

Study of total chromium and water soluble chromium in Indian cement samples

Rekha sharma¹, Devesh K. Sharma^{1#}, N.K. Katyal²

¹ School of Physical Science, Lovely Professional University, Phagwara (Panjab), India. # devsarita@gmail.com

² Ex Incharge "Analytical Lab Service" National Council for Cement and Building Materials, Ballabgarh (Haryana), India

ABSTRACT

Estimation of water soluble hexavalent chromium and total chromium has been devised. For the complete extraction of water soluble hexavalent chromium, leaching period of five days is done. It was ascertained that complete extraction was achieved in five days; the total chromium determination in these samples was done by fusing sample with sodium carbonate up to 1050°C in muffle furnace. Chromium concentration in these samples is determined with spectrophotometer using a redox indicator (1, 5 diphenylcarbazide). Samples investigated are ordinary Portland cement (OPC), Portland pozzolona cement (PPC), Portland slag cement (PSC) and clinker. The content of water soluble and total chromium in these samples ranged from 12 to 33 ppm and from 684 to 1026 ppm respectively. The accuracy of the method has been checked using a standard reference material of National Institute of Standards & Technology (NIST), USA, and found to be in permissible limits.

Keywords : Detection, chromium, redox speciation, extraction, cement.

1 INTRODUCTION

STUDY of chromium content in cement, soil and water has attracted many investigators due to its adverse effect on the environment as well as on human health. Its toxicity mainly depends on its oxidation state. Hexavalent form of chromium is more toxic, as it is water soluble as compared to its insoluble trivalent form [1]. It is an unavoidable trace element present in the raw materials used for formation of cement clinker [2]. At high temperatures of cement rotary kilns, inert trivalent chromium oxidizes to form reactive hexavalent chromium [3, 4].

Cr(VI) can cause cancer, mutations and skin dermatitis [5, 6, 7]. Contact dermatitis is one of the major problems reported in the workers at construction sites, who worked with cement [8, 9, 10, 11, 12, 13]. Due to its toxicity, it is essential requirement to determine and control the content of water soluble chromate in cement. It must not contain more than 0.0002% or equivalent to 2.0 ppm relative to the mass of cement [14].

Many methods have been adopted for estimating concentration of hexavalent and total chromium in cement samples. These methods involve extraction of water soluble Cr(VI) with deionised water followed by mechanical shaking or magnetic stirrer [15, 16, 17]. In harmonized extraction process, Cr(VI) is leached by mixing CEN standard sand [18]. Cr(VI) is also leached by mixing of some chemicals like acetic acid, hydrochloric acid and sodium carbonate and then detected by spectrophotometer, HPLC-ICP-MS, FPLC-ETAAS and adsorptive stripping voltammetry [19, 20, 21, 22, 23, 24]. Recently the extraction and detection of Cr(VI) is done by activated thin layer - WDXRF spectrometer and MIBK- FAAS method, where the hexavalent chromium get separated from interfering elements like Mn, Fe, and Ca before detection [23, 25]. But the selective extraction with MIBK has a drawback, as it forms gel with leached cement. Extraction of total chromium involves diges-

tion through HNO₃, Na₂CO₃ and Na₂O₂ followed by detection using AAS, ICP-OES, ET-AAS and titration methods [26, 27, 28]. In all the above mentioned methods, there is no method to extract the actual quantity of water soluble Cr (VI) which is present in cement samples and therefore the leaching period is not fixed. Chromium (VI) and (III) can interconvert during chemically treated extraction procedure and this behavior poses problems to extract water soluble Cr (VI) quantitatively from the cement matrices without altering its oxidative state.

