

Influence of sample matrix on the alkaline extraction of Cr(VI) in soils and industrial materials

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Abstract An accurate and efficient determination of the highly toxic Cr(VI) in solid materials is important to determine the total Cr(VI) inventory of contaminated sites and the Cr(VI) release potential from such sites into the environment. Most commonly, total Cr(VI) is extracted from solid materials following a hot alkaline extraction procedure (US EPA method 3060A) where a complete release of water-extractable and sparingly soluble Cr(VI) phase is achieved. This work presents an evaluation of matrix effects that may occur during the hot alkaline extraction and in the determination of the total Cr(VI) inventory of variably composed contaminated soils and industrial materials (cement, fly ash) and is compared to water-extractable Cr(VI) results. Method validation including multiple extractions and matrix spiking along with chemical and mineralogical characterization showed satisfying results for total Cr(VI) contents for most of the tested materials. However, unreliable results were obtained by applying method 3060A to anoxic soils due to the degradation of organic material and/or reactions with Fe²⁺-bearing mineral phases. In addition, in certain samples discrepant spike recoveries have to be also attributed to sample heterogeneity. Separation of possible extracted Cr(III) by applying cation-exchange cartridges prior to solution analysis further shows that under the hot alkaline extraction conditions only Cr(VI) is present in solution in

measurable amounts, whereas Cr(III) gets precipitated as amorphous Cr(OH)_{3(am)}. It is concluded that prior to routine application of method 3060A to a new material type, spiking tests are recommended for the identification of matrix effects. In addition, the mass of extracted solid material should to be well adjusted to the heterogeneity of the Cr(VI) distribution in the material in question.

Keywords Cr(VI) · Hot alkaline extraction · Matrix effects · DPC method · Cation-exchange cartridge · Soil · Cement · Fly ash

Introduction

Chromium is a heavy metal of environmental concern at mining sites, industrial sites and waste deposits. Chromium occurs in two stable oxidation states in solid phases and dissolved in groundwater (Adriano 1986; Rai et al. 1989). Whereas Cr(III) is only sparingly soluble, Cr(VI) is easily soluble as oxy-anion (mainly as chromate, CrO₄²⁻), highly toxic and readily bioavailable (Adriano 1986). The presence and concentration of Cr(VI) in effluents of contaminated sites depend on the site-specific processing of Cr compounds. For example, chromic acid (H₂CrO₄) discharged in metal processing activities (Wanner et al. 2012a; Baral and Engelken 2002) may quickly reach the subsoil and groundwater. Similarly, water-soluble dichromate compounds such as sodium dichromate (Na₂Cr₂O₇) and potassium dichromate (K₂Cr₂O₇) are produced during chromite ore processing (Burke et al. 1991; Farmer et al. 1999). This results in a variety of Cr(VI)-bearing mineral phases with different solubilities and dissolution kinetics in the subsurface of contaminated areas. For example, Burke et al. (1991) and Wanner et al. (2012a) report sparingly

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soluble crocoite (PbCrO_4), jarosite [$\text{KFe}_3((\text{SO}_4)_x(\text{CrO}_4)_{1-x})_2(\text{OH})_6$] and chromatite (CaCrO_4) that have formed due to inappropriate handling, poor storage of chromic acid or during chemical manufacturing of chromate. In addition to abandoned industrial sites, present-day sources of Cr(VI) include cement, brick and by-products from municipal solid waste incineration (MSWI fly ash), all produced under oxidising conditions at very high temperatures (e.g. Hills and Johansen 2007; Leisinger et al. 2014). The strong redox control of the Cr system and the kinetically differently reacting secondary mineral phases with different solubilities render the behaviour of Cr(VI) compounds in the environment complex and controlled by the site- and material-specific redox conditions (e.g. Bartlett and James 1979; Christensen et al. 1994; Puls et al. 1999; Flury et al. 2009). This makes the estimation of the various Cr(VI) reservoirs and the assessment of the total Cr(VI) inventory and its release potentially difficult (e.g. Wanner et al. 2012a). The potential of the Cr(VI) release from a contaminated site is often assessed by the amount of Cr(VI) that is extractable with water from the solid material. For example, in Switzerland, threshold values for Cr(VI) concentrations in solid material of contaminated sites and waste deposits are defined by aqueous extraction with deionised water according to the Contaminated Sites Ordinance (CSO test, Swiss Confederation 1998) or the Technical Ordinance on Waste (TOW test, Swiss Confederation 1990, 2013), but no analytical method is prescribed for the determination of the total Cr(VI) inventory in the solid material. Extraction by water over a few hours does neither dissolve less soluble or kinetically slowly reacting Cr(VI)-bearing minerals nor does it capture any Cr(III) minerals that might get oxidised in the subsoil over long time periods (Adriano 1986; Palmer and Puls 1994; James 1996).

The present study focuses on the determination of the total Cr(VI) inventory of contaminated and industrial solid materials based on the US EPA method 3060A (US Environment Protection Agency 1996a). This method attempts a complete release of Cr(VI) from solid materials by extracting the water-extractable Cr(VI) in readily soluble mineral phases and the fraction of sparingly soluble Cr(VI) mineral phases, but without oxidising possibly present Cr(III) phases, under alkaline conditions and at elevated temperature. Up to the present, method 3060A has been systematically tested to a limited degree for the effects of compositional differences in the matrix of Cr(VI)-contaminated materials (e.g. Vitale et al. 1994). To extend the data basis and to allow better understanding of matrix effects and the chemical processes during extraction, a validation study of method 3060A was performed using different contaminated soils and industrial materials. Special emphasis is given on the presence of other redox-

active compounds in the solid materials such as Fe, Mn, S, and total organic carbon (TOC). The study includes multiple extraction of the test materials, matrix spiking and uncertainty estimation accompanied by chemical and mineralogical characterisation of the various solid materials. Additionally, the TOW test was performed to determine the water-extractable Cr(VI) fraction of each test material. The results of this study allow an assessment of the applicability and reliability of EPA method 3060A to a range of Cr(VI)-bearing solid materials of variable matrix compositions.

Materials and methods

Investigated materials

The solid materials used may be divided into two groups. The first group consists of Cr(VI)-contaminated soil samples from three abandoned industrial sites at Niederglatt (ZH), Rivera (TI), and Thun (BE) located in different geological environments in Switzerland. The industrial buildings at Niederglatt (ZH) are located above a fluvial gravel aquifer of the Swiss Molasse Basin. The Cr(VI) contamination of the subsoil is related to chromic acid (H_2CrO_4) that was used in the production of the terpenoid camphor ($\text{C}_{10}\text{H}_{16}\text{O}$) until 1932. The two soil samples were obtained from the unsaturated zone (N1: 0.6–1 m depth) and the transition zone between the unsaturated and saturated zone (N2: 1.3–1.9 m depth) from two different cores of a drilling campaign performed in 2010.

The former industrial site at Rivera (TI) is located in an environment of fluvio-glacial gravel sediments that consists of crystalline and metamorphic rocks with intercalated lenses of organic-rich swamp and bog deposits (Wanner et al. 2012a). Here, the Cr(VI) contamination stems from the production of chromic acid between 1948 and 1960. In this process, chromite (FeCr_2O_4) was oxidised to Na_2CrO_4 and followed by extraction with H_2SO_4 (Wanner et al. 2012a). During the industrial activity chromic acid and H_2SO_4 were spilled and reached the subsoil. Two subsoil samples were obtained from different cores (R1: 2.6–3.55 m depth and R2: 3.6–4.25 m depth) of a drilling campaign performed in 2009.

