Pergamon

Cement and Concrete Research 32 (2002) 435–440

CEMENT AND CONCRETE RESEARCH

Total and soluble chromium, nickel and cobalt content in the main materials used in the manufacturing of Spanish commercial cements

Moisés Frías*, M. Isabel Sánchez de Rojas

Eduardo Torroja Institute (CSIC), c/ Serrano Galvache s/n, 28033 Madrid, Spain

Received 18 April 2001; accepted 1 October 2001

Abstract

One of the problems that some industries, and more specifically cement industries, still have to deal with is the requirement to determine and control the content of some chromium, nickel and cobalt compounds due to their allergenic effects on human health (mainly cement dermatitis). This paper focuses on the quantification of total and soluble chromium, nickel and cobalt content in different materials used normally in the manufacturing of Spanish commercial cements (limestone, clay minerals, raws and clinkers). These materials belong to three different cement factories, which could be representative of Spanish Portland cements. This study is a follow-up of a previous research carried out by the same authors, which provides a valuable contribution to establish possible limitations of these allergenic compounds in future national as well as international standards.

Keywords: Toxic elements; Chromium; Nickel; Cobalt; Cement dermatitis

1. Introduction

The cement manufacturing sector has been always concerned in problems related to the environment, specially those related with the avoidance of gas and dust emissions during the manufacture of cements, because of their harmful effect on plants and animals [1,2].

However, very little has been done concerning measurement and control of harmful trace elements. Currently, this subject is being debated in international forums in order to acknowledge the importance and evaluate the repercussion affecting the cement industry.

Therefore, researchers are engaged in two main research lines: on one hand, to find how the presence of high amounts of some heavy elements (such as Pb, Zn, etc.) affects the formation of clinker, the hydration and the performance of mortars and concretes [3–6] and, on the other hand, to deepen on the influence that some heavy elements have on human health, which is a relevant aspect because of its social repercussions.

Cement dermatitis has been a recurrent problem for many years. It appears as a general irritation of the skin due to the alkaline, abrasive and hygroscopic properties of cement. However, recent studies show that some of these trace elements present in Portland cements could be the cause of allergic contact dermatitis.

Back in the 50s, professionals already recognised that water-soluble chromium was the cause of cement allergy. Total chromium content in cements comes from the starting materials (limestone and clay minerals) used to manufacture cements. This chromate appears in form of Cr (III), which is inert and insoluble, but during the clinkerisation process, the Cr (III) can partly be oxidised to Cr (VI), which is soluble and allergenic.

An important number of medical studies were centred on the harmful effects of Cr (VI) on human health, mainly skin in contact with cement (Fig. 1) [7–10]. Later, Fregert and Rorsman [11] have reported that patients with allergic eczematous contact dermatitis due to metals were often allergic to more than one metal. Since that date until now, this fact has prompted speculation on sensibility of several allergenic metals, especially chromium, nickel and cobalt.

The medical studies carried out until now show the complexity of allergic reaction due to a combination of the Cr, Ni and Co effects. It seems that sensitisation to

* Corresponding author. Tel.: +34-91-302-0440x220; fax: +34-91-302-0700.

E-mail address: mfrias@ietcc.csic.es (M. Frías).

