

Hexavalent chromium and some trace metals in concrete from buildings of different ages in northern Italy

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Abstract The content of total hexavalent chromium (Cr(VI)), total chromium (Cr) and other metals (Fe, Mn, Ni and Co) was determined in the cement matrix of concrete present in samples collected in both old and recent buildings located in the town of Modena (northern Italy). The cement matrix of concrete was obtained by eliminating the aggregate components by means of disaggregation and was ground until it could pass through a 63- μm -sieve. In addition, samples of bagged commercial cements were considered. Metal determination was obtained by inductively coupled plasma optical emission spectroscopy after strong acid dissolution (HCl HNO₃). Total Cr(VI) determination was obtained after mild acid attack (HCl) and analysed by UV Vis spectrophotometry. Analytical data values obtained indicate that the highest concentrations of metals were found in concrete and in bagged cement samples characterized by high Fe concentration. High Cr(VI) concentrations both in the cement matrix of concrete and in cement samples were found in total Cr-rich samples. Cr(VI) concentrations were about 20–30% of total Cr. The data obtained indicate that secondary raw materials and industrial by-product powders utilized in the modern cement industry may significantly increase Cr(VI) in concrete.

Keywords Concrete cement matrix · Analytical method · Metals in concretes · Total Cr(VI) in concretes · Total Cr(VI) in cements

Introduction

Cements utilized in the building industry are usually obtained from natural raw materials like limestone, clay and small amounts of other minerals. Cements are utilized to obtain concretes and mortars. This paper considers an upgrade of analytical methods applied to disaggregated concretes and to commercial cements. Fe, Mn, Ni, Co and Cr have been considered due to their similar geochemical behaviour. They are siderophile elements although Cr also has some lithophile characteristics (e.g. Goldschmidt 1962; White 2013). The occurrence of Cr(VI) and of other metals in concrete powders is a matter of concern for environmental agencies and governments. In particular, Cr(VI) and Ni are carcinogenic for humans (IARC 2011; IPCS 2013) and toxic for aquatic organisms (Frey et al. 1983; Riedel 1985; Persoone et al. 1989). Cr(VI), Ni and Co are characterized by a relatively high oxidizing power and easily penetrate cell membranes. They can cause allergic contact dermatitis in individuals having occupational contact with cements (IARC 2006, 2011; IPCS 2013; Kridin et al. 2016). Fe and Mn are potentially toxic (IPCS 2004; Kovalčíková and Eštoková 2014), but at present, there is no particular concern about the role of Fe and Mn on human health in relation to cement production and to concrete utilization although the cement production cycle has been found to be responsible for a series of health diseases chiefly due to cement dust inhalation (Vestbo 1993; Rafeemanesh et al. 2015; Gizaw et al. 2016; Lee et al. 2016; Nordby et al. 2016). European laws on cement

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Table 1 Main characteristics of the concrete examined in the town of Modena

Sample ID	Material	Localization	Age (year)
PE1c	Reinforced concrete	Decommissioned Power Plant Via Peretti, Modena	1925
PE2c	Reinforced concrete	Decommissioned Power Plant Via Peretti, Modena	1925
PE3c	Cement mortar	Decommissioned Power Plant Via Peretti, Modena	1925
PE5c	Reinforced concrete	Decommissioned Power Plant Via Peretti, Modena	1935
SC1c	Reinforced concrete	Decommissioned Steelworks Via Santa Caterina, Modena	1920
SC1 m	Cement mortar	Decommissioned Steelworks Via Santa Caterina, Modena	1920
SC2 m	Cement mortar	Decommissioned steelworks Via Santa Caterina, Modena	1920
SC cas	Concrete	Decommissioned Power Plant Via Santa Caterina, Modena	1920
MR3c	Concrete	Decommissioned Power Plant Via Morandi, Modena	n.a.
MR cas	Concrete	Decommissioned Power Plant Via Morandi, Modena	1940
AR1c	Concrete	Demolished Block of Flats, Via Archimede, Modena	1985