The decommissioned industrial complex at Thun (BE) is located above the fluvial gravel aquifer of the Aare river, which is composed of carbonate-rich clastic sediments with subordinate silty layers. The Cr(VI) contamination originates from periodic disposal of chromic acid, which was used for acid cleaning of copper alloy surfaces between 1895 and 1990 (Wanner et al. 2012b). Interaction between the disposed chromic acid residues and the aquifer material led to a cementation of the subsoil in the uppermost metres.

The sample used in this study (T1, taken at the surface) was collected from this cemented rock, which forms the hotspot of the contamination.

The second group of materials used in this test series consists of two different industrial materials that are both known to contain some chromium. The first material consists of a non-reduced Portland cement sample (CEM 1 52.5 N, VDZ) from Holcim Technology Ltd., Holderbank. The second material is a MSWI fly ash sample from the waste incinerator Zuchwil which is washed on-site according to the FLUWA-process (Bühler and Schlumberger 2010). The extraction tests were complemented using a standard reference material (National Institute of Standards & Technology 2009; Nagourney et al. 2008) to test the entire extraction and analytical procedure.

Analyses of solid material

Soil samples were dried at 40 °C, homogenised and sieved prior to analysis. Alkaline extraction tests were conducted on the grain size fraction <2 mm. An aliquot of 100 g of dried material of this grain size fraction was milled to a grain size <2 µm using a disc mill for chemical and mineralogical analyses. The chemical composition of the solid materials was first semi-quantitatively analysed by wavelength dispersive X-ray fluorescence analysis using a Phillips PW2400 spectrometer and UniQuant[®] software (Omega Data Systems 2004). The analytical error for XRF measurements is ~0.2 wt % (major elements) and ~20–30 mg/kg (Mn, S). The total Cr content, Cr_(tot), was determined by ICP-OES (Varian 720-ES) after microwave-assisted complete acidic digestions of the solid materials. Mineralogical investigations were performed by powder X-ray diffraction analysis (XRD) using a Panalytical CubiX³ diffractometer with CuKα-radiation ($\lambda = 1.54\text{\AA}$) and the Panalytical Software High Score Plus. The mineralogical characterization is supplemented by scanning electron microscopy (SEM) and optical microscopy. A Zeiss EVO-50 XVP electron microscope coupled with an energy dispersive system (EDS) was used with an accelerating voltage of 20 kV and a spot size of 504 nm for backscattered electron (BSE) images. The total organic carbon (TOC) content was calculated from the total carbon (TC) and the total inorganic carbon (TIC) contents measured by a Stroehlein CS-Mat system on the combusted solid materials. Concentrations of Fe²⁺ were obtained by acidic digestions (mixture of HF 40 % and H₂SO₄ 98 %) of the solid materials in an oxygen-free atmosphere and the digest solutions were analysed by spectrophotometry (Varian Cary 50) after coloured-complex formation with 2,2-bipyridine. Loss on ignition (LOI) was determined by heating the samples to 1050 °C for 1.5 h, except for the fly ash which was heated to 600 °C during 1.5 h.

Extraction procedures

Hot alkaline extraction of total Cr(VI) from the solid materials followed the method 3060A procedure (US Environment Protection Agency 1996a). For the extraction, 2.5 g dry material of a grain size of <2 mm was added to 50 mL of 0.28 mol/L Na₂CO₃/0.5 mol/L NaOH solution in a 250-ml round-bottom flask and heated to 90–95 °C for 60 min under continuous stirring. To prevent oxidation of Cr(III) during extraction, 400 mg MgCl₂ and 0.5 ml phosphate buffer (0.5 M K₂HPO₄/0.5 M KH₂PO₄) were added to the suspension. In contrast to the description given by method 3060A, the hot extract solutions were immediately filtered in their hot state to minimise any temperature-dependent redox and solubility processes possibly interfering with dissolved Cr. Filtration occurred with a pressure filtration device (0.45 µm) using argon gas. The reagents used were all of analytical grade and solutions were prepared with ultra-pure water. The redox potential (Eh), pH and temperature were monitored (Knick Portamess measurement devices) during the entire extraction process to investigate the different behaviour of the test materials during the hot alkaline extraction. Eh values were measured using a Hamilton Oxytrode PTI 120 Pt–Ag/AgCl electrode. Measured values were later corrected relative to the standard hydrogen electrode (SHE, e.g. Stumm and Morgan 1996).

The eluate test according to the Technical Ordinance on Waste (TOW test, Swiss Confederation 1990) is performed by shaking 50 g of homogenised, dry material of a grain size <2 mm in 500 mL of deionised water during 24 h with an end-over-end shaker. After extraction, the solution is filtered (0.45 µm) prior to Cr(VI) determination. No TOW test was performed for the standard reference material (National Institute of Standards & Technology 2009) due to the limited amount of material available.

Analyses of extracts

Method 3060A gives a detailed description of the extraction procedure but does not prescribe the analytical quantification of Cr(VI) in the extract solutions. Therefore, two analytical methods described in the guidelines (Swiss Confederation 2013) for the Cr(VI) determination in TOW extract solutions have been chosen for this study: spectrophotometry (US Environment Protection Agency 1992) and cation-exchange cartridge separation prior to ICP-OES analysis.

Using spectrophotometry dissolved Cr(VI) is reacted with diphenylcarbazide (DPC) at pH 2 to produce a red-violet-coloured Cr–DPC complex. Complexation was performed using a Spectroquant chromate test set (Merck, No. 1.14758) and absorption was measured at 540 nm using a

Merck Pharo 100 spectrophotometer. The reported detection limit and analytical error based on multiple measurements of Cr(VI) standard solution (Merck, No. 1.19780.05) is <0.05 mg/L and ± 10 % for Cr(VI), respectively. Alternatively, Cr(VI) was determined by Cr(III)–Cr(VI) separation using CHROMAFIX® PS-H⁺ (M) cartridges (Macherey–Nagel), followed by ICP-OES analysis (Varian 720-ES). The detection limit and analytical error of this method based on multiple measurements of certified standard solutions (Merck ICP Multi-element Standard CertiPur IV and X) is <0.001 mg/L and ± 5 % for Cr_(tot). The application of such cartridges has been successfully applied to moderately mineralised groundwater samples by Ball and McCleskey (2003). The effectiveness of the cartridges was tested using pure Cr(III) and a mixed Cr(III)/Cr(VI) standard solutions prepared from Cr(NO₃)₃ and K₂CrO₄. The retention of Cr(III) in the cartridge was excellent for both standards with an average Cr(III) retention of about 99.9 %. In contrast to the pure standard solutions, moderately mineralised groundwaters and TOW extract solutions, alkaline extract solutions are of higher ionic strength up to 1.3 mol/L. The high loads of Na⁺ from the extraction agent (0.5 mol/L NaOH and 0.28 mol/L Na₂CO₃) and other components that were dissolved from the solid material during extraction may interfere with the separation efficiency of the cartridge. To inspect such possible interferences and to elaborate the optimal ionic strength of the solution, extract solutions from method 3060A were diluted to different degrees and spiked with 100 µg/L Cr(III) prior to cation-exchange separation. The ideal dilution for all samples was found to be $\sim 1:50$, at which no measurable Cr(III) passed through the cartridge.