0008-8846/02/$ – see front matter
PII: S0008-8846(01)00701-3

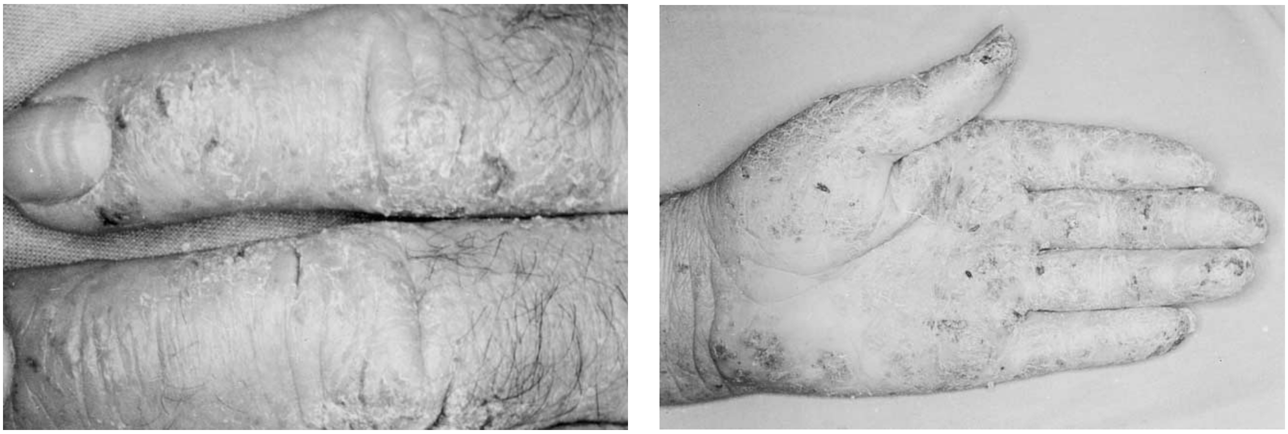

Fig. 1. Two different aspects of construction worker hands with chronic cement dermatitis.

chromate plays an important role in the initial development of allergic contact dermatitis in construction workers, while sensitisation to Ni and Co occur subsequently to chromate sensitivity [10,12]. Professional dermatitis can often become a chronic disease.

Analytical and medical studies found in bibliography state different ways of possible reduction of soluble chromium content in Portland cements: on one hand, the incorporation of ferrous sulfate in order to reduce the water-soluble chromate (Cr^{6+}) to no more than 2 mg/kg. However, right now, even though incorporation of reducing agents raises the prices of cement, it is still the best solution to reduce the Cr^{6+} content in cements. The amount of ferrous sulfate necessary for that effect will vary considerably from cement to cement. So, Tandon and Aarts [13] reported that for a starting cement with 6.20 mg/kg of Cr^{6+}, a 100% reduction was obtained at a stoichiometric ratio of 1:100 of Cr^{6+}/Fe^{2+}.

On the other hand, and from scanty medical works, Eugeniusz [14] reported a limit of 10 mg/kg of Cr^{6+} as a risk of allergic reaction.

From a chemical point of view, the allergenic elements amount (total and soluble) in Portland cements depend on factors such as starting materials, purity, clinkerisation process, nature of steel balls, refractory material used in kiln, cement type, etc. Therefore, on a worldwide scale, an extensive chemical composition can be found for the commercial cements. A typical example can be found in a previous work where Frías and Sánchez de Rojas [15] reported that the total and hexavalent (soluble) chromium content in imported and Spanish Portland cements was between 20 and 110 mg/kg and between 0.9 and 25 mg/kg, respectively. This means that it is not possible to extrapolate results from some cement to another.

The purpose of this paper is to carry out a deep study of total and soluble chromium, nickel and cobalt content in the main materials used in the manufacturing of Portland cements. The materials selected for this study come from three different Spanish factories, which could represent materials normally used to manufacture Spanish Portland cements. Results obtained from this research would be a valuable contribution for the Spanish cement factories as well as forthcoming legal limitations and standardisation.

2. Experimental

2.1. Materials

For this study, different materials related to the manufacture of cement have been tested. Three Spanish commercial clinkers (numbered 1–3) and their starting materials (three limestones (1–3), 3 clay materials (marl 1, slate 2 and clay 3) and three raw materials (1–3) were tested.

2.2. Fineness

A way to express fineness is through the specific surface area of the materials. Different methodologies can be used in order to know this parameter [16]. However, in this paper, Blaine permeability method was used because it is widely employed method to determine the fineness of cements and accepted in standards of most of the European countries, among them Spain [17].

2.3. Extraction test

The method applied in this research corresponds to the one described in the Finnish Standard SFS 5183 [18]. This method consists mainly of the solubilisation of the hexavalent chromium by stirring the samples in water for a predetermined period of time.

Some modifications were introduced in extraction test. For example, samples were stirred vigorously for 60 min instead of 15 min, which is the time recommended in Ref. [18]. Inductively coupled plasma (ICP) was used as analyses technique in order to carry out the quantitative determination of elements. In previous papers, Frías et al. [19] reported that ICP offered greater advantages over the traditional colorimetric method.