composition limit the hydrosoluble Cr(VI) concentration to a maximum value of 2 mg/kg (implemented in Italy by CEN 2006) to prevent contact dermatitis in cement workers (Klemm 2000), whereas at present, there are no limitations for concentrations of metals like Co and Ni. The occurrence of Cr in cements and cement-based materials like concrete has been attributed to raw materials, to refractory bricks utilized in cement kilns, to grinding media, cement kiln fuels and to possible additive minerals (Hills and Johansen 2007). In particular, most raw materials (clay, limestone, Iron hydroxides) contain Cr(III). Oxidation of Cr(III) contained in raw materials at a temperature of around 1200 °C induces Cr(VI) generation (Hills and Johansen 2007). About 8–20% of total Cr in clinker is converted into Cr(VI) (Lizarraga 2003; Hills and Johansen 2007). In recent years, additive minerals or additional materials coming from industrial waste have been added to cements (VDZ 1996; ATILH 2003; CEMBUREAU 2006). Various analytical methods have been adopted for Cr(VI) determination in cements (e.g. Yamaguchi et al. 2006; Eštoková et al. 2012; Sharma and Sharma 2015). Yamaguchi et al. (2006) showed that a significant fraction of Cr (50–80%) in ordinary Portland cements (OPC) is represented by Cr(VI). Persson and Kucera (1998, 2001), Serclérat et al. (2000) and Eštoková et al. (2016) described Cr(VI) leaching phenomena into water from concrete samples. Normally, a set of metals is analysed in cements.

The aim of this paper was the improvement of an analytical procedure proposed by Yamaguchi et al. (2006) modified to allow analyses to disaggregate concrete as well. The method was utilized for the first time to determine the total Cr(VI) concentration in concrete samples. Fe, Mn, Ni, Co have also been analysed in the same ground concrete samples by means of ICP-OES techniques.

Materials and methods

Sample preparation and analysed materials

Concrete samples were taken from walls and pillars belonging to old industrial decommissioned buildings and to a block of residential flats in the town of Modena (northern Italy) (Table 1). Concrete samples were ground by means of a screw press in order to separate the cement matrix of the concrete from the aggregates. Various particle-size fractions were obtained by calibrated sieves. The powders thus obtained were analysed by X-ray diffraction (XRD) for mineralogical characterization (Fig. 1). The most relevant minerals identified were quartz, albite, chlorite, calcite and dolomite and were related to primary raw materials and aggregate component residual fraction. The finest fraction (<63 µm) was enriched in sulphate, sulphoaluminate minerals and portlandite owing to

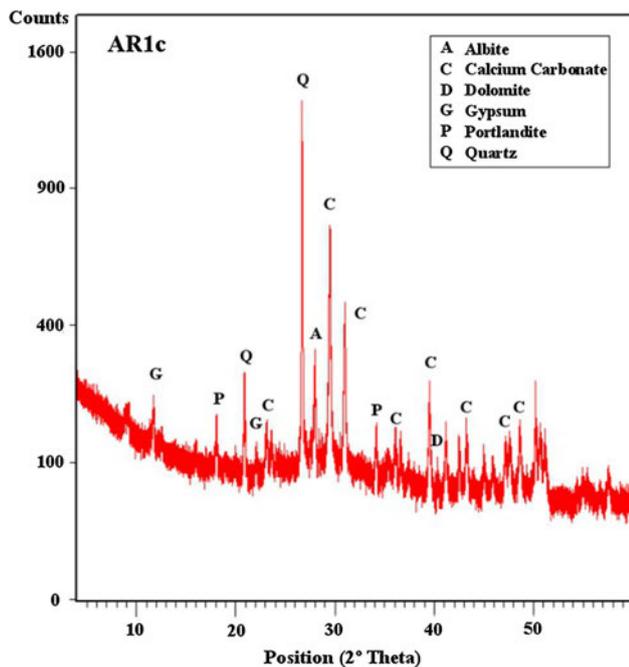


Fig. 1 XRD of the cement matrix concrete sample AR1c. The identified minerals are shown

reactions between cement and water. This fraction (<63 μm) was considered for further chemical analyses. The oldest samples (1925 1940) were representative of concretes obtained from clinker from geological raw

materials. In more recent periods, powders derived from industrial waste and by-products were added to raw materials during the Portland cement clinker process (VDZ 1996; ATILH 2003; CEMBUREAU 2006). The analysis procedure was developed by taking as reference material a Portland cement GTG Italcementi STD. 100/12 free of Cr(VI) reductant (Table 2). Bagged commercial cements, consisting of ordinary Portland cement (OPC), Portland limestone cement (PLC) and Portland pozzolana cement (PPC), were also taken into account (Table 2).