Method validation

The application of method 3060A to solid matrices of different composition and the analysis of the extract solution was evaluated to understand the chemical processes that may take place during alkaline extraction of Cr(VI). The soil and industrial samples were extracted in replicates (precision) and the extract solutions were analysed by ICP-OES with and without prior Cr species separation. The replicate extractions aimed at detecting possible experimentally induced changes in the Cr-speciation related to the different material matrices and so to assess the general applicability and effectiveness of the method to a variety of solid matrices. The accuracy of method 3060A was determined by multiply extracting and analysing the standard reference material NIST 2701 (National Institute of Standards & Technology 2009). An uncertainty estimation of the entire process of the hot alkaline extraction was performed using data obtained from extraction of the standard reference material. To calculate the combined

measurement uncertainty, the contribution of precision and accuracy was combined by Gaussian error propagation.

Matrix effects that may affect the alkaline Cr(VI) extraction by the dissolution of specific compounds from the extracted substance and which would interfere with the extracted Cr by redox and/or complexation reactions were investigated by spiking the matrix with a known amount of Cr(VI) and/or Cr(III) before extraction. Water-extractable (K₂CrO₄) and water-insoluble (PbCrO₄) Cr(VI) spikes were used to confirm that all Cr(VI) phases did dissolve and that no reduction of Cr(VI) took place during extraction. A quantitative recovery of the water-insoluble PbCrO₄ matrix spike would indicate that also sparingly soluble Cr(VI) phases were dissolved under alkaline conditions. Spiking test was conducted by a standard addition with two different concentrations of water-extractable and water-insoluble Cr(VI) (detailed concentrations in Online Resource 1). In a first batch, the concentration equal to the total Cr(VI) concentration determined in the non-spiked materials was added to each material. In the second batch, twice the total Cr(VI) concentration was spiked in form of water-extractable and water-insoluble Cr(VI) prior to the hot alkaline extraction. For the potential oxidation of Cr(III), 50 and 100 mg/kg soluble Cr(III), added as Cr(NO₃)₃, were spiked to each material.

Geochemical modelling

Speciation and solubility calculations of chromium compounds in the hot alkaline extract solutions were calculated with the geochemical computer code PHREEQC (Parkhurst and Appelo 2013) with the thermodynamic database WATEQ 4 (Ball and Nordstrom 1991). The latter was expanded observing internal consistency with the thermodynamic data for Cr-bearing aqueous species and mineral phases recommended by Ball and Nordstrom (1998).

Results and discussion

Sample characterization

For the subsoil materials the total Cr concentrations, Cr_(tot), as determined by total digestion range from 1400 to 11,000 mg/kg (Table 1). Total Cr(VI) concentrations in these soils as determined by hot alkaline extraction range from 40 to 300 mg/kg and water-extractable Cr(VI) determined by TOW eluates range from 0.2 to 18.2 mg/kg Cr(VI) for the subsoil materials. Cr(VI)-bearing mineral phases in amounts quantifiable by XRD (i.e. >1 wt %; Table 2) were not observed.

The total Cr concentration in soil material N2 from Niederglatt is ten times higher than for sample N1. In

Table 1 Chemical analyses of standard reference material (NIST 2701), soil samples and industrial materials

Sample type		NIST 2701	Soil N1	Soil N2	Soil R1	Soil R2	Soil T1	Cement	Fly ash
LOI	wt %	14.3	3.3	12.3	4.7	5.8	11.2	1.0	5.8
SiO ₂	wt %	7.7	72.5	50.9	53.0	57.0	41.8	20.9	13.0
CaO	wt %	11.5	0.6	16.5	2.4	1.6	11.2	62.4	25.4
Al ₂ O ₃	wt %	10.3	12.6	8.8	18.0	19.1	5.3	4.6	6.3
MgO	wt %	10.4	1.7	2.5	2.9	3.0	0.7	1.6	0.9
Na ₂ O	wt %	0.2	1.0	0.7	1.1	2.0	0.5	0.3	0.5
K ₂ O	wt %	0.1	2.2	1.5	3.2	3.0	1.0	0.9	0.7
Fe ₂ O ₃	wt %	36.7	5.0	4.2	10.8	6.4	18.8	2.7	3.8
Fe ²⁺	wt %	4.0	0.6	1.3	2.9	3.4	0.6	0.0	0.6
TOC	wt %	1.9	0.0	0.2	0.4	1.1	0.1	0.2	0.1
Mn _(tot)	mg/kg	2220	555	1520	860	571	198	287	546
S _(tot)	mg/kg	1050	366	221	779	840	8370	17,300	132,425
Cr _(tot)	mg/kg	42,500	1642	10,562	4516	1424	7142	88	708
Total Cr(VI)	mg/kg	401	113	298	58	42	298	45	13
WE Cr(VI)	mg/kg	–	18.2	14.9	2.9	0.2	7.8	0.9	0.8

Cr_(tot) and Fe²⁺ are obtained by complete acid digestion, total Cr(VI) by hot alkaline extraction and water-extractable Cr(VI) by TOW eluate (WE Cr(VI)) followed by ICP-OES analysis. TOC is analysed by coulometric techniques and all other data by XRF techniques (powder pellets)

Table 2 Estimated mineralogical composition of soils and industrial materials based on XRD, SEM and optical microscopy (xxx: >20 wt %, xx: 5–20 wt %, x: <5 wt %)

Phase	NIST 2071	Soil N1	Soil N2	Soil R1	Soil R2	Soil T1	Cement	Fly ash
Quartz	x	xxx	xxx	xxx	xxx	xxx	–	x
Clinker phases ^c	–	–	–	–	–	–	xxx	–
Calcium silicate hydrate ^b	–	–	–	–	–	–	–	xx
Plagioclase	–	x	x	xx	xx	x	–	–
K-feldspar	–	x	x	xx	xx	x	–	–
Biotite ^a	–	–	–	xx	xx	–	–	–
Muscovite ^a	–	x	–	x	x	–	–	–
Clay mineral	–	x	x	xx	xx	–	–	–
Calcite/dolomite	xx	–	xx	–	–	xx	–	–
Anhydrite/bassanite/gypsum	–	–	–	–	–	–	x	xxx
Chromite	xx	–	–	–	–	–	–	–
Fe-hydroxide ^a	–	x	x	–	–	x	–	–

The XRD powder patterns are shown in Online Resource 2

^a Assignment based on optical microscopy

^b SEM observation

^c Alite, belite, ferrite, aluminate

contrast, total Cr(VI) in sample N2 is on average only 2.5 times higher than in sample N1 after multiple hot alkaline extractions of the samples (Tables 1, 3). The water-extractable Cr(VI) fraction of both samples are in the same dimension (18.2 and 14.9 mg/kg) and elevated compared to the other test materials. At the Niederglatt site the most abundant minerals identified in the samples by XRD are

quartz, calcite, dolomite, plagioclase and K-feldspar (Table 2). Less frequently found are clay minerals, muscovite and Fe-hydroxides. The bulk chemical analyses by WD-XRF show high SiO₂ concentrations (>50 wt %), but relatively low in Fe_(tot) content (expressed as Fe₂O₃) compared to samples from Rivera and Thun (Table 1). Concentrations of Fe²⁺ and total organic carbon (TOC) are

