Evaluation of ettringite and hydrocalumite formation for heavy metal immobilization: Literature review and experimental study

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Abstract

The immobilization of heavy metal oxyanions like chromate, arsenate and selenate, has proven to be a challenging task as they are highly mobile in alkaline environments involving S/S of contaminated media. Ettringite, a pozzolanic phase that forms in cementitious materials, has been proposed as a viable immobilization mechanism for oxyanions, wherein the oxyanion may substitute for sulfate in the ettringite structure. A literature review on the immobilization potential of ettringite showed that the substitution potential exists from the thermodynamic point of view where the formation of substituted ettringites occurs under strictly controlled conditions. The pH control over a narrow range is essential for ettringite stability; it becomes even narrower for substituted ettringites, as competing effects with sulfate ettringite and monophases are significantly affected by pH. The presence of sulfate has a catalytic effect on oxyanion incorporation in ettringite. Rapid leaching may occur when the treated media is exposed to sulfate influx. Conversely, monophases seem to be more suitable than ettringite for oxyanion immobilization, mainly as they control oxyanion solubility to lower levels than ettringite. A shift to the thermodynamic equilibrium caused by a shift in environmental conditions may result in monophase conversion to ettringite, which may lead to catastrophic expansion, as widely demonstrated in the cement and soils literature. Overall, the sensitivity of phase equilibria in cement-like systems involving oxyanions is significant with regard to multiple parameters and it is uncertain to what extent these can be predicted and/or controlled in the field.
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1. Introduction

Heavy metal contamination of environmental media due to historical uncontrolled disposal or poor management of industrial wastes is acknowledged as one of the most widespread environmental problems, especially in industrialized areas. Since heavy metals cannot be destroyed, as is the case with organic contaminants, there are two major options for dealing with heavy metal contamination:

1. Chemical transformation into a compound that reduces the potential hazard to tolerable levels for the human health and the environment. This approach is generally referred to as *stabilization* [1] and includes one or more of the following mechanisms:
   - conversion from a toxic to a non-toxic species, e.g., reduction of Cr(VI) to Cr(III);
   - reduction of the mobility by forming highly insoluble compounds, e.g., precipitation of calcium chromate as a Cr(VI) immobilization mechanism;
   - chemical inclusion, through some form of isomorphic substitution, into newly formed pozzolanic products, such as calcium aluminate hydrates (CAH) and calcium silicate hydrates (CSH) [2].
2. Reduction of the metal mobility through physical encapsulation in low-permeability materials, in the *solidification* process [1]. Stabilization and solidification techniques are commonly referred to as S/S techniques.

S/S processes involve the addition of binding agents, among which cement and cementitious materials (lime, fly ash, blast furnace slag, etc.) became increasingly popular in the previous decade, since they are effective both from the environmental and financial point of view [3]. Since then, regulatory efforts, such as the Directives of the European Union, have shifted towards strategies and technologies that promote waste recycling and/or energy recovery. Such approaches are, however, not possible in many cases, whether from the technological or economic

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point of view and, more importantly, due to their high cost of implementation they presently cannot address the extremely high number of contaminated sites across the world (e.g., it was estimated in 1999 [4] that the European Union alone had over 300,000 environmentally impacted sites across its territory, a number that will grow as additional countries joined the EU). It is therefore to be expected that S/S will continue to be a widely applied approach to mitigate contamination problems in a cost-effective way.

Several authors have investigated the immobilization mechanisms and efficiency of S/S treatment involving a variety of binding agents. The behavior of cationic metals is mainly shown to be controlled by adsorption and inclusion mechanisms followed by precipitation as insoluble hydroxides. Dermatas and Meng [2] found, for example, lead retention in cement-stabilized waste to be mainly controlled by adsorption, while trivalent chromium precipitated as hydroxide at pH values above 6. The effective immobilization of oxanions, such as chromate and arsenate is, on the other hand, more problematic, as they often occur in highly alkaline environments and are mobile under these conditions. van der Sloot [5] conducted a study on the leachability of several cations and oxanions in cement mortars and cement-stabilized waste and found that the cementitious matrix is much more tolerant for cations than for oxanions. This was attributed to the lack of immobilization mechanisms at high pH, since sorption efficiency for anions decreases with increasing pH, whereby there is limited to no contribution from solubility-controlling phases for oxanions as is the case with cations. The identification of such precipitates is, therefore, critical in S/S applications that address oxanions.

