

Application of the Rietveld method to assess chromium(VI) speciation in chromite ore processing residue

Maria Chrysochoou*, Dimitris Dermatas

W.M. Keck Geoenvironmental Laboratory, Stevens Institute of Technology, Castle Point on Hudson, Hoboken NJ 07030, USA

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Abstract

The Rietveld method allows the quantification of crystalline phases and amorphous material identified by X-ray powder diffraction (XRPD) and other diffraction methods. The method assists in determining the speciation of contaminants in solid matrices both qualitatively and quantitatively in a statistically defensible approach, as it does not focus on a microscale. Rietveld was applied to chromite ore processing residue (COPR), a cementitious waste containing hexavalent chromium. Calcium aluminum chromium oxide hydrates (CACs) were the crystalline phases identified by XRPD that bind Cr^{6+} in COPR according to their chemical formula. Rietveld quantification, combined with mass balances on Cr^{6+} , showed that CACs may bind Cr^{6+} in variable percentages, ranging from 25% to 85%. Analysis of duplicate samples showed that material variability is the predominant factor of uncertainty in evaluating the role of CACs in Cr^{6+} speciation, provided that a consistent quantification strategy is pursued. The choice of strategy was performed on the basis of the pertinent literature, preliminary analyses of the equipment and the software settings, and mass balances. The correlation between the average CAC-bound Cr^{6+} concentration and the total Cr^{6+} for five samples ($R^2 = 0.94$), extracted from different zones and soil borings, suggests that CACs are a primary sink for Cr^{6+} in COPR.
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1. Introduction

The identification and quantification of hazardous compounds and their leaching behavior in solid matrices are essential features to hazardous material management approaches. The characterization step is essential for risk assessment, treatment design and evaluation, and the identification of treatment alternatives. Stabilization/solidification (S/S) treatment of contaminated solid media is a common approach to immobilize heavy metals [1]. S/S treatment aims to reduce the mobility and/or toxicity of hazardous compounds, by chemical transformation into less toxic and/or soluble forms, or by physical encapsulation in a low-permeability, high-strength media [2]. The speciation of heavy metals will significantly affect their availability to participate in transformation and/or immobilization reactions. Obviously, the determination of contaminant speciation prior to, as well as following treatment, is essential to ensure the success of the treatment, apart from conducting regulatory tests, such as the toxicity characteristic leaching procedure (TCLP).

The current study presents the investigation of contaminant speciation in a cementitious system, in which hexavalent chromium is the contaminant of concern. Chromite ore processing residue (COPR) is generated as a by-product of the chromite ore ((Mg,Fe)(Cr,Al,Fe)₂O₄) processing to isolate and extract chromium. The ore is mixed with quicklime and soda ash and roasted at high temperature (~1200 °C) [3]. The end products of the process are soluble sodium chromate (Na₂CrO₄) and a residue that consists of high temperature oxides (brownmillerite (Ca₂FeAlO₅) and periclase (MgO)), possibly excess hydrated lime, and various impurities, including chromium in both its trivalent and hexavalent form. Million tons of COPR have been deposited in urban environments in the U.S.A. and numerous deposition sites are located in Hudson County, N.J. [4]. This study presents results of an extensive investigation at a COPR deposition site in Hudson County, designated as Study Area 7 (SA7), which focused on the pronounced heaving phenomena observed at the site, as well as the presence, leaching behavior and treatment of hexavalent chromium.

The quantification of the minerals present in COPR is of great importance for the COPR investigation for two reasons: The heaving phenomena observed at SA7 are considered to be a result of mineralogical transformations, see Moon et al.

* Corresponding author. Tel.: +1 201 216 8773; fax: +1 201 216 8212.
E-mail address: mchrysoc@stevens.edu (M. Chrysochoou).

[5]. The determination of the amount of parent and transformation phases, both horizontally and vertically across the site, can, therefore, help identify both the active heaving mechanism, the potential for further volume expansion at the site and possible mitigation methods.

Furthermore, the understanding of the speciation of Cr^{6+} in the solid phase is crucial in developing a site management approach and designing a treatment scheme. Commonly, a reductive treatment to transform toxic Cr^{6+} to non-toxic Cr^{3+} may be pursued. Cr^{6+} has to be available in the aqueous phase and thus dissolved from the Cr-containing phases, in order for redox reactions to occur. A major challenge for assessing treatment efficiency is to recognize that the TCLP test may yield low Cr concentrations even if the reduction does not occur, while the pH remains in the stability field of Cr^{6+} precipitates. However, with time the properties of the solid matrix, such as the buffering capacity, may induce pH changes that subsequently dissolve Cr^{6+} -phases, releasing Cr^{6+} into solution, long after the reductant has been consumed or exhausted. The quantification of Cr^{6+} -containing phases is therefore necessary to determine the target pH and reagent quantities for treatment.