Table 3 Results of multiple extractions of the test materials

Total Cr(VI)—EPA method 3060A										
Replicate (n)	1 mg/kg	2 mg/kg	3 mg/kg	4 mg/kg	5 mg/kg	6 mg/kg	7 mg/kg	x mg/kg	s mg/kg	RSD –
NIST 2701	410	384	425	411	375	420	384	401	20	5
Soil N1	117	114	107	101	105	129	101	113	10	9
Soil N2	248	330	324	323	246	318	–	298	40	13
Soil R1	33	40	62	93	65	46	78	58	20	35
Soil R2	112	1	55	40	29	7	50	42	37	88
Soil T1	289	219	297	323	308	307	343	298	39	13
Cement	45	43	47	43	45	–	–	45	2	4
Fly ash	13	12	13	14	15	–	–	13	1	9

A mean recovery of 73 % (401 mg/kg) for the standard reference material NIST 2701 is determined (certified value: 551.2 mg/kg total Cr(VI)) x mean value, s standard deviation, RSD relative standard deviation

generally low, but sample N2 has the highest total manganese, $Mn_{(tot)}$, concentration of 1520 mg/kg of all other soil samples although it is still lower than that of the NIST standard reference material. Both samples from Niederglatt display lower total sulphur contents ($S_{(tot)} < 400$ mg/kg) than in all other samples (Table 1).

Soil sample R1 of the Rivera site has a three times higher $Cr_{(tot)}$ concentration compared to sample R2. Both samples have total Cr(VI) concentrations of < 60 mg/kg that are significantly lower than those of the other subsoil samples from contaminated industrial sites (Table 1). The concentrations of the water-extractable Cr(VI) are 2.9 mg/kg for R1 and 0.2 mg/kg for R2. The mineralogy of the soil is typical for the Ceneri-Gneiss source rocks of this area and the samples are mainly composed of quartz, plagioclase and K-feldspar and contain substantial amounts of biotite, muscovite and secondary clay minerals such as chlorite (Table 2). The Rivera samples differ chemically from those from the other sites in that they have the highest Fe^{2+} contents at comparable $Fe_{(tot)}$ concentrations and elevated total organic carbon concentrations. In contrast, the concentrations of $Mn_{(tot)}$ and total sulphur are intermediate between the other samples (Table 1). Previous investigations by Wanner et al. (2012a) showed that the aquifer contains lenses of fine-grained sediments with elevated TOC contents (1–2 wt %) thus confirming the elevated TOC contents observed in the two present samples.

The soil sample T1 from Thun site shows high concentrations of $Cr_{(tot)}$ as well as of total Cr(VI). However, the water-extractable Cr(VI) is lower (7.8 mg/kg) compared to the Niederglatt samples. The major mineralogy is similar to that from the Niederglatt site with quartz, calcite, plagioclase and K-feldspars being most abundant (Table 2). The strong Cr contamination resulted, however,

in precipitates of abundant secondary mineral phases in the greenish-brown matrix with amorphous Fe-hydroxides being most prominent. This heavily contaminated subsoil has a high $Fe_{(tot)}$ content of 18.8 wt % (as Fe_2O_3) of which 0.6 wt % are present as Fe^{2+} , a high $S_{(tot)}$ concentration (8370 mg/kg), but low concentrations of $Mn_{(tot)}$ and TOC (Table 1).

The industrial materials, cement and fly ash contain $Cr_{(tot)}$ concentrations of < 1000 mg/kg, total Cr(VI) concentrations of < 50 mg/kg and water-extractable Cr(VI) concentrations of < 1 mg/kg. They are, therefore, less charged with Cr compared to the soil materials from the contaminated industrial sites. The cement sample is an ordinary Portland cement (OPC) that consists mainly of the clinker phases alite, belite, ferrite and aluminat together with anhydrite and bassanite. The washed fly ash contains quartz, amorphous calcium silicate hydrates and sulphate minerals (anhydrite, gypsum) which are responsible for the elevated $S_{(tot)}$ concentration. The heavily contaminated standard reference material NIST 2701 contains in addition to the certified $Cr_{(tot)}$ and total Cr(VI) concentrations also strongly elevated concentrations of $Fe_{(tot)}$, Fe^{2+} , $Mn_{(tot)}$, $S_{(tot)}$ and TOC (Table 1). Our mineralogical and chemical results for NIST 2701 are in agreement with those of Nagourney et al. (2008) who performed an extensive mineralogical and chemical characterisation during the development of this material.

Cr(VI) analyses of extract solutions

The concentration values of total Cr(VI) in the alkaline extract solutions of the different tested soils measured by the spectrophotometric Cr(VI)–DPC method are higher by 12 % (T1), 23 % (N2), and 67 % (R1) compared to the $Cr_{(tot)}$ concentrations obtained by ICP-OES, except for the

standard reference material (National Institute of Standards & Technology 2009; Fig. 1). These results support earlier findings by Milačić et al. (1992), Huo et al. (1998) and Pettine and Capri (2005) who claimed that the presence of extracted compounds from the samples such as humic substances may seriously affect Cr(VI) concentrations obtained with the Cr(VI)–DPC method. Such compounds absorb light at the same wavelength as the Cr–DPC complex (540 nm) causing a positive interference and thus in an overestimation of the real Cr(VI) concentration.

Another issue that interferes with the spectrophotometric Cr(VI)–DPC method is the high pH conditions of method 3060A extract solutions. The Cr(VI)–DPC method requires pH of 2 for correct Cr–DPC complex formation. Such pH value is only attained for solutions with an initial pH between one and nine. However, extract solutions from method 3060A have pH values >10 that interfere with the Cr(VI)–DPC complexation reaction. The observed change from a red–violet to a red–orange colour of the solutions results in a decrease of the extinction intensity at 540 nm that corresponds to the Cr(VI)–DPC complex and thus to an underestimation of the true Cr(VI) concentration. The only option to lower the pH to the required range for correct complex colouration would be a strong dilution of the alkaline extract solution (factor of ≥ 50). Obviously, such a high dilution factor compromises an already rather high limit of detection (LOD) of 0.05 mg/L Cr(VI) of the spectrophotometric Cr(VI)–DPC technique. This limits the application of this technique to contaminated materials with Cr(VI) contents of more than 100 mg/kg of solid material. The subsoil and industrial materials used in this study all have higher total Cr(VI) contents that enabled large dilutions to bring the solutions into the required pH range. In summary, difficulties associated with the pH value of the alkaline extract solutions, interfering compounds such as humic substances, and possible other yet unknown interferences with the complexation reactants limit the spectrophotometric Cr(VI)–DPC technique for

Cr(VI) quantification in alkaline extract solutions prepared according to method 3060A.

