Pergamon

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Cement and Concrete Research 33 (2003) 1589–1593

CEMENT AND CONCRETE RESEARCH

Determination of hexavalent chromium in South African cements and cement-related materials with electrothermal atomic absorption spectrometry

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Received 2 July 2002; accepted 31 March 2003

Abstract

The selective extraction of Cr(VI) in a cement matrix, based on treatment with 0.1 M Na_2CO_3 solution and subsequent determination of chromium by electrothermal atomic absorption spectrometry has been proposed. The proposed method has been applied to South African cement clinkers, natural gypsum, limestone and certified reference materials. The limit of detection of chromium determination in cement samples was found to be 0.14 μg g^{-1}. Between 30% and 80% of the total chromium in South African cement clinkers are Cr(VI) compounds and 8–26% of the total amount of Cr(VI) species is water soluble. The analytical performance of the proposed method has been verified by the analysis of BCS-CRM, a sulphate-resisting Portland cement, and the results obtained were in good agreement with the certified values.

Keywords: Chromium; Cr(VI) extraction; Toxic metal; Cement; Materials

1. Introduction

A great concern in the cement industry is exposure to cement on building and construction sites and during the manufacturing of cement. Skin contact with cement is considered the most common cause of chromium dermatitis [1]. Significant financial implications due to a loss in man-hours because of occupational dermatitis, were reported in the Netherlands [2]. After a study carried out in Copenhagen, Denmark, in 1981 by Avnstorp [3], it was established that workers engaged in the manufacturing of prefabricated concrete building components had the highest prevalence of chromate sensitization (10.5%) and hand eczema (11.9%). Various sources could add chromium to cements, such as the raw materials, refractory bricks lining the kiln, mineral admixtures or the grinding media (normally high-chromium white cast iron) in the final finishing mills. Another concern is the potential leaching of Cr(VI) from cement in the application of cement as part of concrete structures, such as water reservoirs and transport pipes, which can lead to the contamination of drinking water. Although legislation was passed in 1983 in Denmark, stating that the water-soluble chromium content in cement should not exceed 2 mg kg^{-1} [4], no such control measures have been taken in South Africa.

A major problem is however the lack of a reliable analytical method to extract or leach the Cr(VI) species successfully from the solid cementitious matrix, without affecting the dynamic character of the ion. Most publications connected with chromium speciation in environmental samples, are dealing with liquid samples, like natural and waste waters [5], while selective determinations of chromium species in solid samples have not been well described [6]. Determination of the water-soluble fraction of Cr(VI) measured in Swedish [7] and Australian cements [8] are reported to be very low (ranging from 0.2 to 20 mg kg^{-1}). The same procedure applied for the determination of total chromium and water-soluble chromium contents in commercial cements of Spain [9] reported results of 0.9–24 mg kg^{-1} and probably reflects only a fraction of the total Cr(VI) content.

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doi:10.1016/S0008-8846(03)00132-7

The objective of this work was to develop a method to determine the total Cr(VI) in cement and cement-related materials, with the particular aim of ensuring that no changes take place in the original state of chromium, owing to the sample preparation procedure. The extraction of Cr(VI) compounds with Na_2CO_3 in combination with $NaHCO_3$ has been successfully used for the elution of Cr(VI) species from anion-exchanged resin in a liquid matrix [10]. A mixture of Na_2CO_3 and NaOH was used for the leaching of Cr(VI) compounds from steel making solid wastes [11] and soils [12]. This paper describes the successful application of this well-known "classical" wet method of analysis extraction using a Na_2CO_3 solution in a cement matrix. Chromium analysis was done with the use of atomic absorption spectroscopy, since it is not too expensive a technique to apply for routine analyses in factories. The proposed method of Cr(VI) determination was tested on artificial samples with known ratios of Cr(III)/Cr(VI) compounds on raw materials and samples from the cement industry. Several standard reference materials with a known total concentration of chromium were used to verify the results.

2. Experimental

2.1. Analytical method

A Perkin Elmer Atomic Absorption Spectrophotometer model SIMAA 600, equipped with a transversely heated graphite atomizer (THGA) and longitudinal Zeeman-effect background correction system, was used for the measurements. The SIMAA-600 spectrophotometer was equipped with an AS-72 autosampler and the whole system has been controlled by means of AAWinlab control software running under Microsoft Windows programme. The spectrometer was operated in a single element mode, and a Cr hollow cathode lamp (Perkin Elmer), operating at 25 mA, was used for all chromium determinations. The determinations were carried out at the 357.9 nm analytical line and with a bandwidth of 0.7 nm. Standard pyrolitically coated graphite tubes with integrated L'vov's platform (Perkin Elmer, part N B050-4033) for the THGA were applied for chromium atomization at the thermal conditions recommended for Cr determination [13]. Argon (Afrox, South Africa) was used as a protective gas throughout.