Ettringite $(Ca_6Al_2(SO_4)_3(OH)_{12}·26H_2O)$ is a phase that is, generally, present in cement systems, as it forms through the reaction of calcium and alumina, which are available in cementitious matrices, with sulfate either inherently present in the cement paste or introduced into the system through an outside source [6]. Its crystal has a needle-like form, in which $[Al(OH)_6]^{3-}$ octahedra, linked together with Ca^{2+}, make up columns that run parallel to the needle axis, while sulfate and water molecules are accommodated in the channels between them [7]. The channel structure enables the relatively easy replacement of sulfate with oxanions of similar structure and radius, such as chromate, arsenate, vanadate and selenate, to mention only some from the variety of species encountered in the literature [8–11]. Several studies have been conducted in order to investigate oxanion substitution in the ettringite structure, either by synthesis experiments or on artificially contaminated cementitious systems, which will be presented in the following section. These studies have, by and large, demonstrated the theoretical potential of ettringite for waste immobilization. They were conducted, however, under controlled laboratory conditions and included specific parameters (pH and selected type of contamination), while excluding others that may play an important role in the realization of the substitution potential (temperature, competing ion effects and carbonation). Moreover, there is no published large-scale application of this approach.

The present study focuses on the following questions that arise:

1. To what extent will the immobilization potential of ettringite be realized in the field under specific conditions (pH, type and concentration of contamination, materials used as binders)?
2. Are there any other concerns with regard to the field application (geotechnical implications, reversibility of immobilization mechanism)?

The elucidation of these questions is performed on the basis of:

(a) comprehensive literature review;
(b) summary and interpretation of thermodynamic data obtained through the synthesis experiments;
(c) experimental study on a cementitious type of waste containing chromate (Chromite Ore Processing Residue, abbreviated as COPR);
(d) geochemical modeling evaluation of the experimental results on COPR;

2. Literature review

2.1. Formation and properties of ettringite

Ettringite formation has been studied in synthesis reactions, as well as in cement as result of reactions of calcium aluminate phases with sulfate.

Most synthesis experiments reported in the literature are based on the "saccharate" method reported originally by Carlson and Berman [12]. A CaO supersaturated, 10% (v/v) sucrose solution is mixed with $Na_2O·Al_2O_3$ and Na_2SO_4 in stoichiometric amounts. Sodium sulfate can be replaced by an oxanion salt to obtain substituted ettringites (Klemm and Bhatty [8] provide a list of salts to synthesize substituted ettringites). Small amounts of NaOH are used to control the pH at high values that are optimal for ettringite stability.

The same process without the addition of sucrose is referred to as the "paste reaction" method [11]. Poellmann et al. [11] noted a difference in crystal shapes, with a short-prismatic habit noted in ettringites formed by the saccharate method and a more characteristic elongated prism form resulting from the paste reaction method. Cody et al. [13] conducted a study on the effects of different compounds on ettringite nucleation and growth and reported that the presence of sucrose resulted in the formation of very small ettringite needles. In general, the presence of chemicals will affect the formation kinetics, crystal shape and size of ettringite. The crystal morphology has geotechnical implications, such as development of strength and swelling pressures in a cementitious matrix. The size of the crystal is also important with regard to its stability, i.e. small, poorly crystallized crystals will tend to dissolve more easily than large and well-formed crystals and thus be more prone to releasing hazardous compounds into solution. In general, the use of chemicals such as sucrose to facilitate a chemical reaction is not recommended when conducting a feasibility study on immobilization potential, as such conditions would not generally apply to the field.

Other authors [14,15] synthesized ettringite by preparing tricalcium aluminate through a reaction of $CaCO_3$ with Al_2O_3 at 1450 °C and mixing $3CaO·Al_2O_3$ (C_3A in cement nomenclature) with gypsum and water. This method is generally slower and requires more experimental effort, but ensures a final product free of chemical contaminants [14].

Phase equilibria in the $CaO–Al_2O_3–CaSO_4–H_2O$ system, which represents the stability domain of calcium aluminate phases in cements, were studied by Damidot and Glasser [16,17] at 50 and 85 °C, as well as at 25 °C in the presence of alkali (Na_2O).

The following solid phases are possible in this system [16]:

a. ettringite (triphase or AFt in cement nomenclature): $3CaO·Al_2O_3·3CaSO_4·32H_2O$;
b. monosulfate (monophase or AFm): $3CaO·Al_2O_3·CaSO_4·12H_2O$;
c. gypsum: $CaSO_4·2H_2O$;
d. hydrogarnet: $3CaO·Al_2O_3·6H_2O$ (other calcium alumina hydrates are also possible but they are metastable with respect to hydrogarnet);
e. portlandite: $Ca(OH)_2$;
f. gibbsite: $Al(OH)_3$.