COPR is a highly alkaline waste ($\text{pH} > 12$); the pH regime favors the mobility of hexavalent chromium as an oxyanion, i.e., chromate (CrO_4^{2-}). However, the cementitious mineralogy of COPR enables binding of chromate in calcium alumina hydrates, such as ettringite and hydrocalumite [6]. Total analyses are required for total Cr^{6+} estimates. Microscopic and spectroscopic methods are necessary to provide information on Cr^{6+} speciation. X-ray powder diffraction (XRPD), optical microscopy, scanning electron microscopy/energy dispersive X-ray (SEM/EDX) and electron probe microanalysis (EPMA) are commonly applied to investigate the composition of crystalline phases. Among these, XRPD presents the advantage that it allows a statistically defensible (global) analysis of a solid matrix. It is also a widely applied method with extensive databases of XRPD data that facilitate the identification of crystalline phases.

The need for total and contaminant speciation analyses is common for the evaluation of treatment approaches for soil or hazardous waste. For example, the type and amount of clay in a soil is important as an immobilization mechanism for heavy metals as the Al-source in a S/S treatment design to ensure sufficient pozzolanic reaction. The amount of fines in a soil does not necessarily correspond to the amount of clay present, as other minerals (micas and feldspars) may contribute to the fine fraction. The amount of carbonate species (calcite, dolomite) may also provide an indication of the buffering capacity of a soil or solid waste. These are only characteristic examples of useful information extracted from quantitative XRPD analysis for environmental system applications and evaluation.

Several studies have utilized XRPD to investigate heavy metal speciation in S/S matrices [7–10]. The XRPD analysis in mainstream environmental applications is, however, to date mostly qualitative. Although XRPD quantitative analysis methods date back to 1969, with the publication of the Rietveld method [11], quantitative phase analysis (QPA) for environmental applications has been limited. One reason for this is that the

available software was previously difficult to manipulate. However, the progress in computerized powder diffraction and crystal structure data and the advances in XRPD analysis software in the past decade now allow for a wider application of QPA. Training in this regard is therefore essential to understand the physical meaning of quantitative analysis methods, as well as the intricacies of analysis strategies.

Furthermore, the application of QPA on XRPD data of contaminated soils and waste is complicated by the nature of these matrices; the number of crystalline phases is usually high, mixtures are commonly non-uniform and solid phases are not necessarily chemically and structurally well defined, as is the case in materials science applications. COPR is a characteristic example of a complicated cementitious system, as it contains a multitude of crystalline and non-crystalline phases with extensive variability in chemical composition. The present study illustrates how the challenges presented by COPR were successfully overcome to provide first order estimates of Cr^{6+} speciation.

2. Materials and methods

COPR samples were obtained from an extensive subsurface investigation performed at Study Area 7 (SA7), a COPR deposition site located in Jersey City, NJ, USA. A total of 92 discrete disturbed samples were obtained from different depths in 38 soil borings. Twenty-five relatively undisturbed samples were obtained from tube samplers and one block sample was also obtained from a trench excavation. The sampling methods, stratigraphy and physical characteristics of COPR are described in Dermatas et al. [12]. Briefly, four COPR zones extend vertically at the site, designated as Zones A, B1, B2 and C. Zone A is the surficial zone, Zones B1 and B2 contain coarse-grained COPR in the unsaturated and saturated zone, respectively, while Zone C is fine-grained, water-saturated COPR. The sample nomenclature used is “COPR—zone designation”. The investigation involved the collection of samples at ~ 0.7 m intervals, each sample comprising 200–400 g moist COPR material. The contents of each sample container were homogenized manually and about 15 g of each sample were extracted.

Total content values for hexavalent chromium were obtained by using the USEPA alkaline digestion method [13] with colorimetric analysis [14].

All samples were analyzed by XRPD. Representative samples from Zones B1, B2 and C were also analyzed using an internal standard to quantify the amorphous content. The samples were air-dried for 24 h. Two grams of homogenized sample were taken and pulverized manually, using a mortar and pestle, to pass a U.S. #400 standard sieve ($38 \mu\text{m}$ opening). The pulverized sample was mixed with corundum ($\alpha\text{-Al}_2\text{O}_3$) on a 20% (w/w) basis of dry sample (1.6 g of sample with 0.4 g of corundum) and separated into duplicate samples. A Rigaku DXR 3000 computer-automated diffractometer was used, with Bragg-Brentano geometry. The diffractometry was conducted at 40 kV and 40 mA using diffracted beam graphite-monochromator with Cu radiation. The data were collected in the range of two-theta values between 5° and 65° with a step size of 0.02° and a counting time of 3 s per step. XRPD patterns were analyzed by the

Jade software version 7.1 [15], with reference to the patterns of the International Centre for Diffraction Data database [16], version 2002, as well as the Inorganic Crystal Structure Database [17], release 2005. Quantitative phase analysis by the Rietveld method was conducted using the Whole Pattern Fitting function of Jade.

3. Results and discussion

Table 1 shows the total Cr^{6+} concentrations for six COPR samples. These range from $\sim 0.4\%$ by dry weight of COPR in the Zone A sample to over 1% w/w in Zone C samples. These concentrations by far exceed the limit of 240 mg/kg imposed by the New Jersey Department of Environmental Protection. Furthermore, the high concentrations indicate that there is significant probability that Cr^{6+} -containing phases are present in sufficient amounts to be identified by XRPD, exceeding the detection limit. There is no generally accepted detection limit for XRPD, as it depends on phase crystallinity, pattern complexity and counting statistics. In the case of COPR, phases were identified at concentrations as low as 1% (and lower in the case of quartz, which is highly crystalline). The total quantity of Cr^{6+} also dictates the upper limit of Cr^{6+} -containing phases and provides a basis for the assessment of XRPD quantitative results, as will be demonstrated in the following discussion.