Standard stock solutions containing 1000 mg l^{-1} Cr(III) and Cr(VI) as $CrCl_3$ and K_2CrO_4, respectively (Merck, Titrisol), were used for the preparation of working standards for each chromium species. All solutions were prepared using ultra-pure water, obtained with Milli-Q water purification system (Millipore), with a resistivity of 18 MΩ. All other chemicals used were of an AnalaR grade and purchased from Merck.

The reference materials used were: BCS-CRM No. 353 Sulphate-Resisting Portland Cement (Bureau of Analysed Samples, Great Britain), CRM GYP-A (gypsum) (NIST, USA) and PACS-2 marine sediments for trace elements (Institute for National Measurement Standards, National Research Council of Canada). These certified reference materials were used to verify the total chromium determinations.

2.2. Method

2.2.1. Method of sample preparation and verification

The samples were prepared by treating the solid cement clinker, limestone and gypsum samples with a 0.1 M Na_2CO_3 solution. The solution was boiled for 10.0 min and the insoluble carbonates, oxides, hydroxides or basic carbonate, including Cr(III), were removed as precipitates by normal gravitational filtration using No. 540 Whatman filter paper. After filtration the solution was analysed by ET-AAS according to the specifications set out above.

The influence of the volume of sodium carbonate added as well as the heating time was investigated by using one of the gypsum samples. Standard Cr(III) and Cr(VI) solutions each containing 330 pg and each with a volume of 25.0 ml were mixed. A chromium determination on both species was done. This solution was used to spike a 0.5-g gypsum sample and 10.0 ml of 0.1 M Na_2CO_3 solution was added before it was heated. The volume of sodium carbonate was varied between 10.0 and 50.0 ml and the heating time alternated between 15 and 30 min. After filtration the final volume of solution was adjusted to 50.0 ml again and the absorption of Cr(VI) was measured. The results are presented in Table 1.

2.2.2. Analysis of samples and standard reference materials

2.2.2.1. Determination of total amount of chromium. Approximately 0.5 g of cement (OPC—ordinary Portland cement), limestone or natural gypsum was measured out accurately into a glass beaker. Each sample was wetted with 1.0 ml of deionized water and 10.0 ml of 6 M HNO_3. Samples were heated until the excess acid evaporated, diluted with 1% HNO_3 and filtrated as described above.

Table 1
Influence of a variation in volume of Na_2CO_3 and heating time on the absorption signal of a gypsum sample

Test no.	Sample mass (g)	V Na_2CO_3 (ml)	Heating time (min)	Absorbance $n=3$	C_{Cr} (μg l^{-1})	C_{Cr} (μg g^{-1})
1	0.4975	25.00	15.00	0.2443	120.3	24.10
2	0.5055	50.00	30.00	0.2511	123.6	24.30
3	0.5057	12.50	15.00	0.2328	114.6	22.70
4	0.5071	12.50	30.00	0.2392	117.8	23.30
5	0.5031	10.00	15.00	0.2452	120.7	23.80
6	0.5031	10.00	30.00	0.2372	116.8	23.30
Mean						23.58 ± 0.59

Table 2

Summary of the results obtained for total chromium and Cr(VI) ($\mu g\ g^{-1}$) determinations with different digestion methods