Analytical methods

Total metals determination in commercial cements and in the cement matrix of concrete

The main constituents (Fe and Mn) and total Cr, Ni and Co were determined after strong acid dissolution: 1 g of samples was attacked with 5 ml of aqua regia (HCl:HNO₃ = 3:1) at 80 °C and dried out. The residue was dissolved in HNO₃ 0.2 M and the solution filtered by paper (pore size 100 μm) and made up (25 ml) with deionized water.

Metal concentration in these solutions was then determined by ICP-OES (PerkinElmer Optima™ 4200 DV) after vacuum microfiltration.

The operating conditions used for the emission spectrometer in argon plasma source, model PerkinElmer Optima™ 4200 DV, were:

Table 2 Main characteristics of Italian bagged commercial cements examined

Sample ID	Material	Characteristics
CEM STD	Portland cement	Portland clinker 98% Minor components 2%
CEM I 42,5R	Portland cement	Portland clinker ≥ 95% Minor components 0 5%
CEM II/B P 32,5R	Pozzolana cement	Portland clinker ≥ 65 79% Natural pozzolana 21 35% Minor components 0 5%
CEM II A LL 42,5R	Portland limestone cement	Portland clinker ≥ 65 79% Limestone 21 35% Minor components 0 5%
CEM II B LL 32,5R	Portland limestone cement	Portland clinker ≥ 65 79% Limestone 21 35% Minor components 0 5%
CEM IV/A P 42,5R	Pozzolana cement	Portland clinker ≥ 65 89% Natural pozzolana 11 35% Minor components 0 5% Cement resistant to sulphate attack
CEM IV/A V 32,5R	Pozzolana cement	Portland clinker ≥ 65 89% Fly ash 11 35% Minor components 0 5% Cement resistant to sulphate attack

- (a) power of radio frequency = 1100 W
- (b) Argon pressure = 275 kPa
- (c) reflected radio frequency power <5 W
- (d) cooling Argon flow = 16 l/min
- (e) transportation argon flow to the nebulizer = 0.6 l/min
- (f) auxiliary argon flow = 0.5 l/min
- (g) suction flow = 5 ml/min
- (h) radial plasma torch orientation, i.e. perpendicular to the optics of acquisition

The spectral lines of the elements considered for the ICP measures expressed in nm were:

- (i) λ Fe = 259.939
- (j) λ Mn = 294.920
- (k) λ Co = 236.380
- (l) λ Cr = 284.325
- (m) λ Ni = 231.604

Total hexavalent chromium determination in commercial cements and in the cement matrix of concrete

Cr(VI) has been analysed partly following the method proposed by Yamaguchi et al. (2006). This method involves an acid attack at ambient temperature by HCl 2N (1 g/10 ml) and the determination of Cr(VI) by UV Vis spectrophotometry (PerkinElmer LambdaTM 45 UV/Vis spectrometer) measuring absorbance at 540 nm of solution obtained after the addition of diphenylcarbazide (C₆H₅-NHNH)₂CO. After the initial (60 min) acid attack, the

precipitation of Iron hydroxides and of further interfering metals was obtained by adding 10 ml of NH₄OH (25%) at 60 °C for 2 h and made up (25 ml) with NH₄OH 4N. After 24 h, the solution obtained was filtered by paper (pore size 7 µm) and the clear and colourless solution utilized for Cr(VI) analysis by diphenylcarbazide in acetone standard method (e.g. Clescerl et al. 1999).

Hydrosoluble hexavalent chromium determination in standard reference and in commercial cements

Mortar samples were prepared by mixing 450 g of cement, 1350 g of certified sand (CEN EN 196-10 SNL Société Nouvelle du Littoral) and 225 ml of deionized water (CEN 2006). Twenty millilitres of eluate were obtained by filtering.