The mineralogy of COPR, as identified by qualitative XRPD analysis, consists of the following minerals: brownmillerite ($\text{Ca}_2\text{FeAlO}_5$) and periclase (MgO) are the COPR “parent” materials from the roasting process. Hydrogarnets (katoite ($\text{CaO}_3\text{Al}_2\text{O}_3(\text{H}_2\text{O})_6$ being the main phase), hydrotalcites (sjoegrenite $\text{Mg}_6\text{Fe}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ and quintinite $\text{Al}_2\text{Mg}_4(\text{CO}_3)(\text{OH})_{12}\cdot 3\text{H}_2\text{O}$ are representative compounds), calcium aluminum chromium oxide hydrates ($\text{CACs}-\text{Ca}_4\text{Al}_2\text{O}_6(\text{CrO}_4)\cdot n\text{H}_2\text{O}$) are the main transformation products derived from brownmillerite, while brucite ($\text{Mg}(\text{OH})_2$) is the main periclase hydration product apart from hydrotalcites that also scavenge part of the magnesium. Portlandite ($\text{Ca}(\text{OH})_2$) is the product of quicklime (CaO) hydration. Ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$) and calcite (CaCO_3) form when sulfate and carbonate are introduced to the system by means of water and/or air infiltration. Fig. 1 shows a characteristic example of a COPR XRPD pattern labeled with the peak positions of the identified phases.

Apart from the crystalline phases identified by XRPD, COPR also contains amorphous material. The quantification of the amorphous content is important in order to reduce the uncertainty in the estimation of the concentrations of the crystalline

Table 1
Total Cr^{6+} concentrations in mg/kg for six COPR samples

	Cr^{6+} (mg/kg dry COPR)
COPR-A-1	3720
COPR-B1-1	4840
COPR-B1-2	7216
COPR-B2-1	6560
COPR-C-1	11600
COPR-C-2	10300

phases; the internal standard (corundum) was used as a known variable that interpolated the unknown amorphous content from the quantification algorithm.

From the phases identified in the SA7 COPR XRPD patterns, only CACs contain Cr^{6+} explicitly in their chemical formula. These are cementitious phases, similar to monosulfate ($\text{Ca}_4\text{Al}_2\text{O}_6(\text{SO}_4)\cdot 12\text{H}_2\text{O}$) found in concrete, with chromate substituted for sulfate in the crystal interlayer. They were found at different hydration states (9, 12 or 14 H_2O). Palmer [18] identified CAC in Cr^{6+} -contaminated concrete as $\text{Ca}_4\text{Al}_2\text{O}_6(\text{CrO}_4)\cdot 15\text{H}_2\text{O}$ and highlighted the relevance of this compound for highly alkaline systems containing Cr^{6+} , including COPR. However, CACs were never previously reported as the primary Cr^{6+} -containing phases in COPR. Weng et al. [19] and Meegoda et al. [20] studied COPR obtained from N.J. deposition sites, but were not able to identify Cr^{6+} -containing phases by XRPD. Hillier et al. [21] investigated COPR deposited in Scotland and reported the following phases as candidates for Cr^{6+} speciation: hydrogarnet, hydrocalumite and ettringite. Hillier et al. [21] concluded that hydrogarnet and hydrocalumite retain most of the chromate in COPR, based on electron probe microanalysis observations, coupled with recalculation of structural formulae for these phases. In the case of SA7 COPR patterns, hydrotalcites are reported as the minerals matching the peak at 11.3° (Fig. 1), as they produced a better fit in the structural model for Rietveld analysis. Hydrotalcites and hydrocalumite have identical structure and belong to the general group of layered double hydroxides; they differ in the chemical composition (hydrocalumite consists of calcium, aluminum and chloride, while hydrotalcites are magnesium–aluminium–iron carbonate compounds). It is possible that layered double hydroxides also retain chromate in the interlayer, apart from carbonate and/or hydroxyl. The composition of hydrotalcites and their role in Cr^{6+} speciation cannot, however, be independently resolved by XRPD. Similarly, the role of hydrogarnets and ettringite requires microscopic analyses, as these compounds do not explicitly contain chromate in their chemical formula. Cr^{6+} -ettringite was not identified in any of the COPR XRPD patterns; a geochemical