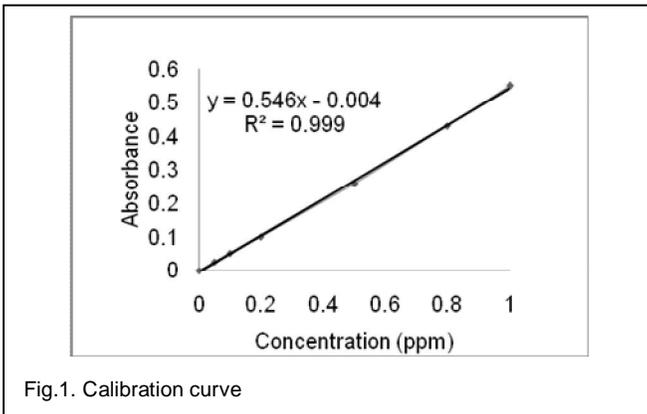
In the present work, we tried to develop a method for extraction of water soluble hexavalent chromium without heating and chemical treatment and the successful application of wet method of analysis for complete extraction of chromium (total chromium) from cement samples. The proposed method of total chromium and water soluble Cr (VI) determination was tested on recognized samples with known ratio of Cr (III) and Cr (VI).

2. EXPERIMENT PROCEDURE

2.1 REAGENTS AND SOLUTIONS PREPARATION

All the reagents and chemicals used in the study are of analytical/G.R. grade. Deionised water was used in all the experiments. 1.0 gram diphenyl carbazide (DPC) is dissolved in 75 mL ethanol. To this was added 5 gram phthalic anhydride and 6 drops of concentrated H₂SO₄ and made up to 100 mL with ethanol. Standard stock solution of 1000 ppm Cr₂O₃ was prepared by dissolving 1.9353 gram of K₂Cr₂O₇ in 1000 mL of distilled water. The reference solution of 10 ppm was made by dilution of stock solution (1000 ppm). Further dilution of 10 ppm solution forms 0.05, 0.1, 0.5, 0.8, 1 ppm reference solutions of appropriate volume. In 10 mL of reference solutions, was added 10 mL H₂SO₄ (1:4), 2.5 mL of 0.25% diphenylcarbazide and solution was made to 100 mL. Calibration curve of chromium reference solution were prepared in the range from

0.05 ppm to 1.0 ppm with reagent blank as initial value. The calibration curve is shown in Figure 1.



Cement samples under study are, ordinary Portland cement (OPC), Portland pozzolona cement (PPC), Portland slag cement (PSC) have been taken from construction site at Delhi and clinker samples from cement manufacturing plant. The main component of cement is clinker in all.

2.2 PREPARATION OF SOLUTIONS AND VERIFICATION

The samples were leached with deionised water for extraction of water soluble Cr (VI). Total chromium was estimated by fusing the samples with sodium carbonate at high temperature and dissolving in deionised water. Chromium content was detected by spectrophotometer [29]. For verification a recovery study was performed with known concentration (50 mg/L) of both chromium species (Cr (VI) and Cr (III)) added to the clinker sample in a proportion of 1:1 in three replicates (Table 1). The influence of the amount of sodium carbonate added as well as the heating temperature was investigated by using one of the clinker samples (Table 2).

	Total chromium	Water soluble Cr (VI)
Initial concentration of clinker sample	1200±15.30	31±3.43
Concentration spiked (mg/l)	1300	131
concentration calculated (mg/l)	1354±14.56	145±8.6
% Recovery	104±2.4	110±3.3

x±s (n = 3), x: average value for three determinations; s, standard deviation.

TABLE 2
INFLUENCE OF A VARIATION IN AMOUNT OF Na₂CO₃

Na ₂ CO ₃ (g)	Concentration (Cr ₂ O ₃ %) at different range of temperature *(n=3)			
	250-500°C	500-750°C	750-1000°C	1000-1250°C
2.00	0.05±0.03	0.08±0.04	0.06±0.04	0.09±0.02
4.00	0.06±0.02	0.07±0.03	0.07±0.03	0.09±0.03
6.00	0.07±0.05	0.07±0.03	0.10±0.05	0.11±0.03
8.00	0.10±0.05	0.11±0.06	0.13±0.03	0.10±0.06
10.00	0.10±0.03	0.10±0.04	0.13±0.02	0.10±0.05

*Heating time (20 min)

2.3 EXTRACTION AND ESTIMATION OF WATER SOLUBLE CHROMIUM

2.0 g cement sample was taken in a 250mL beaker. To this 100 mL distilled water was added. The contents were thoroughly mixed with a glass rod. The beaker was covered with a watch glass. The contents were mixed intermittently after every hour in day time. This process was continued for seven days. The contents were filtered through Whatman42 in a 100 mL volumetric Flask. Washing was done. As the hexavalent chromium is soluble in water, it was found that within a period of 5 days all the chromium gets leached out and comes in the filtrate. There was no further release of chromium is presented in Table 3.