To ensure that no measurable Cr(III) was left in solution after the hot alkaline Cr(VI) extraction, method 3060A extracts were measured by ICP-OES with and without prior Cr species separation by the application of cation-exchange cartridges. Chromium concentrations obtained for the same solutions with and without the application of cation-exchange cartridges agree within the $\pm 5\%$ uncertainty range of the ICP-OES measurement (Fig. 2). This indicates that under the strongly reducing extraction conditions of method 3060A only oxidised Cr(VI) was present in the extract solution whereas all Cr(III) was precipitated. Based on the thermodynamic data compiled by Ball and Nordstrom (1998), the equilibrium concentration of the major Cr species, $\text{Cr}(\text{OH})_{3(\text{aq})}$ is $\sim 5 \cdot 10^{-11}$ mol/L, above which amorphous $\text{Cr}(\text{OH})_{3(\text{am})}$ will precipitate under the given extraction conditions (i.e. pH ~ 10.5 , IS ~ 1.3 M, T = 90 °C, $E_{\text{SHE}} \sim 0$ mV; see section identification of chemical processes below). This is considerably lower than that at low ionic strength and ambient temperature, but at similarly high pH values where the solubility limit of amorphous $\text{Cr}(\text{OH})_{3(\text{am})}$ is at $\sim 1.4 \cdot 10^{-7}$ mol/L of $\text{Cr}(\text{OH})_{3(\text{aq})}$. This illustrates that under the applied alkaline extraction conditions, precipitation of amorphous Cr(III) hydroxide is indeed promoted which would decrease the risk of having Cr(III) in the alkaline extract solution as already pointed out by Rai et al. (1987). Based on this evidence that only Cr(VI) is present in method 3060A extraction, a cation-exchange separation does not appear mandatory for the analyses of the tested subsoil, cement and fly ash samples. Therefore, the validation of method 3060A was performed without the application of cation-exchange cartridges prior to the ICP-OES analyses. Nevertheless, one extract solution of each material type was additionally prepared using cation-exchange cartridges prior to analysis as a control.

Fig. 1 Total Cr(VI) determined by the spectrophotometric technique (Cr(VI)–DPC method) and Cr_(tot) determined by ICP-OES in alkaline extract solutions prepared according to method 3060A. The error bars show the analytical uncertainty for Cr of each method ($\pm 10\%$ for spectrophotometry and $\pm 5\%$ for ICP-OES)

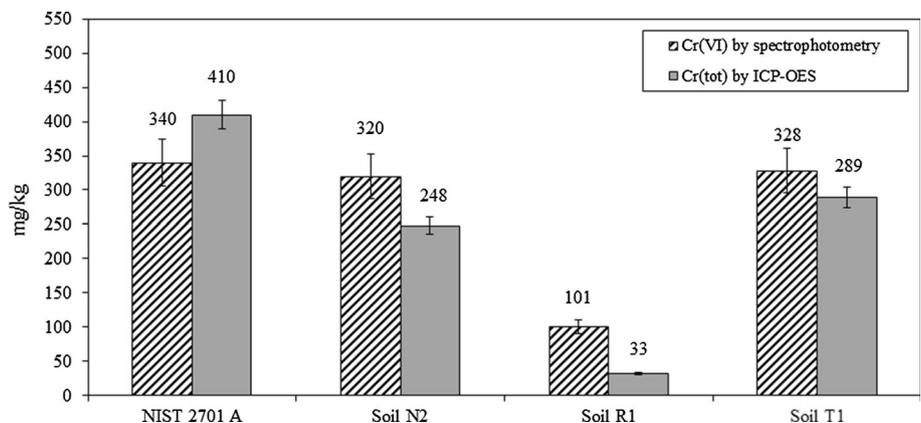
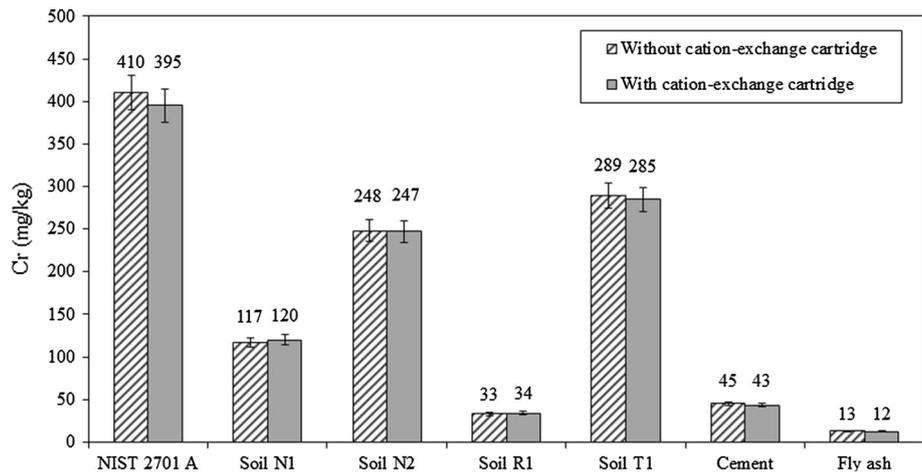


Fig. 2 Cr concentrations measured by ICP-OES with and without prior cation-exchange separation of Cr(III) in alkaline extract solutions prepared by method 3060A. After species separation (*hatched bars*) only total Cr(VI) is detected whereas without cation-exchange separation (*grey bars*) possibly present Cr(III) is measured together with the total Cr(VI). The *error bars* show the analytical uncertainty of $\pm 5\%$ for Cr



Reasonable results of Cr(VI) for the TOW extract solutions are achieved by the Cr(VI)–DPC method because the pH value of the solutions were in the range of pH 9. Only the cement sample eluate showed an elevated pH value of 12.5 and no spectrophotometric Cr(VI) determination was possible. The results of water-extractable Cr(VI) could be confirmed using cation-exchange cartridges followed by ICP-OES analysis.

Method validation

For the replicate alkaline extractions a relative standard deviation (RSD) $<10\%$ for the total Cr(VI) concentration was achieved for the standard reference material NIST 2701 and the industrial materials cement and fly ash. In addition, the subsoil samples N1, N2 and T1 from the Niederglatt and Thun site yielded an RSD between 9 and 13%. In contrast, samples R1 and R2 from the Rivera site yielded large RSDs of 35 and 88% for the replicate extractions. The poor precision obtained for the Rivera samples suggests either a sample heterogeneity due to the small sample size (2.5 g) in spite of exactly the same preparation of the <2 mm grain size fraction for all samples, and/or a different behaviour of the sample matrix during the hot alkaline extraction compared to all other tested materials (see below).

The accuracy of method 3060A was determined by extracting and analysing the standard reference material NIST 2701 seven times. An average recovery of total Cr(VI) of 73% was achieved for these extractions. This corresponds to the recoveries listed in the certificate of analysis (National Institute of Standards & Technology 2009) using detection methods such as colorimetry (US Environment Protection Agency 1992; recovery 69.7%) or ion chromatography (US Environment Protection Agency 1996b; recovery 70.5%). In contrast, a 30% higher recovery compared to these analytical methods was

reported by the National Institute of Standards and Technology (NIST) using isotope dilution mass spectrometry (US Environment Protection Agency 2007; recovery 100.4%). The value obtained by this latter technique is currently adapted as the certified Cr(VI) value (551.2 mg/kg) in method 3060A extract solutions for the standard reference material. The rather large differences obtained by different detection techniques highlight the complexity attached to the quantification of Cr(VI) in the hot alkaline extract solutions and this asks for further research.

The precision (replicate extraction) and accuracy (recovery of certified value) data obtained from the standard reference material are additionally used to calculate a combined measurement uncertainty of 15% and an expanded uncertainty of 30% for the entire process of total Cr(VI) determination using method 3060A and ICP-OES analysis.