Ten millilitres of filtered eluate were added to 40 ml of deionized water and to 10 ml of diphenylcarbazide in acetone (e.g. Clescerl et al. 1999); pH was adjusted in the range 2.1–2.5 by HCl 1.0 mol/l. Calibration solutions were prepared according to CEN 2006. Hydrosoluble Cr(VI) concentrations were determined by UV Vis spectrophotometry (PerkinElmer LambdaTM 45 UV/Vis spectrometer) according to CEN 2006.

Analytical results and comments

Analytical data regarding total metals and total hexavalent chromium concentration are reported in Table 3. Hydrosoluble Cr(VI) data obtained by the present study have been reported in Table 4. In Table 5, repeated measurements

Table 3 Metal concentrations in commercial cements and in concrete cement matrix (in mg/kg Fe% mass)

Sample ID	Fe (%)	Mn (mg/kg)	TOT Cr (mg/kg)	TOT Cr(VI) (mg/kg)	Ni (mg/kg)	Co (mg/kg)
CEM STD	1.6	722.5	50.8	4.4	58.1	65.7
PE1c	1.6	1000.3	74.7	11.8	66.9	106.7
PE2c	1.6	923.2	69.3	10.0	64.7	101.5
PE3m	1.5	637.3	71.5	10.4	65.2	106.8
PE5c	1.6	845.7	48.1	9.4	66.9	107.1
SC1c	1.7	789.6	60.5	8.0	84.2	118.3
SC1m	1.7	1404.9	62.1	10.9	68.7	140.8
SC2m	1.0	488.3	56.3	12.1	52.3	66.7
SC cas	2.2	1511.2	50.5	12.4	68.8	138.1
MR3c	0.4	562.4	27.7	11.1	36.1	45.8
MR cas	1.6	1139.6	86.1	11.1	71.8	111.1
AR1c	1.6	1057.5	46.9	9.2	61.7	111.9
CEM I 42,5R	1.5	752.1	64.8	11.5	84.2	114.8
CEM II/B P 32,5R	1.5	193.4	32.4	9.4	50.2	101.2
CEM II/A LL 42,5R	0.9	567.1	75.4	8.7	81.7	73.8
CEM II/B LL 32,5R	0.2	332.5	37.2	8.0	80.3	47.3
CEM IV/A P 42,5R	0.6	664.8	57.4	10.1	83.8	58.3
CEM IV/A V 32,5R	2.4	751.0	91.3	15.1	79.4	156.2

Table 4 Concentration of hydrosoluble Cr(VI) in six commercial cements and in Portland cement standard (GTG Italcementi STD 100/12) free of Cr(VI) reductant usually utilized as a laboratory standard in Italy (in mg/kg)

Sample ID	HYD Cr(VI) (mg/kg)
GTG Italcementi STD 100/12	4.3
CEM I 42,5R	2.7
CEM II/B P 32,5R	2.2
CEM II/A LL 42,5R	1.3
CEM II/B LL 32,5R	0.6
CEM IV/A P 42,5R	1.3
CEM IV/A V 32,5R	4.4

obtained in the present study and by the certified laboratory of the Environmental Protection Agency of Emilia-Romagna Region (ARPAE) are reported. Those data refer to hydrosoluble Cr(VI) in cement mortar samples (Portland cement GTG Italcementi STD 100/12 free of Cr(VI) reductant usually utilized as a laboratory standard in Italy). The values obtained do not indicate significant differences between the two laboratories. All samples shown in Table 3 were characterized by relatively high metal concentrations. In particular, samples characterized by high Fe concentration were enriched in almost all metals. Total Cr concentration found in concrete samples was in the range 25–90 mg/kg. Total Cr(VI) concentration was in the range 8–15 mg/kg. Similar values were found in bagged cement samples (Table 3). Total Cr(VI) concentrations found in the cement matrix of concrete were slightly lower than the values found by Yamaguchi et al. (2006) in OPC samples. In particular, abundance levels of Fe, Mn and trace elements in cement matrix of concretes and in analysed commercial cements were comparable with data