3. Results and discussion

3.1. Physical characterisation

Fineness is a physical parameter, which plays an important role in the leaching of the water-soluble metals. It is well known that one of the main factors to study the leaching phenomenon is to know the minimum fineness of materials to avoid a possible interference during extraction tests. The starting point was a previous paper carried out by the same author [19]. They recommended specific area values above 1500 cm^2/g for hexavalent chromium. Beyond this value, the fineness did not have any influence on the quantitative determinations Fig. 2 shows the maximum and minimum value of the specific surface area, obtained from Blaine permeability data. It can be seen here that all samples have fineness above 4000 cm^2/g, except for clinkers, which show an interval between 2000 and 3000 cm^2/g.

3.2. Chemical characterisation of major elements

Table 1 shows the chemical composition of different materials selected in this work, expressed as chemical interval. It is well known that, depending on the nature and purity of materials, the chemical composition can vary substantially from one to another. It is important to note that raw materials show chemical compositions very similar despite its different origin, quality, etc.

3.3. Total and water-soluble contents of allergenic elements

Figs. 3 and 4 and Table 2 present the total and water-soluble chromium, nickel and cobalt contents in mg/kg, corresponding to materials and products from different factories.

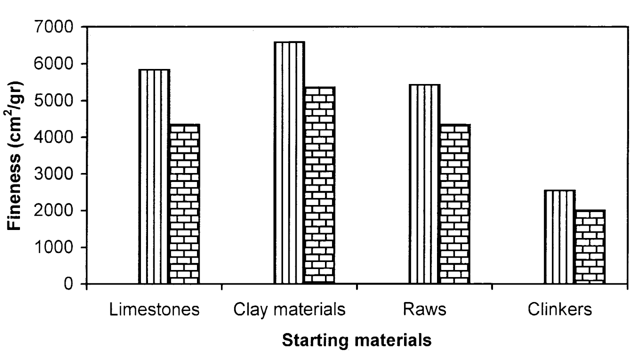

Fig. 2. Fineness interval of materials studied.

Table 1
Chemical composition interval for the materials studied

Oxides (%)	Limestones	Clay materials	Raw	Clinkers
SiO_2	1–12	46 –57	13–14	20–23
Al_2O_3	1–3	10–20	3–4	5–6
Fe_2O_3	0.5–1	4–10	1.5–2.5	3–4
CaO	45–55	1–18	42–44	65–66
MgO	0.5–1.5	1–2.7	0.5–1.5	0.5–1.5
SO_3	0.1–0.3	0.2–0.3	0.1–0.2	0.8–1.8
K_2O	0.1–0.5	2–3.5	0.3–0.8	0.5–1.6
LOI	38 –45	17 –20	34–36	0.1–0.4

3.3.1. Total contents

The results revealed that the total content of allergenic elements vary in function of its origin, purity and nature (Fig. 3), as mentioned above.

3.3.1.1. Chromium. The total chromium contents of the selected materials were between of 0 and 10 mg/kg for the limestones, 60 and 120 mg/kg for clays materials, 15 and 20 mg/kg for the raw materials and 20 and 80 mg/kg for the clinkers.