TABLE 3
WATER SOLUBLE Cr (VI) CONCENTRATION (IN PPM) AT DIFFERENT INTERVALS

Time interval	Clinker	OPC/1	OPC/2	PPC	PSC
1st day	14	18	25	11	5
3rd day	16	20	27	13	7
4th day	19	24.5	30	16	8
5th day	20	24	33	20	12
6th day	20.5	23	34	20	11.5
7th day	20	24	32	20.5	11

To the filtrate 2.5 mL of 1, 5 diphenylcarbazine solution was added. 10 mL of sulphuric acid (1:4) was added. Volume was made to 100 mL with distilled water. A pink color was developed due to the presence of chromium. A blank was made using all the reagents except the sample. Optical density (OD) of all the solutions was noted using a HACH Spectrophotometer (Made in USA) at wavelength of 540 mμ. From the OD corresponding concentration in ppm was found from the calibration curve.

2.4 EXTRACTION AND ESTIMATION OF TOTAL CHROMIUM

0.5g sample was taken in a platinum crucible. To this about 6-8g sodium carbonate was added. The contents were thoroughly mixed with a glass rod. The crucible was kept in a Muffle Furnace at ambient temperature. Then temperature was raised to 1050°C. The fusion was carried for 20 minutes. After this the crucible was cooled to room temperature and transferred to a 250 mL beaker. To this about 40 mL of water and 15 mL concentrated sulphuric acid was added. The beaker was heated on a hot plate at low temperature till the mass inside was completely dissolved. The solution was then filtered through Whatman No 42 filter paper in a 100 mL volumetric Flask. Washing was done with hot distilled water. Then 5 mL phosphoric acid (1:3) was added. To this 2.5 mL 1, 5 diphenylcarbazide was added. Then the volume was made to 100 mL. A blank was made adding all the reagents except the sample in exactly same manner as with the sample. OD was noted at 540 mμ using the spectrophotometer.

3.0 RESULTS AND DISCUSSION

The detection limit of proposed method was calculated based on three times the standard deviation of three runs of the blank solution. The detection limits were found 0.5 mg/L and 0.7 mg/L for both water soluble Cr (VI) and total chromium (as Cr (VI)). The calibration graph for Cr₂O₃ is linear and described by the equation $y = 0.546x - 0.004$, where x is the analyte concentration and y is the integrated absorbance. Results showed linearity with a good correlation co-efficient of 0.999.

Standard Reference Material 1886a, Portland cement made by National Institute of Standards & Technology (NIST), USA, was used to check the accuracy of results. The results, presented in Table 4, indicate the reference sample using the sodium carbonate leaching procedure is in good agreement with the certified value (percentage of total chromium as Cr₂O₃ was 0.0026 ± 0.0003 found and 0.0024 ± 0.0008 was certified) and water soluble chromium was found below from permissible limit as per COSHH (Control of Substances Hazardous to Health) regulations [14].

Each type of sample was investigated three times and found to have a good agreement in repeatability and reproducibility for proposed method. It was found that total chromium was recovered as 1354 mg/l from 1300 mg/l containing sample, and 145 mg/l of Cr (VI) was recovered from the 131mg/l containing sample. From the percentage recovery calculated as 104±2.4 (for total chromium) and 110±3.3 (for water soluble Cr (VI)) respectively Table 1.