available in the literature (e.g. VDZ 1996; ATILH 2003; CEMBUREAU 2006; Hills and Johansen 2007). No significant differences were found between the data of commercial cement and that of the cement matrix of concretes. This confirms that the material used for analysis was representative of the cement component of concretes. The concentration of siderophile trace elements (Ni, Co) was relatively high (Table 3) when compared to data relative to common natural raw material (limestones, clays, Iron hydroxides) (Burns et al. 1974a, b). This suggests that some of these metals in cements were derived from other industrial sources, i.e. steel mills during raw material grinding or by possible addition of refractory bricks, etc. (Hills and Johansen 2007). The content of total Cr(VI) found in commercial cements was 0.6–4.4 mg/kg (Table 4). Some of these values were higher than those of hydrosoluble Cr(VI) admitted in Europe for commercial cements (<2 mg/kg according to CEN 2006). The total Cr(VI) both in commercial cements and in concretes was a significant fraction (20–30%) of total Cr and was significantly lower than the values found by Yamaguchi et al. (2006) in Japanese OPC (50–80%). Total Cr and total Cr(VI) concentrations were positively correlated with Fe concentration both in cements and in the cement matrix of concrete (Figs. 2, 3). Furthermore, total Cr(VI) concentration was positively correlated with total Cr concentration of cement matrix of concrete (Fig. 4).

Possible environmental impacts and effects on human health

Hexavalent chromium was mostly bound in mineral phases formed during the hydration process of the cement paste

Table 5 Concentration of hydrosoluble Cr(VI) in standard Portland cement standard (GTG Italcementi STD 100/12) free of Cr(VI) reductant

Present study sample ID	Present study HYD Cr(VI) (mg/kg)	ARPAE sample ID	ARPAE HYD Cr(VI) (mg/kg)
GTG Italcementi STD 100/12 1	4.42	GTG Italcementi STD 100/12 A	4.50
GTG Italcementi STD 100/12 2	4.50	GTG Italcementi STD 100/12 B	4.45
GTG Italcementi STD 100/12 3	4.38	GTG Italcementi STD 100/12 C	4.35
GTG Italcementi STD 100/12 4	4.40	GTG Italcementi STD 100/12 D	4.33
GTG Italcementi STD 100/12 5	4.52	GTG Italcementi STD 100/12 E	4.35
GTG Italcementi STD 100/12 6	4.47	GTG Italcementi STD 100/12 F	4.36

Column on the left refers to data obtained at the Department of Chemistry and Geological Sciences laboratories, University of Modena. Column on the right refers to data obtained at ARPAE laboratories in Reggio Emilia (in mg/kg)

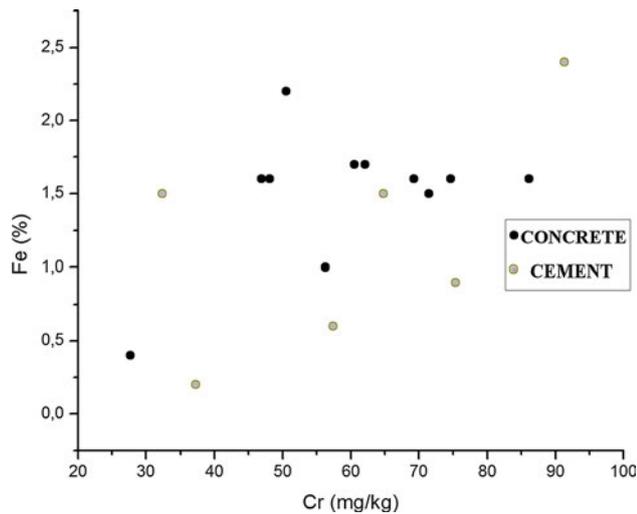


Fig. 2 Relations between Fe and total Cr concentration in commercial cements and in concrete cement matrix

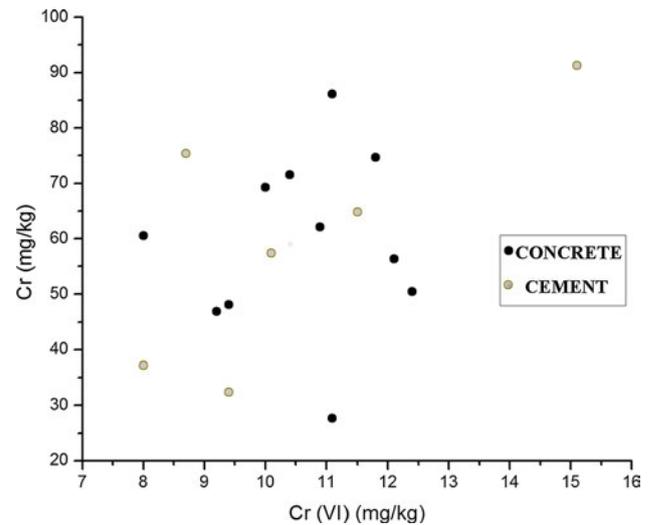


Fig. 4 Relations between total Cr and total Cr(VI) in cements and in concrete cement matrix

