4. Study of changes in speciation

A very important issue when performing extraction is to ensure that there are no changes in speciation during the process. Therefore, the purpose of our research was to examine whether during the extraction procedure we propose, based on the mixture 0.01 mol dm^{-3} DTPA + 0.2 mol dm^{-3} $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{OH}$ (pH = 8) (extraction procedure A), there are no changes in speciation. We conducted experiments in which we examined whether there was no oxidation of Cr(III) to Cr(VI) or a reduction of Cr(VI) to Cr(III). For this purpose, we carried out additional extractions of all three cements with the addition of Cr(III) as CrCl_3 or Cr(VI) as K_2CrO_4 to the cements. The obtained results are presented in Table 4. As can be seen, the addition of Cr(III) to the extraction mixture did not result in

Table 4. The results obtained for Cr(VI) determination in cements using extraction procedure A with the addition of Cr(III) or Cr(VI) to the extraction mixture. Relative standard deviations in % given in brackets (n=5)

Type of cements	Cr(III) added ($\mu\text{g/g}$)	Cr(VI) added ($\mu\text{g/g}$)	Cr(VI) concentration determined in cement ($\mu\text{g/g}$)
CEMENT a	-	-	34.9 ± 1.7
	100	-	35.4 ± 1.4
	-	100	132.1 ± 4.3
CEMENT b	-	-	28.1 ± 1.4
	100	-	27.1 ± 1.6
	-	100	130.1 ± 4.1
CEMENT c	-	-	40.4 ± 1.5
	100	-	41.8 ± 1.8
	-	100	137.6 ± 5.2

increase of the Cr(VI) value determined in the tested cements. The obtained differences in the values of Cr(VI) determined with or without addition of Cr(III) are insignificant and are in the range of the relative standard deviation. This indicates that during the proposed extraction procedure for the determination of the total Cr(VI) content in cement there is no oxidation of Cr(III) to Cr(VI). In the case of adding Cr(VI) to cement, the determined content of Cr(VI) in cement increased respectively by the value of Cr(VI) added, which means that during the extraction there was no reduction of Cr(VI) to Cr(III). It allows to assume that during the proposed extraction procedure there are no speciation changes.

4. Conclusions

Summarizing the results obtained, the following conclusions can be drawn:

- the extraction procedure based on the mixture 0.01 mol dm^{-3} DTPA + 0.2 mol dm^{-3} $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{OH}$ (pH = 8) and thermostating at $40 \text{ }^\circ\text{C}$ for 10 min. is suitable for the determination of Cr(VI) in cements;
- the extract is in an easy-to-analyze form;
- DTPA present in the extraction mixture simultaneously ensures selectivity during voltammetric Cr(VI) determination;
- no speciation changes occur during extraction;
- the procedure is simple and quick to carry out.

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