Sample	Total Cr C ($\mu g\ g^{-1}$) HNO_3 digestion	Total Cr C ($\mu g\ g^{-1}$) HNO_3 and Na_2CO_3 digestion	Cr(VI) C ($\mu g\ g^{-1}$) Na_2CO_3 extraction	Cr(VI) C ($\mu g\ g^{-1}$) H_2O extraction	Cr(VI)/Cr_T (%)	
					Na_2CO_3 extraction	H_2O extraction
Limestone						
1	12.1 ± 0.80	13.6 ± 0.9	< DL	< DL	nd	–
2	29.8 ± 2.20	34.4 ± 2.3	0.26 ± 0.10	< DL	0.81	–
3	154 ± 6.00	157 ± 5.6	1.09 ± 0.02	< DL	0.71	–
4	7.30 ± 0.30	6.70 ± 0.3	< DL	< DL	nd	–
5	33.8 ± 1.30	35.4 ± 1.6	0.16 ± 0.06	< DL	0.50	–
6	72.8 ± 3.60	67.2 ± 4.4	1.36 ± 0.12	< DL	2.0	–
Clinker						
1	165 ± 9.00	144 ± 10.0	124 ± 6.2	10.2 ± 0.9	80.6	8.0
2	179 ± 8.60	186 ± 7.3	69.2 ± 3.1	18.1 ± 2.8	37.3	26.0
3	94.5 ± 5.30	84.0 ± 6.6	66.6 ± 3.1	9.72 ± 0.7	79.7	14.6
4	124 ± 6.50	126 ± 5.5	34.3 ± 1.1		27.5	nd
5	93.0 ± 4.80	96.5 ± 3.0	48.6 ± 2.1	4.72 ± 1.3	51.2	9.6
6	108 ± 8.30	124 ± 10.0	39.7 ± 2.2	5.4 ± 1.7	34.0	13.6
Gypsum						
1	1.20 ± 0.21	1.27 ± 0.06	0.23 ± 0.21	2.31 ± 1.0		
CRM						
Cement	101 ± 6.6	102 ± 8.3	95.5 ± 2.3	26.6 ± 3.1	94.9	26.4
Gypsum	0.66 ± 0.10	0.69 ± 0.10				
Sediment	92.6 ± 3.8	–	–	–		

The final volume was adjusted to 100.0 ml with deionized water. The results are given in Table 2.

For the determination of total chromium in the gypsum samples about 0.5 g of the natural gypsum sample was accurately measured and boiled with 20.0 ml of 0.1 M Na_2CO_3 solution. After cooling, the sample was completely dissolved in 20.0 ml of a 6 M HNO_3 solution. This procedure was also used to determine the total chromium content in cement samples, as an alternative way of total chromium determination via the acid digestion procedure. For this determination a 0.2-g cement sample was treated with 10.0 ml of 0.1 M Na_2CO_3 solution. After filtration, the wet filter paper was placed in 10.0 ml of 6 M HNO_3 solution. The final results are given in Table 2.

2.2.2.2. Determination of water-soluble Cr(VI). Approximately 0.2 g of cement (OPC), limestone or natural gypsum was accurately measured and added to 25.0 ml of deionized water. The samples were boiled for 10 min, cooled, treated for 2 min in an ultrasonic bath and filtered. The final volume of the solution was adjusted to 100.0 ml with deionized water. The final results are given in Table 2.

2.2.2.3. Determination of the total Cr(VI) content. About 0.2 g of cement (OPC), limestone or natural gypsum was accurately measured and treated with 10.0 ml of a 0.1 M Na_2CO_3 solution. The samples were boiled for 10 min, cooled, treated for 2 min in an ultrasonic bath and filtered. The final volume of the solution was adjusted to 100.0 ml with deionized water. The results are presented in Table 2. The heating period was varied between 10 and 30 min to test for complete Cr(VI) dissolution.

3. Results and discussions

The detection limit (DL) of Cr(VI) determination has been established using a blank solution of 0.1 M Na_2CO_3, which were analyzed together with standards and samples. Calculated according to the equation: $DL = X_{bl} + 3\ S_{bl}$ out of 25 measurements, the value of the DL was found to be 0.7 $\mu g\ L^{-1}$ for a 20 μl of sample solution. This value of DL is comparable to the values reported earlier [11,14]. With respect to the cement samples, assuming that 0.5 g of cement after digestion has been adjusted to the volume of 100.0 ml, the DL of Cr(VI) determination was estimated as 0.14 $\mu g\ g^{-1}$.

The calibration graph for both Cr(III) and Cr(VI) is linear up to 100 ng ml^{-1} and is described by the equation: $y = 0.006x + 0.0025$ for Cr(III) and $y = 0.0061x + 6 \times 10^{-5}$ for Cr(VI), where x is the analyte concentration and y is the integrated absorbance, with a correlation coefficient (R^2) of .9996 and .9985, respectively. These results were in agreement with that found by Chakraborty et al. [14] for chromium species atomized off a graphite furnace. From the results it is evident that both oxidation species can be used for calibration purposes. In practice, all the results were based upon a direct comparison with the aqueous Cr(III) standard solution.