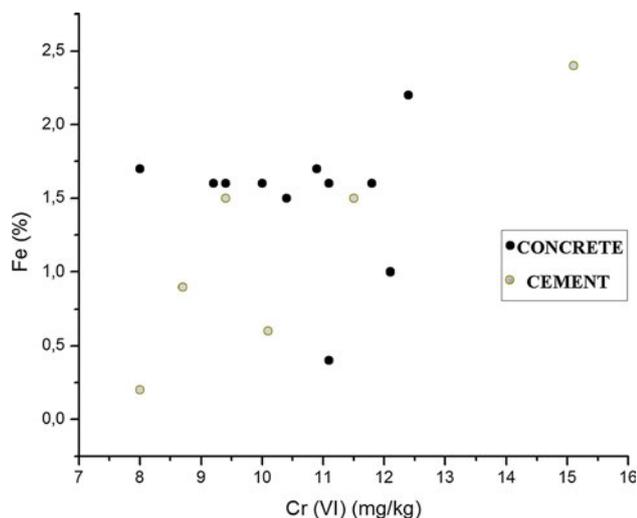


Fig. 3 Relations between Fe and total Cr(VI) concentration in commercial cements and in concrete cement matrix

(calcium sulphoaluminates and calcium silicate hydrates) in the form of chromates mainly in the 10.5–13.5 pH range (Laforest and Duchesne 2005; Peysson et al. 2005; Giergiczny and Król 2008; Leisinger et al. 2014) and consequently immobilized in cement-based materials like concrete. Persson and Kucera (1998) analysed metal concentrations in runoff water from building concrete materials and found hydrosoluble Cr(VI) values in the range 4–28 $\mu\text{g/l}$. Sercl rat et al. (2000) obtained similar values in laboratory experiments on leaching phenomena, while E stokova et al. (2016) obtained higher values in laboratory leaching experiments by utilizing different leaching solutions. A consistent fraction of Cr in concretes analysed in this study was represented by Cr(VI); thus, the possible increase of reaction surfaces in concrete due to possible

grinding, cleavage or to other chemical and physical degradation processes and any subsequent weathering may induce the release of significant amounts of Cr(VI) (about 0.1% of the total Cr concentration in concretes) to aqueous media and possible environmental pollution processes. Further cause for concern might be related to Ni and Co concentrations in cements and in concrete since the present study found Ni concentrations in the range 36–84 mg/kg, while Co concentrations were found in the range 45–156 mg/kg. Ni effects on skin and on the lungs have been studied by Kiilunen (1997), IARC (2011), etc. Furthermore, IARC (2006) etc. described Co effects on human health. Ni, Co and Cr(VI) follow similar biochemical pathways; thus, the skin and lungs could be considered the most vulnerable organs in humans subject to the effects of considered siderophile elements, although only limited amounts of Ni and Co were expected to be found in leachate solutions (e.g. Koval ckova and E stokova 2014). Accidental exposure of humans to cement or concrete dusts should be limited, especially for workers (e.g. Kiilunen 1997).

Conclusions

The analytical method has allowed Cr(VI) and metals (Ni, Co, Fe and Mn) to be determined in the cement matrix of concrete as well as in commercial cements. The data obtained showed that significant concentrations of Cr(VI), about 20–30% of total Cr, were ubiquitously present in concretes and in cements. Possible degradation processes of concrete may induce Cr(VI) release into the environment. The release of significant amounts of metals in general was also expected from concrete debris resulting from demolition wastes. Grinding, cleavage or other

chemical and physical degradation processes of concrete may induce environmental pollution phenomena.

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