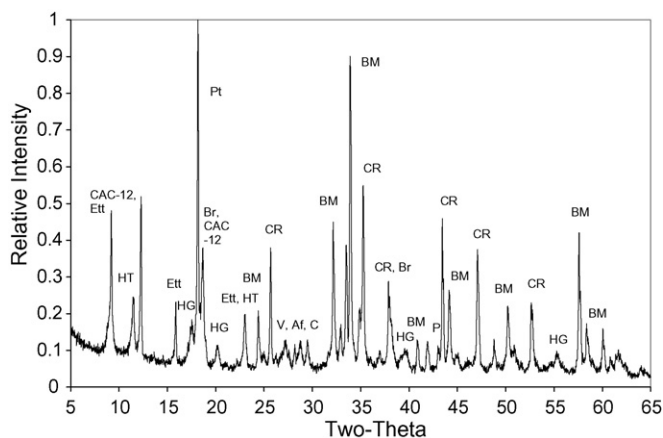


Fig. 1. XRPD pattern of sample COPR-B1-2 (BM: brownmillerite; P: periclase; Br: brucite; Pt: portlandite; C: calcite; V: vaterite; HG: hydrogarnet; HT: hydrotalcite; Et: ettringite; Af: afwillite; CR: corundum; CAC-12: calcium aluminum chromium oxide hydrate).

modeling study also demonstrated that this phase is not thermodynamically favored at the present COPR conditions [6]. Consequently, the focus of this study was to quantitatively assess to what extent CACs acted as the Cr⁶⁺-reservoir in SA7 COPR.

Quantitative XRPD analyses coupled with mass balances for Cr⁶⁺ were conducted for selected samples. The results are presented from two perspectives: (a) the refinement procedure, the difficulties and uncertainties in quantitative analysis, and (b) the role of CACs in Cr⁶⁺ speciation according to the Rietveld analysis.

3.1. Refinement procedure and evaluation of uncertainties

With the chief Cr⁶⁺-containing phase identified, its quantification by the Rietveld method entails the production of a synthesized diffraction pattern, which fits to the experimentally obtained pattern as closely as possible. The synthesized pattern is produced through the calculation of XRPD reflections from a known crystal structure for each of the identified phases and the merging of the calculated reflections of all phases to produce the best pattern in a least-square fitting analysis. A comprehensive overview of XRPD principles and the Rietveld method is provided in Bish and Post [22] and Young [23].

Quantitative XRPD analysis poses several questions and challenges, related both to the experimental settings that produce the actual XRPD pattern and the mathematical model that produces the calculated pattern. The primary issues identified in this study were:

- (a) Sample preparation: sample preparation is significant for the accuracy and precision of Rietveld analysis, as it aids in minimizing systematic errors, such as preferred orientation. A comprehensive overview of sample preparation methods and the issues associated with particle size are presented in Bish and Post [22]. Knowing that COPR is susceptible to mineralogical changes upon the influence of heat and chemicals, sample preparation methods such as mechanical pulverization and spray drying were avoided in this study.
- (b) Choice of scan parameters: the range of two-theta values, step size and counting time have a significant effect on the quality of the obtained data and thus, on the accuracy and precision of Rietveld analysis. The range 5–65° was selected because all COPR phases reveal their main peaks in this range of two-theta values; higher angles present extensive peak overlap between different phases and complicate, rather than facilitate, the Rietveld analysis. The step size was chosen according to the recommendations of McCusker et al. [24] to be more than five times smaller than the inherent peak broadening of the instrument (which was measured to be 0.158°). The chosen scan parameters were found to produce good peak resolution and intensity and low noise; the detection limit decreases and random errors associated with counting statistics are minimized in this way [22,23].
- (c) Choice of structural model: the structural model consists of the individual structures of the crystalline phases present in the mixture and identified in the XRPD pattern. Qualitative analysis of a XRPD pattern is therefore necessary

prior to any quantitative analysis method. The quality of the structural model is essential to the success of the method, i.e., a poor choice of input phases will result in poor fitting. Conversely, poor fitting will assist in pinpointing false identification of crystalline phases in a pattern; thus, qualitative and quantitative analysis act in a complementary, self-correcting manner. Furthermore, there may be a variety of published structures for a single phase, e.g. there are 125 structural files for quartz in the ICSD. The criteria to select the structures used in this study were that they should: (i) produce a good fit, (ii) be published in a crystallography journal, and (iii) have been studied under normal temperature and pressure conditions that are the most pertinent for the COPR matrix at deposition sites. Overall, common phases, such as quartz, calcite, corundum, etc., are widely studied and a multitude of structural files are available; the less common the compound, the less choice available. In the case of the CACs in COPR there is no published structure for these compounds, so that their powder diffraction files (PDFs) were used as input for the Rietveld model.

- (d) Choice of refinable parameters: the production of the synthesized pattern requires the choice of global parameters, which refer to the entire pattern, and phase parameters that address each phase in the structural model. A comprehensive overview of refinable parameters and issues is presented in Young [23]. The choice of parameters depends on pattern complexity, the purpose of the refinement and the experience of the user. For example, quantitative phase analysis in environmental applications does not require the precise determination of atomic positions or lattice constants, especially for well studied minerals, such as quartz; these can be kept constant at their initial values, simplifying the mathematical model. In general, the set of parameters should be chosen to produce the best fit, while maintaining the physical meaning of the refined parameters, i.e., avoiding erroneous curve fitting. The current study was based on the Rietveld refinement guidelines of McCusker et al. [24], and the refinement strategies proposed by Young [23] and Winburn et al. [25]. The latter group studied coal-combustion by-products, a cementitious system analogous to COPR.