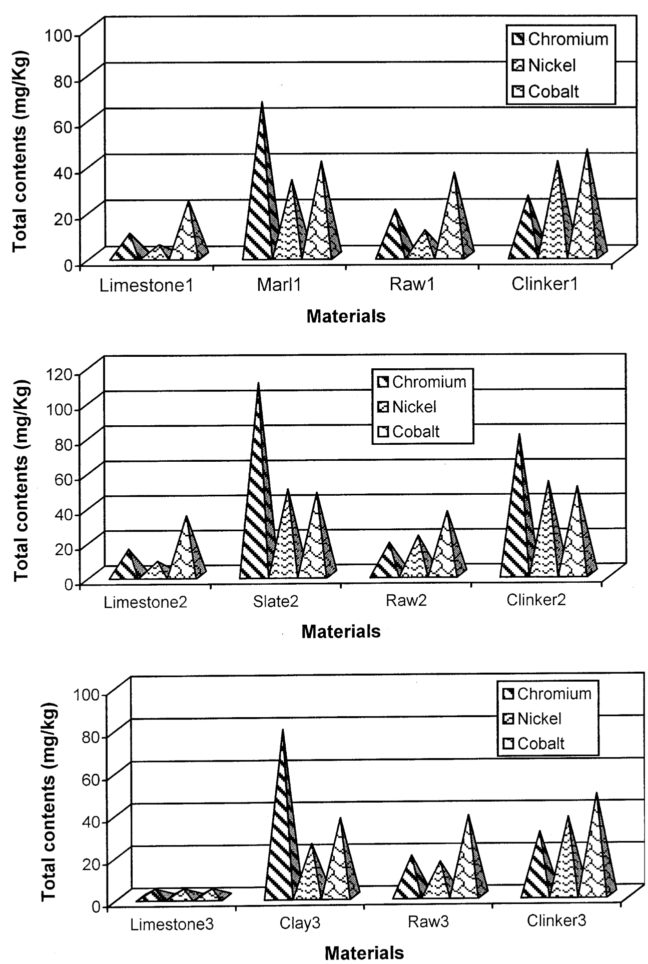

Fig. 3. Total Cr, Ni and Co contents in starting and raw materials.

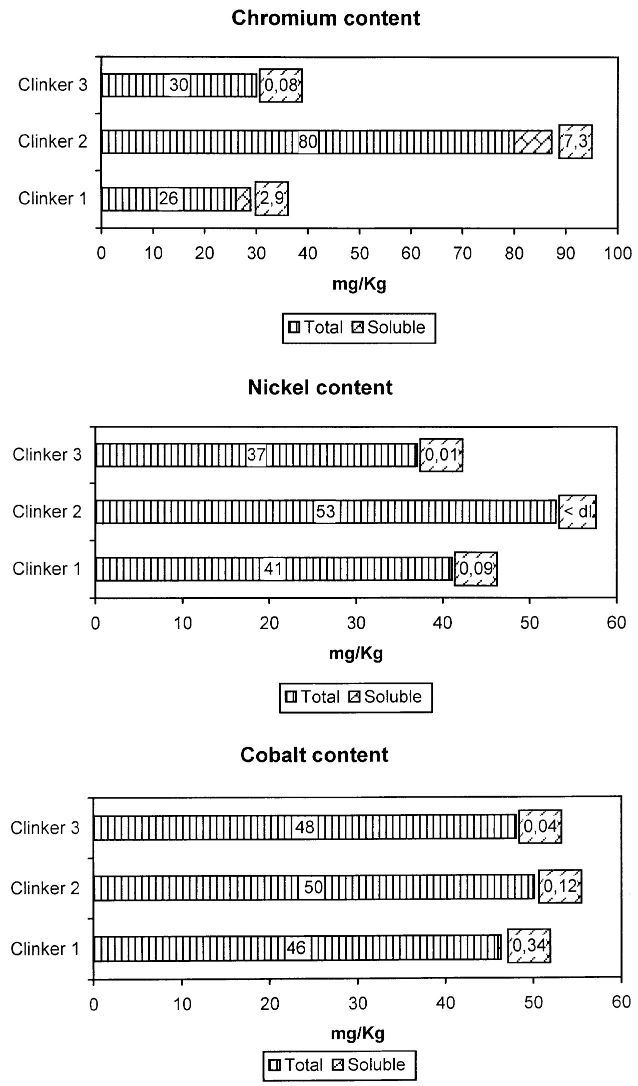

Fig. 4. Total and soluble Cr, Ni and Co contents in three Spanish commercial clinkers.

3.3.1.2. Nickel. Materials selected for this study presented total nickel values below 10 mg/kg for limestones and between 20 and 50 mg/kg for clay minerals. Value for raws and clinkers range between 10 and 25 mg/kg and between 30 and 55 mg/kg, respectively.

3.3.1.3. Cobalt. As for total cobalt contents, limestones showed values between 20 and 35 mg/kg, except for the limestone 3, which showed a lower value (4 mg/kg). Clay minerals showed higher total contents with respect to limestones: between 35 and 50 mg/kg are detected. In raw materials, the total content ranged between 35 and 40 mg/kg. Finally, total contents between 45 and 50 mg/kg were detected in clinkers.

The analytic results revealed (as expected) that chromium, nickel and cobalt elements catalogued as allergens because their repercussions on human health were supplied mainly by clay minerals (marl, slate and clay). However, some limestones can also be materials with an important contribution in cobalt.