For interpretation of the Cr(VI) and Cr(III) spiking results, the mean value of the recoveries from the two spiked concentrations to each material was calculated and the deviation between the single spike recoveries are plotted as error bars in Fig. 3. Recoveries for the water-extractable and water-insoluble Cr(VI) spikes between 90 and 125% were obtained for all alkaline extracts, except for soil N2 and the two Rivera soil samples. Whereas the water-insoluble spike recovery of sample N2 (76%) from Niederglatt is within the expanded measurement uncertainty of 30% of the method, those for the two Rivera soil samples R1 and R2 show consistently poor and highly diverging spike recoveries for water-extractable Cr(VI) (R1: 0 and 153%; R2: 16 and 6%) and water-insoluble Cr(VI) (R1: 70 and 6%; R2: 43 and 117%). No correlation is established with the large relative standard deviations of 35 and 88% obtained for the total Cr(VI) contents is evident. The recoveries of water-extractable and water-insoluble Cr(VI) spikes of the Rivera samples, therefore, indicate a dependence on the composition of the extracted

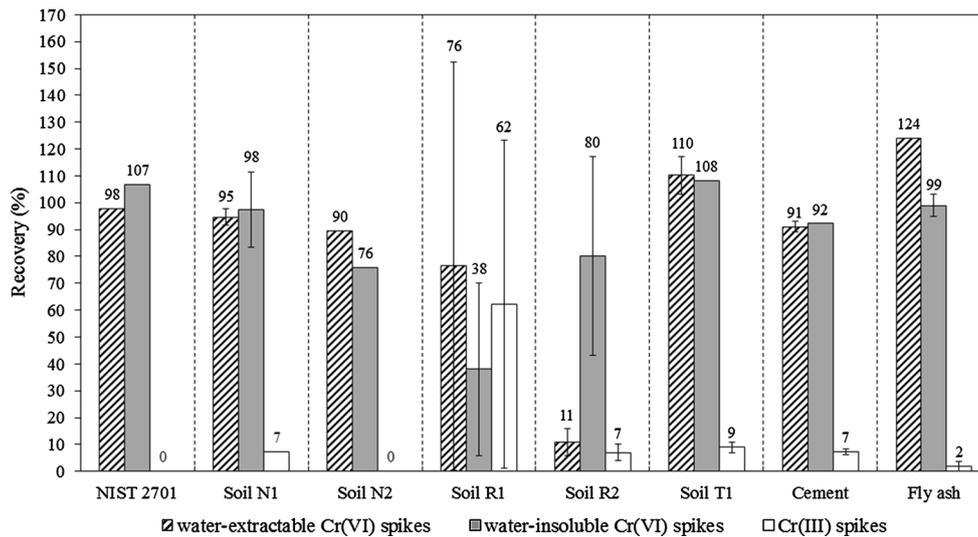


Fig. 3 Recovery of Cr(VI) and Cr(III) spikes from alkaline extract solutions prepared from the various solid materials. *Hatched bars* indicate the mean ($n = 2$) Cr recovery in % after water-extractable Cr(VI) spiking, *grey bars* after water-insoluble Cr(VI) spiking and the *white bars* represent the mean Cr recovery after

spiking the alkaline solutions with Cr(III). The *error bars* show the deviations between spike recoveries of replicate samples performed for each spiking type. The Cr(VI) and Cr(III) spike recoveries for soil N2 and the standard reference material (NIST 2701) are only based on single spike experiments

material as will be outlined in more detail in the next section.

Addition of soluble Cr(III) spike revealed 2–9 % higher Cr concentrations compared to non-spiked solutions for the alkaline solutions of all materials, except for the subsoil sample Rivera R1 (see below). Some insight into this elevated Cr recovery is gained from the spiked extraction of a non-contaminated blank sample from the Niederglatt site. This sample N3 was spiked with 100 mg/kg of Cr(III) prior to extraction and 10 % of this spiked Cr were still found in the solution after extraction. Interestingly, the same amount of spiked Cr was also analysed in the solution after passing it through a cation-exchange cartridge that removed all Cr(III) from this solution. This indicates that in this extraction some 10 % of the added Cr(III) spike were oxidised to Cr(VI) during extraction. Within this context it is important to note that the Cr(III) spike was added to the extract solution at ambient temperature as dissolved $\text{Cr}(\text{NO}_3)_3$. It thus appears that under the initial oxidising conditions of the extract solutions at ambient temperature the oxidation of spiked and dissolved Cr(III) is quicker than its precipitation as amorphous Cr(III) hydroxide. It is concluded that the 2–9 % higher Cr concentrations obtained in Cr(III)-spiked alkaline extract solution compared to non-spiked solutions are due to partial oxidation of the added Cr(III) spike during the initial phase of the alkaline extraction process. While the interpretation of partial oxidation of the Cr(III) spike is in agreement with the findings by Vitale et al. (1994), we associate this oxidation to faster reaction kinetics of the Cr(III) oxidation in

the solution compared to that of the Cr(III) precipitation from the alkaline extract solution. The present data do not allow to either support or reject the hypothesis by Eary and Rai (1987) who proposed the oxidation of Cr(III) by $\beta\text{-MnO}_2$ during extraction. However, the similar degree of observed oxidation of spiked Cr(III) in the extract solutions (i.e. 2–9 %) of samples with strongly variable $\text{Mn}_{(\text{tot})}$ contents ($\sim 290\text{--}2220$ mg/kg, Table 1) seem to argue against the oxidation by MnO_2 as a dominant process. Such oxidation is inhibited during extraction at 90 °C by the lowering of the redox potential of the extract solution and the lowering of the solubility of Cr(III), by several orders of magnitude.

Soil R1 showed an anomalous mean Cr(III) spike recovery of 62 % (Fig. 3) in contrast to all other samples. This value results from a recovery of 123 % of Cr(III) after spiking with 50 mg/L of Cr(III) and a recovery of 2 % of Cr(III) after spiking with 100 mg/L of Cr(III). A repeat extraction with 50 mg/L of Cr(III) spike added to sample R1 resulted in an even higher recovery of 144 %. This erratic behaviour can hardly be related to chemical reactions taking place during the alkaline extraction. For instance, the extract solution of this sample showed the lowest redox potential ($E_{\text{hSHE}} \sim 50$ mV, Fig. 4) just after addition of the spike. Combined with the intermediate $\text{Mn}_{(\text{tot})}$ content (860 mg/kg), this extract solution is thus expected to have a Cr(III) oxidation capacity during the initial phase of the extraction that is at least as low as in all other extract solutions. The much lower redox potential during the continuation of the extraction at 90 °C