From all of the presented issues, the greatest challenge to assess the accuracy of quantitative results proved to be the lack of structural information for the CACs. The major difference between using crystal structure data and powder diffraction files to conduct Rietveld quantification is that the latter requires an experimental value, termed as reference intensity ratio (RIR) [22]. If this value is not reported in the PDF, the quantification of the phase is not possible, regardless of the software or the experimental conditions. Furthermore, this value is subject to experimental aberrations and is heavily dependent on the conditions used to obtain it. A round robin study conducted by the International Union of Crystallography to assess the sources of error in QPA [26,27], showed that the use of inappropriate reference intensity ratios played the greatest role in error propagation, along with user inexperience and excessive microabsorption correction.

Table 2
Quantitative XRPD results and Cr⁶⁺ mass balance for sample COPR-A-1 using RIR values 0.9 and 3 for the phase CAC-9

Rietveld results	PDF ^a	RIR 0.9	RIR 3.0
Brownmillerite	30-0226	34.1	42
Periclase	45-0496	1.3	1.6
Brucite	07-0239	7.0	9.0
Portlandite	04-0733	1.0	1.2
Calcite	05-0586	5.7	6.9
Hydrogarnets	24-0217	10.6	14.9
Hydrotalcites	24-1091	4.9	4.0
Ettringite	41-1451	4.0	4.2
Afwillite	29-0330	7.8	9.7
CAC-9	42-0063	23.6	6.6
CAC-12	41-0478	n.d.	n.d.
CAC-14	52-0654	n.d.	n.d.
Mass balance for Cr ⁶⁺ in mg/kg			
Cr ⁶⁺ in CAC-9		20768	5808
Cr ⁶⁺ total		3720	3720

n.d.: non-detected.

^a From ICDD [16].

A similar challenge was encountered in the case of COPR and CACs. Despite the fact that the three CAC compounds are identical except for the state of hydration, the PDFs provide an RIR of 0.9 for CAC-9 (42-0063), 1.0 for CAC-12 (41-0478) and 3.0 for CAC-14 (52-0654). A change in the RIR from 3.0 to 1.0 will yield a weight percentage about three times higher. Table 2 presents the quantitative results for sample COPR-A-1 using the published value of RIR 0.9 and an estimated RIR 3.0 for the identified CAC-9. The mass balance for Cr⁶⁺ was performed by calculating the percentage of Cr⁶⁺ contained in CAC-9 based on its chemical formula (Ca₄Al₂O₆(CrO₄)·9H₂O) and extrapolating it to 1 kg dry COPR.

The results show that the RIR 0.9 yields an unrealistically high weight percentage for CAC-9; the mass balance shows that the Cr⁶⁺ bound in 23.6% (w/w) CAC-9 by far exceeds the total Cr⁶⁺, as measured by alkaline digestion (Table 2). Conversely, the weight percentage for CAC-9 using the RIR 3.0 corresponds to a Cr⁶⁺ concentration that is close to the total Cr⁶⁺ (Table 2). It should be noted that the amorphous content was not measured in

that pattern. An amorphous content of 35% in the quantification results with RIR 3.0 would bring the Cr⁶⁺ concentration bound in CAC-9 to 3775 mg/kg, or roughly the total Cr⁶⁺. However, 35% is a realistic number for the COPR amorphous content, as will be discussed in subsequent sections. A similar discussion holds for the phase CAC-12. Therefore, the same RIR (3) was used to quantify all three CAC phases in COPR, as it yielded realistic results, and because it is also close to the calculated RIR (2.5) for the kuzelite structure (file 100138 in the ICSD). This phase is similar to the CACs, with sulfate instead of chromate in the crystal and is encountered as monosulfate in the cement literature [6].

3.2. Evaluation of the role of CACs in Cr⁶⁺ speciation

CACs were identified in 75% of the COPR patterns obtained from 120 discrete samples spatially distributed across the site. The frequency of CAC presence increases to 85%, if non-COPR (native soil) samples are excluded from the statistics. In other words, the presence of CACs was predominant across the entire site. Rietveld quantification of the obtained patterns yielded concentrations that ranged from 1% to 28% (w/w) CAC. However, these results did not include the estimation of the amorphous material. Therefore, mass balances were conducted for selected samples, for which total Cr⁶⁺ and internal standard analyses were performed.

Table 3 presents the quantitative results for five COPR samples, two from Zone B1, one from Zone B2 and two from Zone C. The average value and standard deviation of the duplicate analyses are given for each mineral group. Calcium carbonate includes the results for all crystalline forms, calcite, aragonite and vaterite; hydrogarnets were modeled as the sum of the two end members, one Al-rich (katoite) and one Fe- and Si-rich (hydroandradite). Hydrotalcites include sjoegrenite and quintinite, while CACs are the sum of CAC-12 and CAC-14. No CAC-9 was detected in any of the samples, and CAC-14 was the predominant form encountered in all samples, with the exception of COPR-B1-2, where CAC-12 was the primary CAC phase identified. The modification of the RIR from 1.0 to 3.0 was, therefore, only significant for this sample. The analysis with the

Table 3
Average and standard deviation values for major mineral groups in % w/w dry COPR for five COPR samples