A detailed study of the total content showed that values found for raw materials and clinkers are logical with respect to values found for starting materials (limestones and clays). Nevertheless, it is important to note that for raw 3, the total cobalt content was slightly higher than for clay 3. At first sight, it is obvious that this value is not consistent with general idea of raw dosage. Different explanations apply to this fact: (1) An analytical mistake; (2) The incorporation of corrective components. It is well known that in the manufacturing process of Portland cement, the incorporation of corrective compounds is necessary to correct the bulk composition: sands, aluminum oxides (bauxite), iron oxides, iron ore, etc. are normally the compounds used [20]. Some of these compounds could contain significant amounts of minor elements as, for example, cobalt; (3) The clay used in the manufacture of raw 3 did not exactly correspond to clay 3 analysed in this paper.

3.3.2. Water-soluble content

Table 2 represents the water-soluble Cr, Ni and Co contents for starting and raw materials, and Fig. 4 shows total and soluble Cr, Ni and Co contents for clinkers selected.

These analytical results show the wide interval of water-soluble contents.

3.3.2.1. Chromium. The water-soluble chromium content obtained for each one of the materials considered had a wide range of values. As Table 2 shows, insignificant values of soluble chromium (below 0.1 mg/kg) are detected for limestone, clay minerals and raw materials. Clinkers showed higher soluble contents. Values between 0.1 and 7.5 mg/kg were detected (Fig. 4).

These results revealed that in the manufacturing process, the hexavalent chromium content only comes from materials that have undergone an oxidation process and high temperatures. These facts ratify results published in the previous paper [19].

Table 2
Soluble contents of chromium, nickel and cobalt for the starting materials

Materials	Soluble chromium (mg/kg)	Soluble nickel (mg/kg)	Soluble cobalt (mg/kg)
Limestone 1	< dl	< dl	< dl
Marl 1	0.04	0.41	0.12
Raw 1	0.03	0.03	0.1
Limestone 2	0.02	< dl	0.07
Slate 2	0.02	< dl	0.03
Raw 2	0.07	< dl	0.03
Limestone 3	0.09	0.01	0.26
Clay 3	0.02	0.03	0.04
Raw 3	0.03	0.02	0.05

dl = detection limit of ICP.

3.3.2.2. Nickel. Regarding the soluble nickel content in materials studied, the values indicated that nickel compounds are insoluble. So, values of soluble nickel very close to the limit of detection were found (or below), except for marl 1 (Table 2). Clinkers also had very low contents. Values below 0.1 mg/kg were quantified (Fig. 4).

3.3.2.3. Cobalt. Water-soluble cobalt contents indicated a similar behaviour to this of nickel. Insignificant values of soluble cobalt were detected in all starting materials from the three factories. It is important to point out that soluble Co content in raw 3 was only 0.04 mg/kg, while soluble Co content in limestone 3 was 0.26 mg/kg. In clay 3, it was 0.04 mg/kg. This fact could be associated with different factors, as mentioned above. Thus, the same considerations can apply for it.

However, for clinkers (mainly 1 and 2), soluble cobalt contents of 0.34 and 0.12 mg/kg were detected (Fig. 4). This fact would indicate a slight increase of cobalt compound solubility in water after they were submitted to high temperatures (1400 °C) and oxidising conditions during the clinkerisation process.

Considering results obtained, it is possible to state that clinkerisation process affects in different ways the solubility of allergenic elements. For the case of chromium, it is well known that the trivalent form (inert and insoluble) is partially converted to hexavalent form (soluble and allergenic) during kiln processing, when the raw materials are heated to 1400 °C in an oxidising atmosphere. These conditions might have a slight influence on cobalt and none on nickel.

As for allergens studied, it has been impossible to observe a direct relation between total and soluble content in materials used today in the manufacture of commercial cements, mainly in clinkers. According to bibliographical documentation, different factors could be related to the absence of correlation between both contents: nature, solubility of compounds, storage time, leaching test, pH value of leachate, capacity of fixation with hydrated phases of Portland cement (mainly with silicates and aluminates), etc. [21–24]. In another hand, analytical methodology can also play an important role on quantitative determination of elements. In a previous work, Frías et al. [19] reported that the quantification of hexavalent chromium using a colorimetric method had some associated interference in Portland cement matrices due to the presence of agents that reduce or/ and mask the chromium (VI) content.