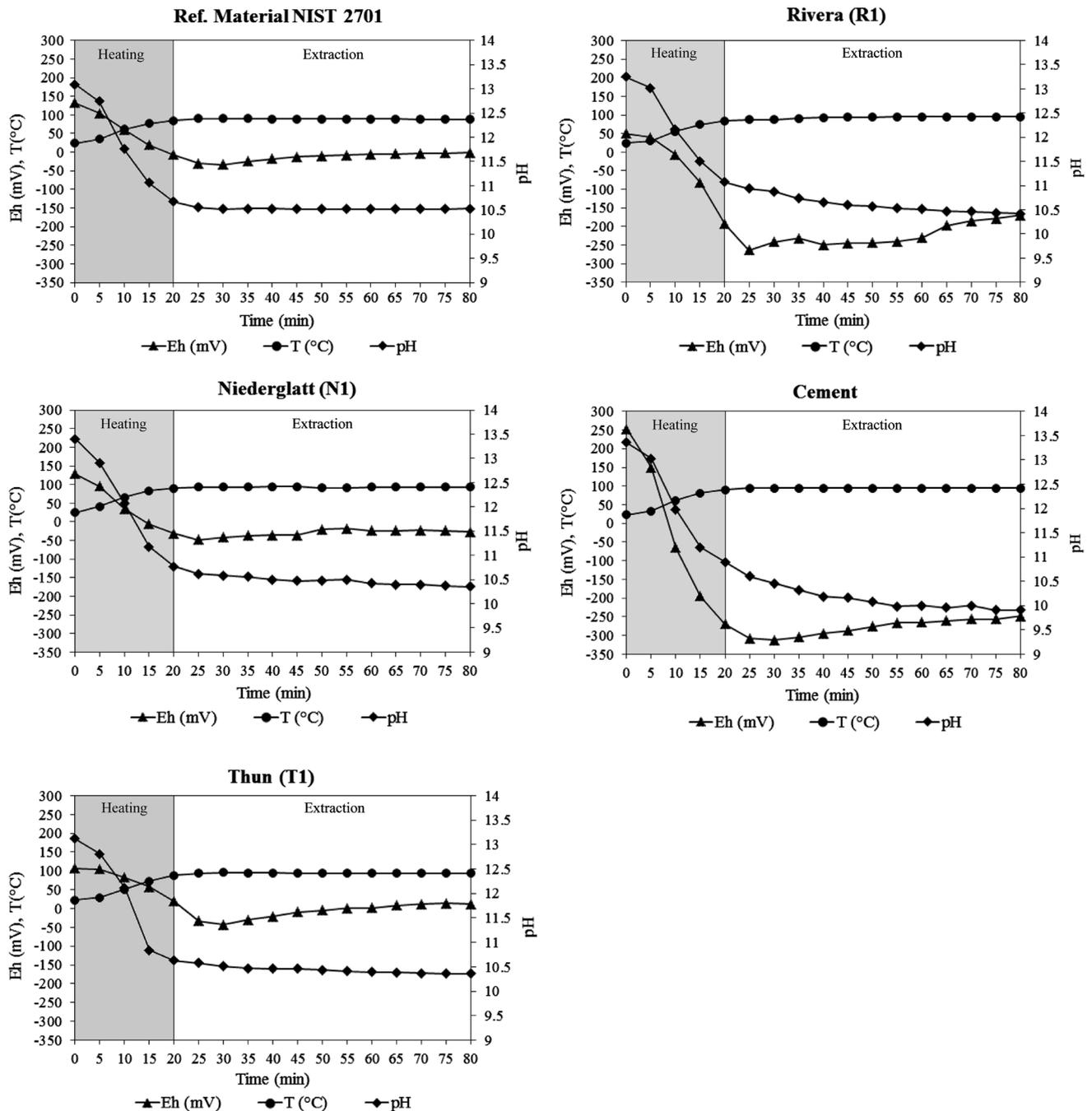


Fig. 4 Variation of the parameters Eh (relative to SHE and corrected for temperature), pH and temperature as a function of extraction time during the alkaline extraction

compared to all other solutions (Fig. 4) also argues against an oxidation of Cr(III) during this phase of extraction. Therefore, the observed Cr concentration in the Cr(III)-spiked extract solutions can only be attributed to the presence of a different amount of soil-derived Cr(VI) in this sample aliquot compared to the non-spiked sample aliquot. Such sample heterogeneity is supported by the large standard deviation of multiple extractions of the Rivera samples (Table 3). The Rivera R1 sample aliquots

thus indicate how sensitive the determination of Cr(VI) in small soil aliquots of 2.5 g is, even if the preparation occurs with great care.

Identification of chemical processes during extraction

The water-extractable Cr(VI) concentration is about one order of magnitude smaller compared to the total Cr(VI)

concentration independent of the type and origin of the material (Table 1). Water-extractable Cr(VI) does not correlate with the total inventory of Cr(VI) present in a contaminated or newly manufactured solid material. The true Cr(VI) inventory is thus underestimated by simply applying the TOW eluate test. After 24 h of extraction, pH values between 9 and 10 and E_{SHE} values between 360 and 450 mV have been measured. At these conditions, the dominant Cr species in solution is chromate (CrO_4^{2-}) (Ball and Nordstrom 1998). No relation between the total Cr(VI) and the water-extractable Cr(VI) exists and the measured concentrations of the TOW test do not help to understand the aberrant behaviour of the Rivera soil samples by performing method 3060A.

Some insights into the chemical interaction between the sample matrix and the hot alkaline solution may be obtained from monitoring pH, Eh and temperature during the extraction process and from geochemical modelling. Stable measurements were obtained during monitoring within less than a minute for all samples except for the fly ash sample, which is composed of highly reactive sulphides, sulphates, oxides, carbonates, salts and silicates.

The target extraction temperature of 90–95 °C was reached for all test materials within ~20 min (Fig. 4). The initial solution pH of about 13.2 decreased to a value near 11 during this heating period for all soil samples. Subsequently, pH smoothly decreased to a value near 10.5 without reaching an obvious steady state until the end of the extraction after 80 min. Geochemical model calculations indicate that for the pure extract solution (0.5 mol/L NaOH and 0.28 mol/L Na_2CO_3) the temperature increase from 20 to 90 °C results in a decrease of the solution pH from 13.2 to 11.5. Solely the additional decrease by one log unit between 30 and 80 min is, therefore, related to buffering reactions within the solid material. Modelling further reveals that neither the carbonate system (calcite, dolomite) nor the Mg system (Mg added as buffer), nor the Si system (quartz) can reduce the pH to the observed values. It appears that the dissolution of relatively abundant Al-silicates (feldspars, mica, clays) is responsible for the pH reduction. Under the prevailing alkaline conditions, Al released from dissolving Al-silicates is highly soluble and forms $\text{Al}(\text{OH})_4^-$ (aq) and $\text{Al}(\text{OH})_3$ (aq) complexes until saturation with amorphous Al-hydroxide ($\text{Al}(\text{OH})_3$ (am)) is reached. For example, the dissolution of about 40 mmol/L of K-feldspar would result in a decrease of the extract solution pH from 11.5 to 10.6 near equilibrium with gibbsite, but not yet with $\text{Al}(\text{OH})_3$ (am). This latter observation and the still decreasing pH indicate that after 80 min the system is not yet at equilibrium and is still kinetically controlled with respect to the interaction with the sample matrix. The only approximately stable high pH conditions for the quartz–feldspar–calcite dominant subsoil samples

will, however, not directly interfere with the systematics of the Cr system. A similar behaviour is also observed for the cement sample, although there the final pH is slightly lower (near 10) and the decreasing trend is more pronounced (Fig. 4).

In contrast to pH, changes in the redox conditions will directly influence the Cr system during the alkaline extraction. The initial E_{SHE} of extract solutions at 20 °C without soil was 330 mV. According to the Nernst equation, an increase of the E_{SHE} by about 34 mV would result due to the decrease in pH induced by heating the solution to 90 °C. By adding the different soil materials to the extract solution at 20 °C this initial E_{SHE} is quickly reduced to about 110–130 mV for all materials, except for the Rivera R1 soil samples where a decrease occurred to $E_{\text{SHE}} \sim 50$ mV. Monitoring of the redox potential during the ~20 min of heating up to 90 °C revealed another pronounced decrease in Eh for all materials, but to a different extent (Fig. 4). For the standard reference material (NIST 2701) and the soil samples Niederglatt N1 and Thun T1, the decrease in E_{SHE} amounts to ~160 mV, whereas a decrease of >300 mV and >500 mV was observed for the Rivera R1 and the cement sample, respectively. The most reducing conditions were attained after 20–30 min of extraction time independent of the material. The most negative E_{SHE} value was obtained for Rivera R1 sample (–249 mV, corrected for temperature) and the Portland cement sample (–312 mV), whereas samples from Niederglatt and Thun yielded minimum E_{SHE} values of only about –50 mV.