As a result, Percentage of recovery were found slightly higher which means that the DPC method suffers from the presence of interfering metal species (such as Mo(VI), Cu(II), Fe(III), Hg(II), and V(V)) which can react with DPC

giving positive interference [30, 31]. Therefore need of an alternative for DPC reagent, moreover transformation of Cr (III) into Cr (VI) in alkaline medium within 5 days of maximum leaching process [32].

Total chromium is obtained after the digestion procedure, which ensures the oxidation of all the chromium species present in cement sample. It is also clear that the obtained values are in close proximity to the certified values. The results indicate that the concentration for the same sample mass were dependent of the amount of sodium carbonate as well as the heating temperature, as is indicated in Table 2.

Water-soluble chromium as well as the total chromium concentrations for all these samples is given in Table 4, and a comparison of water soluble chromium and total chromium content in different cement samples is given in Figures 2 and 3 respectively.

TABLE 4
Water soluble and total chromium concentration in cement and clinker

Sample ID	Total Chromium		Water soluble Chromium		Leaching ratio
	Cr ₂ O ₃ (%)	Cr (VI) ppm	Cr ₂ O ₃ (%)	Cr (VI) ppm	Cr (VI)
OPC NIST	0.0026±0.0003	16	0.00016±0.00002	1.09	6.05
OPC /1	0.14±0.03	958	0.0037±0.001	25	2.62
OPC /2	0.15±0.02	1026	0.0048±0.001	33	3.20
PPC	0.14±0.02	958	0.0029±0.001	20	2.07
PSC	0.1±0.02	684	0.0018±0.0004	12	1.80
Clinker	0.13±0.03	889	0.0029±0.0004	20	2.23