	COPR-B1-1		COPR-B1-2		COPR-B2-1		COPR-C-1		COPR-C-2	
	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.	Average	S.D.
Brownmillerite	25.9	0.1	21.7	0.2	19.4	0.7	1.8	0.0	2.7	0.3
Periclase	2.3	0.2	1.0	0.0	2.7	0.2				
Brucite	4.7	1.1	6.8	0.6	6.9	0.9	1.7	0.1	3.2	0.2
Portlandite			1.4	0.3					11.1	0.2
Calcium carbonate	7.0	0.4	6.5	1.3	7.0	1.2	15.8	1.4	18.5	0.1
Quartz	2.4	0.5	n.d.	n.d.	5.2	1	n.d.	n.d.	0.4	0.5
Hydrogarnets	13.5	0.4	10.4	0.7	6.5	0.8	18.8	0.2	7.3	0.1
Hydrotalcites	4.8	1.7	3.2	0.7	5	0.6	4.8	0.6	8.5	0.9
Ettringite	1.2	0.2	5.6	1.1	2	0.3	4.6	0.1		
Afwillite	3.0	0.2	3.3	0.5	3.8	0			9.3	0.5
CAC	3.0	1.3	5.2	0.1	2.8	0.4	11.5	0.8	10	1.5
Amorphous	32.2	1.7	34.8	4.4	38.7	0.2	41	1.3	28.7	1.3

n.d.: non-detected.

RIR 1.0 given in the original PDF file of CAC-12 yielded a high amount of CAC-12 that could not conform with the mass balance on Cr^{6+} . The RIR 3 was used, therefore, for all CAC quantifications.

The standard deviation values (Table 3) show that there is very good agreement between the duplicate analyses for all samples. They are generally in the range of values of the estimated standard deviation (ESD) values that are calculated by the software for each set of quantification results based on random error statistics. Random error statistics are associated with the errors introduced by counting statistics, so that they represent the minimum possible error if all other effects are excluded [22]; they are generally low compared to errors introduced by sample variability, systematic errors in the quantification strategy, user inexperience, etc. [23]. ESD values for the COPR phases were between 0.1% and 0.5% (w/w), with the higher values corresponding to phases with higher amount, such as brownmillerite and corundum. The standard deviation values calculated based on the duplicate analyses were higher than the ESD values only when there were actual differences in the two patterns. Ettringite and CACs were the phases with the highest standard deviations in all samples due to sample variability, as evidenced by the different relative intensities of these phases in the duplicate patterns. This highlights the extremely variable composition of the COPR material, as the sample preparation involved a relatively small amount of material with high degree of homogenization. The amorphous phase also presents high standard deviations, because it is calculated based on the internal standard (20% corundum). Any error in the quantification of corundum propagates in the quantification of the amorphous phase and is magnified because of the high amorphous content. Consequently, the difficulty in evaluating quantitative results from different COPR samples arises mainly from the non-uniformity of the material, rather than from the analysis method itself, provided that a consistent refinement strategy is pursued. Other effects, such as the variable preferred orientation observed in portlandite, or the shift in two-theta values due to experimental aberrations, were not found to affect the quantitative results to a higher extent compared to the error predicted by the ESD values. Obviously, other systematic errors induced by the refinement strategy itself cannot be assessed by this type of analysis; complementary methods to evaluate the results are necessary, such as the mass balances.

Fig. 2 presents the amount of Cr^{6+} bound in CACs in mg/kg, as compared to the total Cr^{6+} concentration measured by alkaline digestion and colorimetric analysis. CACs were found to bind ~50% of the total Cr^{6+} in both B1 samples, ~33% in the B2 sample and ~75% in the two Zone C samples, based on the average values of the Rietveld results. These numbers vary between 25% and 70% for sample COPR-B1-1 if the average value and the standard deviation are considered. The range of values for sample COPR-C-2 is also relatively large, between 65% and 85% of the total Cr^{6+} bound as CACs. The remaining three samples present a narrower range of values, due to the lower standard deviation in the CAC concentration.

Overall, CACs seem to play a major role in Cr^{6+} speciation in COPR. Fig. 3 shows the correlation between Cr^{6+} bound in

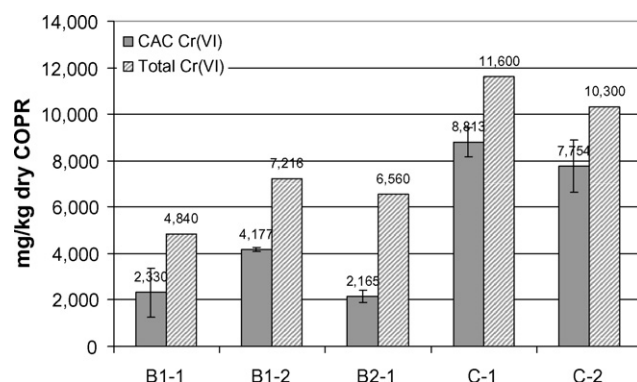


Fig. 2. CAC-bound vs. total Cr^{6+} in mg/kg dry COPR for five COPR samples.