3.1. Leaching procedure and verification for Cr(VI) determination

The use of the solution of Na_2CO_3 has been carefully studied in order to ensure that no change in the original oxidation state of chromium in cement samples occur during the pretreatment. A study of the pretreatment of the samples, using mixtures that were spiked with equal quantities of Cr(III) and Cr(VI), was investigated. The absorption data, presented in Table 3, indicate that the treatment of cement with 0.1 M Na_2CO_3 allows separating both species of chromium, previously added to the sample in a proportion of 1:1. Calculating from the results, it was found that from the 33 μg g^{-1} of total chromium added, 32.7 μg g^{-1} was recovered and from the 16.5 μg g^{-1} of Cr(VI) added 16.8 μg g^{-1} was recovered. From the percentage recovery calculated (99.1% and 101.8%, respectively) it is evident that the leaching procedure is quantitative in terms of absorption signals. Furthermore, the results indicate that the absorption signals for the same sample mass were independent of the volume of sodium carbonate as well as the heating time, as is indicated in Table 1.

The concern that at high pH values (pH above 12) some of the Cr(III) compound can be dissolved as negatively charged $Cr(OH)^{4-}$ complex ions seems to be reasonable according to Coedo et al. [11]. Special investigations by Rai et al. [15], showed that the actual solubility of $Cr(OH)_3$ at high pH values remains constant and that the possibility of $Cr(OH)^{4-}$ formation was overestimated. The stability of Cr(VI) in an alkaline solution with chromium concentrations from 1 to 50 μg l^{-1} stored for at least two months was verified by the repeated analysis of solutions.

3.2. Analytical results of chromium determination

3.2.1. Total chromium determination

The results in Table 2 represent the total chromium concentration of different types of limestone samples from different geological regions in the country. Limestone 1,4 and 5 are primary deposits from the southern part of the country. Limestones 2 and 6 are primary deposits from the northern part of the country, while limestone 3 is a secondary limestone originating also from the northern part of the country. It is seen that the total chromium concentration of the limestone, originating from the southern part of the country, was in general lower than those originating from the northern part of the country. Furthermore, the secondary limestone has a much higher total chromium concentration than any of the primary deposits. The gypsum had very little chromium (1.2 μg g^{-1}). The total chromium in the limestone originating from different deposits was in general much lower than in the cement clinkers (ranging from 7.2 to 157.1 μg g^{-1} for limestone and 83.1–179.1 μg g^{-1} for clinker). These results indicate that the raw materials are not the only source of chromium in cement and that the manufacturing process makes a significant contribution. The contamination is probably due to the refractory bricks that lines the kiln, the grinding media (normally high-chromium white cast iron) in the final finishing mills and/or the use of chromium containing fuels, such as tannery wastes.

Table 3
Recovery of Cr(VI) from a 1:1 Cr(VI) / Cr(III) mixture added to artificial gypsum

	Cr(VI) + Cr(III)	Cr(VI)
Average integrated absorbance	0.1060	0.2058
Concentration calculated (μg g^{-1})	32.7	16.8
Concentration spiked (μg g^{-1})	33.0	16.5
% Recovery	99.1	102

From the results, it is also clear that the obtained values are in close proximity to the certified values. That is, 135 μg g^{-1} certified for the cement sample versus 100.6 μg g^{-1} found, 0.7 ± 0.2 μg g^{-1} for the gypsum standard versus 0.66 ± 0.10 μg g^{-1} found and 90.7 ± 4.6 μg g^{-1} for the sediment standard versus 92.6 ± 3.8 μg g^{-1} found.

The results for the sodium carbonate dissolution presented in Table 2 indicate that the results are similar to those obtained with the acid dissolution. The correlation between the two methods for cement clinkers is illustrated by the paired *t* test, whereby $t_{0.95} = 0.45$, for $n = 12$ and $t_{table} = 2.18$. The results obtained for the gypsum sample using the sodium carbonate leaching procedure is in good agreement with the certified value (0.66 ± 0.10 μg g^{-1} found and 0.7 ± 0.2 μg g^{-1} certified).

3.2.2. Determination of total Cr(VI)

The results obtained for the sodium carbonate dissolution method presented in Table 2 indicate that the amount of Cr(VI) in the raw materials, limestone and gypsum was very low and mostly below the detection limit (0.14 μg g^{-1}). On the other hand, the amount of Cr(VI) in the cement clinker was at measurable levels and significantly higher (ranging from 34.3 to 124.5 μg g^{-1}). These results substantiate the observation made with the total chromium determinations, which the presence of Cr(VI) and (III) in cement clinker is mainly due to contamination that occurs during the manufacturing process.

The results obtained for the water leaching method, as reported in Table 2, showed that the water-soluble Cr(VI) values were markedly less than those obtained with the sodium carbonate leaching method. The results showed that between 30% and 80% of the total chromium content of cement clinker existed in the form of Cr(VI). These findings are in agreement with previous studies done by Lee et al. [16], in which it was indicated that the chromium in Portland cement are mostly in the chromate form.