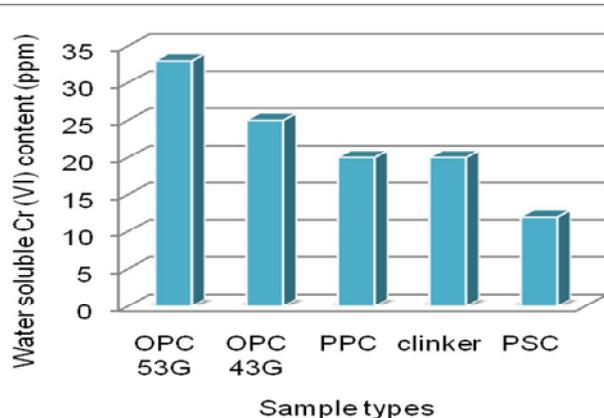


Fig. 2. Water soluble Cr (VI) content

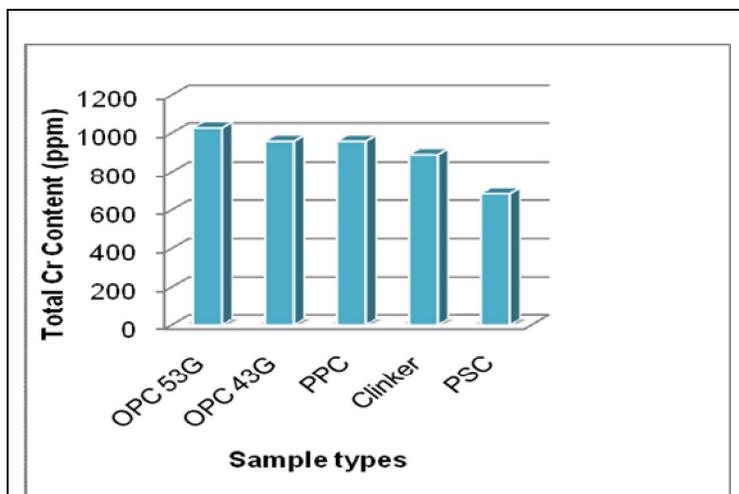


Fig. 3. Total chromium content

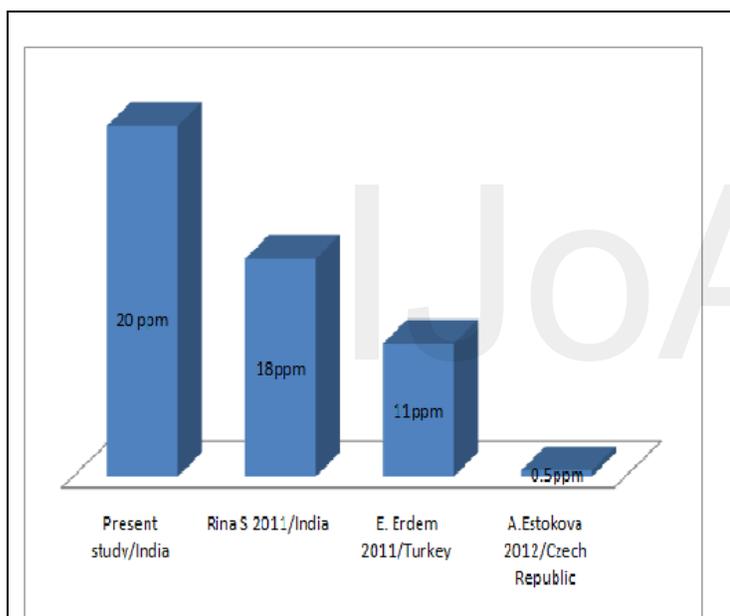


Fig. 4. Water soluble Cr (VI) from different research work

Different concentration of chromium (water soluble and total) is found in different cement samples. Selection of raw material and manufacturing conditions can be the main reason for the above said difference. The main component of cement is clinker. The concentration of chromium varies with % age of clinker and additives.

The water soluble chromium and total chromium in clinker is 20 ppm and 889 ppm respectively. Addition of 5% gypsum in clinker (OPC) and grinding of clinker in chrome alloy increased the chromium concentration [33]. PPC sample is formed by reducing clinker content and adding fly ash. Chromium content of PPC, 20 ppm (water soluble) and 958 ppm (total chromium) is higher than clinker. Fly ash can be one of the reasons for this.

Chromium content is found to be lowest in PSC, amongst the sample studied. In PSC sample, the air-cooled

blast furnace slag powder was used as additive, which is effective in diminishing hexavalent chromium since the replacement of 25% of the Portland cement by blast furnace slag was found to decrease the (OH⁻) of the pore solution, resulting decrease of the Chromium concentration hence giving lower value of water soluble chromium i.e. 12 ppm [34, 35].

The water soluble chromium concentration in Indian samples and samples from Turkey and czech Republic are given in Figure 4. Although the total chromium concentration and water soluble chromium is found to be more as compared to the chromium content reported earlier, but the leaching ratio is comparable. The leaching ratio for PSC cement is 1.80%, which is comparable 1.38% found by A. Estokova et al (2012). Leaching period of five days has also extracted water soluble chromium incorporated in cement [36].

Hexavalent chromium is hazardous to the health of worker at construction site thus European countries has limited the content of hexavalent chromium to 2 ppm, but no such law or legislation is made in India. Thus the estimation of chromium and its reduction is essential for the health of workers. A lot of research is required in this area.

4 CONCLUSION

As a result of the present study, the following conclusions have been drawn:

- Present method indicates the complete (maximum) extraction of water soluble chromium, as compare to short time pre-extraction processes used previously.
- Fusion with sodium carbonate at high temperature ensures the conversion of all chromium (incorporated Cr also) species into water soluble Cr (VI) and hence probably giving the complete total chromium. It may be due to high solubility of sodium chromate formation.
- High concentration of water soluble Cr (VI) in cement and clinker indicate the high content of alkali present in cement, therefore further research should be carried out to confirm a correlation in between chromium and alkalis.
- High concentration of chromium in Indian cement gives an alert to the health of workers; therefore a suitable reagent for its reduction should be enforced in India.
- Looking to the high concentration of chromium in the samples Furthermore research should be carried to confirm chromium content in different brands of cement samples with cement types, collected from different regions of India.

ACKNOWLEDGMENT

The authors wish to thanks Dr. N. K. Katyal (Ex Incharge "Analytical Lab Service" National Council for Cement and Building Materials, Ballabgarh (Haryana), India for providing the facilities for analysis of cement samples.