In spite of different factors directly related to the solubility and concentration of these elements, results obtained in the current work showed that Ni and Co elements were practically insoluble in water and therefore would not have a harmful effect on cement dermatitis. However, Fregert and Gruvberger [12] reported experimental data about the solubility of Ni and Co oxides in different solutions. They demonstrated that Co oxides were partly dissolved by substances present in body fluids such as amino acids. This finding would explain in part the principles of the formation of cobalt complexes and their capacity of eczematous reactions.

For this reason, it would be necessary to have a better understanding of a possible negative effect of these elements on human health, paying also special attention on the solubility of these elements in different media. This fact would be considered an important advance for both cement producers and society for choosing corrective measurements, since right now there is no general recommended limitation for these allergenic elements on cement dermatitis.

4. Conclusions

The following conclusions can be summarised from this experimental work:

1. Total Cr and Ni contents present in clinkers are mainly supplied by clay minerals, while total Co content can come either from clay materials or some limestones.

2. Soluble contents vary substantially in materials under study, depending on the minor element and nature and origin of materials (limestone, clay, raw and main clinker). The highest contents were detected in clinkers. In this case, maximum values of 7.3, 0.09 and 0.34 mg/kg were found for Cr, Ni and Co, respectively. Taking into account the maximum value recommended by Northern European Countries (2 mg/kg Cr^{6+}), two of the three Spanish clinkers had higher contents but values below the limit value (10 mg/kg) considered a risk of allergic reaction by Eugeniusz [14].

3. From the water-soluble contents, clinkerisation conditions (high temperature and oxidising atmosphere) are closely related to the solubility of chromium in water, while solubility of Co is slightly related and not at all for nickel compounds. Variation of conditions during clinkerisation process could be one of the causes of the absence of a linear relation between total and soluble content for Cr, Ni and Co.

4. Water-soluble content/total content ratio was of 7%, 0.06% and 0.33% for Cr, Ni and Co, respectively. Taking into account these percentages, Cr is the main allergen in construction works, followed by Co and then by Ni. From analytical point of view, Ni and Co compounds, due to their insignificant solubility in water, would not show any incidence on cement dermatitis. However, from medical point of view, these elements have an important negative repercussion on allergic reaction. This fact is related to the capacity to elicit eczematous reactions in media different to water. This possibility does not take into account at present.

5. For this reason, at the moment of carrying out some corrective measurements in Portland cements, in order to reduce or eliminate the allergenic effect that Cr, Ni and Co has on cement dermatitis, authors recommend to pay attention to the sum of three allergens and not only for the case of Cr (according to medical works mentioned above, the cement dermatitis takes place by the presence of three allergens elements).

From all results exposed here, exhaustive controls of Cr, Ni and Co contents in Portland cements are necessary because of the scanty knowledge about its contribution to the allergic reaction as well as solubility in different media, mainly in body fluid.

Therefore, this line requires much more experimental research, which would permit a better understanding about possible mechanisms of interaction between allergenic elements and skin and, on the other hand, to know and establish the maximum concentrations of these elements in commercial clinkers (and/or cements) in order to avoid and reduce the cement dermatitis in construction works.

For these reasons, a mere limitation in the water-soluble chromium content would not be enough even though it is fundamental as first step. Possible limitations would also extend to total and soluble Cr, Ni and Co contents.

Acknowledgments

The authors of the current paper want to thank Dr. L. Conde-Salazar from Service of Dermatology of the Spanish National Institute of Medicine and Safety for his information and photographs about cement dermatitis and Artemio Alcañiz for his contribution in experimental tests.