4. Conclusions

The extraction of Cr(VI) with a sodium carbonate solution can be successfully applied in a cement matrix. Furthermore, the data obtained with the water leaching procedure, are only representative of a small portion of the total Cr(VI) present in South African cement clinkers and only about 15% of the total Cr(VI) species is water soluble. The general perception that exists amongst cement chemists, that all the Cr(VI) in cement and cement-related materials is water soluble, has been proven suspect.

The method of sodium carbonate leaching results in a very basic environment and simulates the pH range that normally prevails during the hydration process of cement. Therefore, the much higher values obtained for the Cr(VI) in this basic environment illustrate more realistically the potentially hazardous environment created by the cement manufacturers and users, for their workers.

Cement clinkers contain significantly more total chromium and Cr(VI) than limestone and gypsum and chromium in natural samples of limestone and gypsum mostly exists as Cr(III). The majority of Cr(VI) present in cement clinkers seem to originate from production processes.

Acknowledgements

The Technikon Pretoria and the NRF (National Research Foundation) are gratefully acknowledged for supplying financial assistance.

References

[1] D. Burrows, R.M. Adams, Metals, in: R.M. Adams (Ed.), Occupation Skin Disease, WB Saunders, Philadelphia, PA, 1990, p. 349.

[2] P.J. Coenraads, Prevalence of hand eczema. Association with occupational exposure, especially in construction workers, Thesis, Groningen, The Netherlands: University of Groningen, 1983, pp. 70–84B.

[3] C. Avnstorp, Risk factors for cement eczema, Contact Dermatitis 25 (1991) 81–88.

[4] C. Avnstorp, Prevalence of cement eczema in Denmark before and since addition of ferrous sulphate to Danish cement, Acta Derm.-Venereol. 69 (1989) 151–155.

[5] M.J. Marques, A. Salvador, A. Morales-Rubio, M. de la Guardia, Chromium speciation in liquid matrixes: a survey of the literature, Fresenius' J. Anal. Chem. 367 (2000) 601–613.

[6] M.J. Marques, A. Salvador, A. Morales-Rubio, M. de la Guardia, Analytical methodologies for chromium speciation in solid matrixes: a survey of literature, Fresenius' J. Anal. Chem. 362 (1998) 239–248.

[7] J.E. Wahlberg, G. Lindesedt, O. Einarsson, Chromium, cobolt and nickel in Swedish cement, detergent, mould and cutting oils, Berufs-Dermatosen 25 (1977) 220–228.

[8] R. Tandon, B. Aarts, Chromium, nickel and cobalt contents of some Australian cements, Contact Dermatits 28 (1993) 201–205.

[9] M. Frias, M.I. Sanchez Rojas, Determination and quantification of total chromium and water soluble chromium contents in commercial cements, Cem. Concr. Res. 25 (1995) 433–439.

[10] H. de Beer, P.P. Coetzee, Chromium (III)/chromium (VI) speciation analysis by ion chromatographic separation and direct atomic absorption spectrometric detection, S.-Afr. Tydskr. Chem. 41 (4) (1988) 152–156.

[11] A.G. Coedo, T. Dorado, I. Padilla, F.J. Alguacil, Speciation of chromium in steelmaking solid wastes by selective retention on ion-exchange media and determination by isotope dilution inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom. 15 (2000) 1564–1568.

[12] B.R. James, J.C. Petura, R.J. Vitale, R. Mussoline, Hexavalent chromium extraction from soils: a comparison of five methods, Environ. Sci. Technol. 29 (1995) 2377–2381.

[13] The THGA Graphite Furnace: Techniques and Recommended Conditions, Bodenseewerk Perkin-Elmer, Germany, 1995.

[14] R. Chakraborty, A.K. Das, M.L. Cervera, M. de la Guardia, Determination of chromium by electrothermal atomic absorption spectrometry after rapid microwave-assisted digestion of sediments and botanical samples, J. Anal. At. Spectrom. 10 (1995) 353–358.

[15] D. Rai, B.M. Sass, D.A. Moore, Chromium (III) hydrolysis constants and solubility of chromium (III) hydroxide, Inorg. Chem. 26 (1987) 345–349.

[16] J.F. Lee, S. Bait, S.B. Clark, G.M. Lamble, C.A. Langton, L. Oji, Chromium speciation in hazardous, cement-based waste forms, Phys., B 208–209 (1995) 577–578.