REFERENCES

- Dayan AD and Paine AJ (2001), "Mechanisms of chromium toxicity, carcino-

- genicity and allergenicity: review of the literature from 1985 to 2000", *Human & Experimental Toxicology*, 20(9), 439-51.
- [2] Estokova A, Palasackova L, Singovszka E and Holub M (2012), "Analysis of chromium concentration in cement materials", *Procedia Engineering*, 42, 146-154.
- [3] Hills L and Johansen VC (2007), "Hexavalent Chromium in Cement Manufacturing: Literature Review", Portland cement Association, Skokie, IL.
- [4] Barros AM, Espinosa DCR and Tenorio JAS (2004), "Effect of Cr₂O₃ and NiO additions on the phase transformations at high temperature in Portland cement", *Cement and Concrete research*, 34, 1795-1801.
- [5] Wetterhahn KE and Hamilton JW (1989), "Molecular basis of hexavalent chromium carcinogenicity", effect on gene expression. *Sci. Total Environ*, 86(1-2), 113.
- [6] Witmer CM, Park HS and Shupack SI (1989), "Mutagenicity and desorption of chromium", *Sci. Total Environ.*, 86(1-2), 131-148.
- [7] Katz SA and Salem H (1994), "The Biological and Environmental Chemistry of Chromium.", *VCH New York*, 97-103.
- [8] Jager H, Pelloni E, (1950), "Tests epicutanes aux bichromates, positifs dans l'eczema au ciment". *Dermatologica* 100: 207
- [9] Halbert AR, Gebauer KA, Wall LM (1992), "Prognosis of occupational chromate dermatitis". *Contact dermatitis* 27, 214- 219.
- [10] NIOH (National Institute of Occupational Health) (2003), "Epidemiological assessment of the occurrence of allergic dermatitis in workers in the construction industry related to the content of Cr(VI) in cement". National Institute of Occupational Health, Oslo, Norway. Unpublished report dated May 2003, sponsored by CEMBUREAU, Chromium allergy in the construction industry an epidemiological review.
- [11] Geier J and Schnuch A (1995), "A comparison of contact allergies among construction and non construction workers attending contact dermatitis clinics in Germany". *Amer J Contact Derm* 6, 86-94.
- [12] Guo YL, Wang BJ, Yeh KC, Wang JC, Kao HH, Wang MT, Shih HC and Chen CJ (1999), "Dramatises in cement workers in Southern Taiwan", *Contact Dermatitis* 40, 1-7.
- [13] Kaufman JD, Cohen MA, Sama SR, Shields JW and Kalat J (1998), "Occupational skin diseases in Washington State, 1989 through 1993, Using workers' compensation data to identify cutaneous hazards", *Am J Public Health* 88, 1047-1051.
- [14] CSTEE (The Scientific Committee on Toxicity, Ecotoxicity and the Environment) (2002), "Risk to Health from Chromium Hexavalent in Cement", CSTEE, Brussels
- [15] FIOSH (Federal Institute for Occupational Safety and Health of Germany) (2002), "Industrial regulations for hazardous materials TRGS-613". Dortmund, Germany.
- [16] Hagedorfer H and Goessler W(2008), "Separation of chromium (III) and chromium (VI) by ion chromatography and an inductively coupled plasma mass spectrometer as element-selective detector", *Talanta* 76 , 656-661.
- [17] Vaity RS, Verma JK (2011), "Portland pozzolana cement in India with respect to total chromium and hexavalent chromium content", *Adv Cem Res* 23(3), 145 -149.
- [18] CEN (European Committee for Standardization) (2006) EN196-10 Methods of testing cement - Part 10: Determination of the water soluble chromium (VI) content of cement, Brussels, 2006.
- [19] Wang S, Vipulanandan C (2000), "Solidification/stabilization of Cr (VI) with cement: Leachability and XRD analyses". *Journal of Cement and Concrete Research* 3(30), 385-389.