The strong lowering of the redox potential to $E_{\text{SHE}} \sim 50$ mV of the alkaline extract solution immediately after addition of the Rivera R1 sample at 20 °C indicates a high reduction capacity with quickly reacting reducing components in this soil. This is supported by the observation that the initially colourless extract solution changed rapidly to dark-brown colour after getting in contact with the Rivera soils at room temperature. This indicates the release of organic material from these soils, which continues with increasing temperature until an almost black colour was reached after 60 min. Analysis of TOC shows that the Rivera materials contain elevated TOC contents (0.5 and 1.1 wt %) compared to soil material from the Niederglatt and Thun sites (Table 1). Elevated TOC contents are consistent with the locally anoxic conditions due to the degradation of organic matter in lenses of organic-rich swamp and bog deposits at this site. Therefore, the different behaviour of the Rivera samples during extraction is associated mainly with the strong reducing potential of these soils because of the presence of organic matter.

Furthermore, it is known that apart from organic-rich sediments also minerals containing reduced sulphur (i.e.

sulphides) and/or ferrous iron (e.g. magnetite, biotite, chlorite, hornblende) may function as Cr(VI) reducing agents (Palmer and Puls 1994; Bishop et al. 2014). In sulphide minerals such as pyrite (FeS_2), both the iron and the sulphide are able to act as electron donors. Materials from Rivera show increased concentrations of biotite and secondary sheet silicates (e.g. chlorites) compared to the other samples (Table 2). This is supported by the higher Fe^{2+} concentrations obtained for the Rivera soils (2.9 and 3.4 wt %) compared to soils from the Niederglatt (0.6 and 1.3 wt %) and Thun (0.6 wt %) sites (Table 1). Wanner et al. (2012a) tested the Cr(VI) reduction potential of the gravel aquifer material at the Rivera site with a simple batch experiment. They milled a sample of uncontaminated, weathered Ceneri-Gneiss and shook it with K_2CrO_4 solution (10 mg/L) for 10 days. This batch experiment resulted in a Cr(VI) concentration below detection for the spectrophotometer (<0.05 mg/L Cr(VI)). The authors concluded that the entire aquifer material has the potential of operating as a Cr(VI) reducing agent. Although the milling of the Gneiss material possibly produced fresh, reactive and non-oxidised, Fe^{2+} -bearing mineral surfaces and the reactions might occur more slowly with naturally weathered material, this experiment combined with the above Fe^{2+} concentrations are clear evidence that such reactions may occur.

The elevated TOC and Fe^{2+} concentrations in the soil material and the observed Cr(VI) reducing potential of the extract solutions of the Rivera samples explain the discrepant behaviour of the Rivera samples, whereas the hot alkaline extraction according to method 3060A worked fine for all other test materials including the standard reference material. Matrix effects and the strong reducing potential of the Rivera soil samples reduce the spiked Cr(VI) with subsequent precipitation of $\text{Cr}(\text{OH})_{3(\text{am})}$ as discussed above. This is in agreement with findings by Vitale et al. (1994) who observed low Cr(VI)-spike recoveries by applying method 3060A to anoxic, sulphidic sediments that contained 27 wt % of organic carbon and 100 mg/kg sulphides. The results of water-extractable and water-insoluble Cr(VI)-spike recoveries indicate that soils with elevated amounts of reducing minerals (e.g. Fe^{2+} -bearing phases) and/or organic matter will induce matrix effects that interfere with Cr(VI) spikes. A strong negative redox potential as observed for the Rivera samples is, however, not an unambiguous indicator for a low Cr(VI)-spike recovery. This is exemplified by the Portland cement sample (CEM I), which reached an even more negative redox potential of $E_{\text{H}_{\text{SHE}}} -312$ mV during extraction (Fig. 4), but yielded an excellent Cr(VI)-spike recovery (92 %). This suggests that the reduction of Cr(VI) does not primarily depend on the reducing potential of a material, but more on the reducing agents present in such materials.

The present data do, however, not allow a more detailed description of the involved processes and further investigations are required for such special types of industrial materials.

Conclusion

The results of this study demonstrate that the determination of Cr(VI) in extract solutions from US EPA method 3060A by the spectrophotometric diphenylcarbazide (DPC) method likely leads to discrepant results due to interfering substances arising from the extraction process and due to the high pH conditions ($\text{pH} > 10$). Tests under hot alkaline extraction conditions with and without cation-exchange cartridges to remove Cr(III) reveal that only oxidised Cr(VI) is present in the alkaline solution and that dissolved Cr(III) precipitated presumably as amorphous $\text{Cr}(\text{OH})_{3(\text{am})}$. A cation-exchange procedure prior to determination of Cr in the extract solution by spectrometric techniques is a priori not indicated. Nevertheless, a redox-sensitive analytical technique is recommended to assure that no Cr(III) is erroneously quantified in samples of unknown matrix composition.

The applicability of method 3060A in combination with ICP-OES analysis was successfully tested and validated for subsoil samples from oxidising, weathered environments with matrices mainly composed of quartz, calcite, plagioclase and K-feldspar and low contents of Fe^{2+} , TOC and $\text{Mn}_{(\text{tot})}$. For such type of soils and including standard reference material (NIST 2701) a good reproducibility of Cr(VI) determinations was obtained and the recovery of Cr(III)- and Cr(VI)-spikes was within the expanded uncertainty of 30 % of the method. This indicates that no substantial matrix effects interfered with soil-derived Cr(VI) and Cr(III) during extraction. A similar behaviour was found for a Portland cement (OPC-1) and an MSWI fly ash sample.

The poor reproducibility of soil-derived Cr(VI) and the anomalous and heterogeneous Cr(III)- and Cr(VI)-spike recoveries obtained for Rivera subsoil samples is attributed to severe matrix effects during the alkaline extraction and compositional heterogeneity between different sample aliquots. Matrix effects are responsible for the anomalous recovery of Cr(VI) spike in the alkaline extract solutions of the Rivera samples and can be related to differences in the mineralogical and chemical composition, notably the elevated Fe^{2+} and TOC contents. Sample heterogeneity is indicated by the poor reproducibility of soil-derived Cr(VI) in combination with the anomalous recovery of the Cr(III) spike in these alkaline extract solutions. In addition, the comparison of the total Cr(VI) and the water-extractable Cr(VI) concentrations do not show simple dependencies on phase composition.

To circumvent some of the experienced problems related to the application of method 3060A alkaline extraction to differently composed materials it is recommended that (a) prior to routine application to a new material type, spiking tests are to be performed for the identification of possible matrix effects, (b) that the mass of solid material to be extracted is adjusted to the heterogeneity of the Cr(VI) distribution in the material in question, and (c) that the solid material is added to the alkaline extract solution not until the solution has reached 90 °C. Point (c) requires further confirmation. However, the chemical reactions identified appear to take place during the initial phase of the alkaline extraction during heating from 20 to 90 °C. This seems to support such a modification of method 3060A.

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