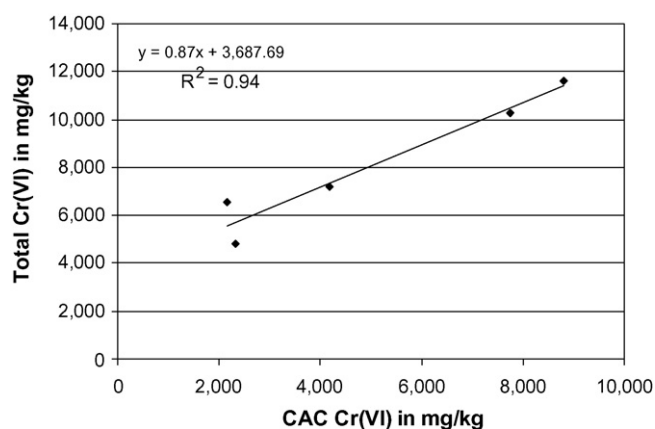


Fig. 3. Correlation between CAC-bound and total Cr^{6+} based on five COPR samples.

CACs and total Cr^{6+} . The linear correlation coefficient is 0.94, which indicates that CACs are an important sink for hexavalent chromium in COPR and tend to form in higher amounts, when higher concentrations of Cr^{6+} are present within the matrix. This mechanism is similar to the formation of calcite, when carbonate enters the system, i.e., carbonate will be scavenged predominantly by calcite, when it is introduced in the high pH, Ca-rich environment of COPR. However, CAC formation depends also on other factors, such as the availability of alumina, which is considered to be the limiting factor for hydration product formation in COPR. The presence of sulfate is also significant, as CACs are metastable with respect to ettringite, based on COPR geochemical modeling [28].

The mass balances also show that there is Cr^{6+} unaccounted for in all samples. As pointed out previously, other phases may also bind part of Cr^{6+} , while the amorphous phase is also of unknown composition. Further studies with methods alternative to XRPD are necessary to evaluate the remaining Cr^{6+} speciation.

4. Conclusions

The application of quantitative X-ray powder diffraction analysis on media contaminated with trace elements offers the

potential to both qualitatively and quantitatively determine the speciation of the contaminants. The methodology to investigate metal speciation by qualitative and quantitative XRPD was demonstrated in the case of chromite ore processing residue (COPR), which is a cementitious waste containing hexavalent chromium; its mineralogy and chemistry resembles that of an S/S treated soil.

The immobilization mechanisms in a cementitious matrix include precipitation, physical and chemical inclusion, and sorption. XRPD aids in identifying precipitates containing the contaminant explicitly in their chemical formula and also other components that may immobilize the metal by means of isomorphous substitution. In the case of COPR, the precipitates containing hexavalent chromium were calcium aluminum chromium oxide hydrates (CACs), cementitious phases similar to monosulfate in concrete. They were identified in 85% XRPD patterns from COPR samples obtained over the entire vertical and horizontal extent of COPR deposition site. Their quantitative contribution to Cr⁶⁺ speciation in COPR was then assessed by means of XRPD quantitative analysis by the Rietveld method, coupled with mass balances.

The Rietveld results showed that CACs immobilize Cr⁶⁺ in COPR to variable extent, ranging from 25% up to 85% of the total Cr⁶⁺. The variability in the CAC content arises mainly from sample variability, rather than the uncertainty in the analysis itself. When the average values of duplicate analyses were considered, the linear correlation between the CAC-bound and total Cr⁶⁺ yielded a correlation coefficient of 0.94, indicating that the CAC content increases proportionally with total Cr⁶⁺ content. In other words, CACs constitute an important sink for hexavalent chromium in COPR.

However, the mass balances also showed that CACs do not account for all Cr⁶⁺ present in COPR. As no other mineral phase explicitly contains Cr⁶⁺ in its structure, other phases that could include it as isomorphous substitution are hydrotalcites and hydrogarnets. Complementary microscopic analyses (SEM/EDX, EMPA) are therefore necessary to further refine Cr⁶⁺ speciation in COPR.

Overall, the Rietveld analysis of COPR showed that a consistent analysis strategy yields results with lower estimated standard deviations compared to the standard deviations induced by sample variability. The main uncertainties in the method arise from the availability of crystal structure data, the accuracy of published powder diffraction data and the choice of the refinement strategy itself. The application of complementary analyses, such as mass balances, microscopic, chemical and thermal analyses, may be of assistance in identifying systematic errors in quantitative XRPD analysis.