- [20] Yamaguchi O, Ida M, Uchiyama Y and Hanehara S (2006), "A method for the determination of total Cr(VI) in cement", *J Eur Ceram Soc* 26, 785-790.
- [21] Potgietera SS, Panichevb N, Potgieterc JH, Panicheva S (2003), "Determination of hexavalent chromium in south African cements and cement-related materials with electrothermal atomic absorption spectrometry", *Cement and concrete research* 33, 1589-1593.
- [22] Trezza MA and Ferraiuolo MF (2003), "Hydration study of limestone blended cement in the presence of hazardous wastes containing Cr(VI)", *Cem Concr Res* 33, 1039-1045
- [23] Janez S, Radmila M, Fabienne S and Donard OFX (2005), "Determination of hexavalent chromium in cement by the use of HPLC-ICP-MS, FPLC-ETAAS, spectrophotometry and selective extraction techniques", *J Anal. At. Spectrom* 20, 871-875.
- [24] R.B. Lokothwayo (2007), "M.Sc Thesis, University of Withwatersrand, Johannesburg (2007)", Available at <http://witsetd.wits.ac.za:8080/dspace/bitstream/123456789/4649/1/Msc%202007%20-%20Chromium%20studies%20-%20final.pdf>.
- [25] Eva M, Claudia fonta S, Marta T, Manel G, Manuela H and Ignacio.Q (2010), "Determination of Water-Soluble Hexavalent Chromium in Clinker Samples by Wavelength-Dispersive X-ray Fluorescence Spectrometry After Concentration in Activated Layers", *Applied Spectroscopy* 64, 547-551.
- [26] Khmiri A and Samet B (2009), "Chromium in cement: development of an analytical method and investigation of contamination sources *Adv Cem Res* 21(1), 39-44.
- [27] Erdem E, Donat R, Esen K and Tunc T (2011), "Removal of soluble Cr (VI) in cements by ferrous sulphate monohydrate, solid lignin and other materials" *Journal Ceramics - Silikaty* 55 (1) 85-93.
- [28] ASTM (1983) C572-81, Standard test Method for Chemical Analysis of Chrome-Containing Refractories and Chrome Ore ASTM International, USA.
- [29] Voinavitch IA, Debras J, Guedon and Iouvier J.(1966), "The Analysis of Silicates. Israel Program", Jerusalem.
- [30] Unceta N, Séby F, Malherbe J and Donard OFX (2010), "Chromium speciation in solid matrices and regulation: a review", *Anal Bioanal Chem* 397: 1097-1111.
- [31] Narayana B and Cherian T (2005) Rapid Spectrophotometric Determination of Trace Amounts of Chromium Using Variamine Blue as a Chromogenic Reagent. *J. Braz. Chem* 16 (2):197-201.
- [32] Eary LE, Rai D (1987) Kinetics of chromium (III) oxidation to chromium(VI) by reaction with manganese dioxide. *Envir Sci Technol* 21: 1187-1193.
- [33] Klemm, Waldemar (1994), "Hexavalent Chromium in Portland cement. Cement", *Concrete and Aggregates* 16 (1), 43-47.
- [34] Morioka M, Nakashima Y, Higuchi T, Takahashi M, Yamamoto K, Sakai E and Daimon M (2003), "Cement Admixture, Cement Composition, and Cement Concrete Made Therefrom", World Intellectual Property Organization, publication number WO/2003/035570, 2003.
- [35] Jeffrey H, Boy, Timothy D, Race, Keturah A, Reinbold, Bukowski J and Xiaofengzhu (1995), "Chromium Stabilization Chemistry of Paint Removal Wastes in Portland Cement and Blast Furnace Slag". *Hazardous Waste and Hazardous Materials* 12: 83.
- [36] Sinyoung S, Songsiriritthigul P, Asavapisit S and Kajitvichyanukul P(2011), "Chromium behavior during cement-production processes", A clinkerization, hydration, and leaching study *Journal of Hazardous Materials* 191: 296-305.