References

[1] W. Hinz, Problems associated with the environmental upgrading of old installations in the cement industry, Zem.-Kalk-Gips 42 (3) (1989) 136–141.
[2] W. Krefta, Environmental protection concepts in the cement industry, Zem.-Kalk-Gips 41 (4) (1988) 193–201.
[3] W. Lieber, The Influence of Lead and Zinc Compounds on the Hydration of Portland Cement, 5th Int. Symp. on the Chemistry of Cement, The Cement Association of Japan, Tokyo, 1968, pp. 444–454.
[4] D. Stephan, H. Maleki, D. Knofel, B. Eber, R. Hardtl, Influence of Cr, Ni and Zn on the properties of pure clinker phases: Part I. C_3S, Cem. Concr. Res. 29 (1999) 545–552.
[5] M. Murat, F. Sorrentino, Effect of large additions of Cd, Pb, Cr, Zn to cement raw meal on the composition and the properties of the clinkers and the cement, Cem. Concr. Res. 26 (3) (1996) 377–385.
[6] J.I. Bhatty, Role of minor elements in cement manufacture and use, Research and Development Bulletin RD 109T, Portland Cement Association, 1990.
[7] L. Conde-Salazar, D. Guimaraens, C. Villegas, A. Romero, M.A. Gonzalez, Occupational allergic contact dermatitis in construction workers, Contact Dermatitis 33 (1995) 226–230.
[8] C. Irvine, C.E. Pugh, E.J. Hansen, R.J. Rycroft, Cement dermatitis in underground workers during construction of the Channel Tunnel, Occup. Med. 44 (1994) 17–23.
[9] S. Fregert, Occupational dermatitis in a 10 year material, Contact Dermatitis 1 (1975) 96–107.
[10] C.L. Goh, S.F. Kwork, S.L. Gan, Cobalt and nickel content of Asian cements, Contact Dermatitis 15 (1986) 169–172.
[11] S. Fregert, H. Rorsman, Allergy to chromium, nickel and cobalt, Acta Derm.-Venereol. 46 (1966) 144–148.
[12] S. Fregert, B. Gruvberger, Solubility of cobalt in cement, Contact Dermatitis 4 (1978) 14–18.
[13] R. Tandon, B. Aarts, Chromium, nickel and cobalt contents of Australian cements, Contact Dermatitis 28 (1993) 201–205.
[14] S. Eugeniusz, Chromium in Portland cement, Cem.-Wapno-Gips 1 (1985) 1–16.
[15] M. Frías, M.I. Sánchez de Rojas, Determination and quantification of total chromium and water soluble chromium contents in commercial cements, Cem. Concr. Res. 25 (2) (1995) 433–439.
[16] M. Frías, M.I. Sánchez de Rojas, N. García, Determination of specific surface area by the laser diffraction technique. Comparison with the Blaine permeability method, Cem. Concr. Res. 21 (5) (1991) 709–717.
[17] Standard UNE 80-106:Métodos de ensayo de cemento. Ensayos físicos, determinación de la finura con el permeabilimétro Blaine, 1986.
[18] Finnish standardisation Organisation, SFS 5183. Determination of water soluble chromium (VI) in cement.
[19] M. Frías, M.I. Sánchez de Rojas, N. García, M.P. Lúxan, Contribution of toxic elements: Hexavalent chromium in materials used in the manufacturing of cement, Cem. Concr. Res. 24 (3) (1994) 533–541.
[20] H.F.W. Taylor, Cement Chemistry 2, Thomas Telford Publishing, Thomas Telford Services, London, 1997 (437 pp.).
[21] S. Wang, C. Vipulanandan, Solidification/stabilisation of Cr (VI) with cement, leachability and XRD analysis, Cem. Concr. Res. 30 (2000) 385–389.
[22] O.E. Omotoso, D.G. Ivey, R. Mikula, Quantitative X-ray diffraction analysis of chromium doped tricalcium silicate pastes, Cem. Concr. Res. 26 (9) (1996) 1369–1379.
[23] I. Moulin, J. Rose, W. Stone, J.Y. Bottero, F. Mosnier, C. Haehnel, Lead, zinc and chromium (III) and (VI) speciation in hydrated cement phases, in: G.R. Woolley, J.J.M. Goumans, P.J. Wainwright (Eds.), International Conference on the Science and Engineering of recycling for environmental protection (WASCON 2000), Harrogate, England, I (2000) pp. 269–280.
[24] J. Bensted, A discussion of the paper determination and quantification of total chromium and water soluble contents in commercial cements, Cem. Concr. Res. 26 (2) (1996) 329–330.