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References

- [1] J.R. Conner, *Chemical Fixation and Solidification of Hazardous Wastes*, Van Nostrand Reinhold, New York, 1990.
- [2] U.S. EPA 549-B-99-002, U.S. Environmental Protection Agency (EPA), *Solidification/Stabilization Resource Guide*, 1999.
- [3] *Process Descriptions Baltimore Plants*, Allied Signal, 1982.
- [4] P.J. Lioy, N.C.G. Freeman, T. Wainman, A.H. Stern, R. Boesch, T. Howell, S.I. Shupack, *Microenvironmental analysis of residential exposure to chromium-laden wastes in and around New Jersey homes*, *Risk Anal.* 12 (1992) 287–299.
- [5] D.H. Moon, D. Dermatas, P. Dutko, M. Chrysochoou, C. Christodoulatos, *Ettringite-induced laboratory swelling in chromite ore processing residue*, in: *In-situ and On-site Bioremediation Symposium, Conference Proceedings*, Battelle, Columbus, OH, 2005.
- [6] M. Chrysochoou, D. Dermatas, *Evaluation of ettringite and hydrocalumite formation for heavy-metal immobilization: a literature review and experimental study*, *J. Hazard. Mater.* 136 (2006) 20–33.
- [7] D. Dermatas, X. Meng, *Utilization of fly-ash for stabilization/solidification of heavy metal contaminated soils*, *Eng. Geol.* 70 (2003) 377–394.
- [8] J. Duchesne, E.J. Reardon, *Lime treatment of fly ash: characterization of leachate composition and solid/water reactions*, *Waste Manage.* 19 (1999) 221–231.
- [9] M.Y.A. Mollah, F. Lu, D.L. Cocke, *An X-ray diffraction XRD and Fourier transform infrared spectroscopic FT-IR characterization of the speciation of arsenic V in Portland cement type-V*, *Sci. Total Environ.* 224 (1998) 57–68.
- [10] D.H. Moon, D. Dermatas, N. Menounou, *Arsenic immobilization by calcium–arsenic precipitates in lime treated soils*, *Sci. Total Environ.* 330 (2004) 171–185.
- [11] H.M. Rietveld, *A profile refinement method for nuclear and magnetic structures*, *J. Appl. Crystallogr.* 2 (1969) 65–71.
- [12] D. Dermatas, R. Bonaparte, M. Chrysochoou, D.H. Moon, *Chromite ore processing residue: hazardous contaminated soil or solid waste?* *J. ASTM Int.* 3 (7) (2006).
- [13] U.S. EPA, SW-846, Method 3060A, *Alkaline digestion for hexavalent chromium*.
- [14] U.S. EPA, SW-846, Method 7196A, *Chromium, hexavalent (colorimetric)*.
- [15] *Jade Version 7.1*, Material's Data Inc. California, USA, 2005.
- [16] *Powder Diffraction File, PDF-2 Database Release*, announcement of new database release, International Centre for Diffraction Data (ICDD), 2002.
- [17] *Inorganic Crystal Structure Database (ICSD)*, Fachinformationszentrum Karlsruhe, Germany, 2005.
- [18] C.D. Palmer, *Final Report: attenuation of chromium in alkaline environments chromium substitution in ettringites and C4AH12-monosulfates*, EPA Grant Number: R823388, 1998.
- [19] C.H. Weng, C.P. Huang, H.E. Allen, P.B. Leavens, P.F. Sanders, *Chemical interactions between Cr⁶⁺ and hydrous concrete*, *Environ. Sci. Technol.* 30 (1996) 371–376.
- [20] J.N. Meegoda, W. Kamolpornwijit, D.A. Vaccari, A.S. Ezeldin, B.A. Noval, R.T. Mueller, S. Santora, *Remediation of chromium-contaminated soils, bench scale investigation, practice periodical of hazardous, Toxic Radioact. Waste Manage.* 3 (3) (1999) 124–131.
- [21] S. Hillier, M.J. Roe, J.S. Geehoed, A.R. Fraser, J.G. Farmer, E. Paterson, *Role of quantitative mineralogical analysis in the investigation of sites contaminated by chromite ore processing residues*, *Sci. Total Environ.* 308 (2003) 195–210.
- [22] D.L. Bish, J.E. Post, *Reviews in mineralogy*, *Modern Powder Diffraction*, vol. 20, Mineralogical Society of America, Washington, 1989.
- [23] R.A. Young, *The Rietveld Method*, Oxford University Press, New York, 1993.
- [24] L.B. McCusker, R.B. von Dreele, D.E. Cox, D. Louer, P. Scardi, *Rietveld refinement guidelines*, *J. Appl. Crystallogr.* 32 (1999) 36–50.
- [25] R.S. Winburn, S.L. Lerach, B.R. Jarabek, M.A. Wisdom, D.G. Grier, G.J. McCarthy, *Quantitative XRD analysis of coal combustion by-products by the Rietveld method. Testing with standard mixtures*, *Adv. X-ray Anal.* 42 (2000) 387–396.

- [26] I.C. Madsen, N.V.Y. Scarlett, L.M.D. Cranswick, T. Lwin, Outcomes of the international union of crystallography commission on powder diffraction round robin on quantitative phase analysis: samples 1a to 1h, *J. Appl. Crystallogr.* 34 (2001) 409–426.
- [27] N.V.Y. Scarlett, I.C. Madsen, L.M.D. Cranswick, T. Lwin, E. Groleau, G. Stephenson, M. Aylmore, N. Agron-Olshina, Outcomes of the international union of crystallography commission on powder diffraction round robin on quantitative phase analysis: samples 2,3,4, synthetic bauxite, natural granodiorite and pharmaceuticals, *J. Appl. Crystallogr.* 35 (2002) 383–400.
- [28] M. Chrysochoou, D. Dermatas, D.H. Moon, C. Christodoulatos, M. Wazne, C. French, J. Morris, M. Kaouris, Investigation of barium treatment of chromite ore processing residue (COPR), *J. ASTM Int.* 3 (6) (2006).