The equilibrium of interest for an oxyanion immobilization mechanism is that of ettringite versus monophase. Gypsum is stable at pH values lower than 10.5 or when soluble alumina is scarce. Hydrogarnet, gibbsite and portlandite are phases that contain no sulfate and will not be considered further, as they cannot play a significant role in the immobilization of hazardous oxyanions.

Damidot and Glasser [16] found as a result of thermodynamic calculations that ettringite was always stable with respect to the monophase at 25 °C, while sulfate remained in solution at low concentrations and hydrogarnet formed instead of ettringite. However, in Portland cement, monosulfate has been observed to be stable at low sulfate concentrations during the early hydration state [6]. Damidot and Glasser [16] attributed this phenomenon to non-equilibrium conditions during cement hydration and to kinetic inhibition of the monosulfate conversion to ettringite.

An experimentally derived rule in cement literature for ettringite formation over monosulfoaluminate is that the alumina-to-sulfate ratio in the solid has to be lower than 1 [18].

The type of chemical binder influences significantly the availability of soluble calcium, aluminum and sulfate that comprise the three axes of the stability diagram. Overall, the main types of materials to consider in a S/S application are:

(1) *Cement*: There are different types of cement, such as Portland cement (which has subcategories with different physicochemical properties) and high-alumina cement. Klemm and Bhatty specifically studied the immobilization potential of hazardous oxyanions in the ettringite structure in what was a thorough and comprehensive research project of the Portland Cement Association [8]. In the framework of that study, they examined different combinations of cements and proposed a mixture of Portland cement type V with high-alumina cement and gypsum or anhydrite in order to achieve early formation of ettringite, when heavy metals are still mobile and can easily be incorporated into the ettringite structure. The Cement Association of Canada [19] mentions "ettringite cements" as a specific category of calcium sulfoaluminate (CSA) cements that can be used for waste stabilization. They are formulated to form large amounts of ettringite and stabilize particular metallic ions within the ettringite structure. CSA clinkers are based on yeelimite ($4CaO·3Al_2O_3·SO_3$) mixed with belite ($2CaO·SiO_2$) and an aluminate or ferrite phase, with further addition of 16–25% gypsum or anhydrite [20]. The main hydration products of this formula are ettringite and CSH, so that early strength development can be achieved at room temperature faster compared to Portland cement [21]. CSA cements have been developed and used in China, while increasing interest is demonstrated in the rest of the world due to the economical and mechanical advantages that these cements offer [21,22]. The application of CSA cements in waste immobilization is, however, a new area, which requires additional testing and research to demonstrate its ability to substantially increase the capacity to immobilize heavy metals and oxyanions as compared to other types of cements.

(2) *Lime*: Lime is widely used as a stabilizing agent for expansive clays. It acts as a cementitious agent by producing highly alkaline conditions, in which silica and alumina go into solution and react with the available calcium to form pozzolanic products, increasing strength, impermeability and durability to chemical attack [23]. In the case of S/S applications, addition of solely lime is possible when an alumina and silica source is available within the waste itself in order for the cementing action to take place. Otherwise, the use of further admixtures is necessary, such as those considered in the following paragraph.

(3) *Pozzolanic/cementitious materials*: These can be natural products or by-products from industrial processes. Natural products include volcanic ashes and clays, such as bentonite. Modified clays, like metakaolin, have also been developed as stabilization agents [24]. Klemm and Bhatty [8] tested the use of metakaolin as an admixture to cement and found that it showed very good strength development and no evidence of expansion. It reduced, however, the amount of ettringite formed, as soluble silica scavenged the available calcium to form CSH. Solem and McCarthy [25] compared the reactivity of four types of cementitious materials, with regard to their ability to form ettringite:
a. fly ash of different compositions;
b. flue gas desulfurization (FGD) residue;
c. fluidized bed combustion (FBC) residue;
d. limestone injection multistage burner (LIMB) residue.

All of the materials, with the exception of low-calcium fly ash, proved to be satisfactory sources of soluble calcium for ettringite formation. The limiting factors were soluble alumina and sulfate. Sulfate is not considered further, as it should be replaced by oxyanions in the case of S/S treatment. Soluble alumina was sufficient in the cases of fly ash, FGD residue and LIMB material.

The latter formed the highest amount of ettringite, which was estimated to be 20% by quantitative XRPD. FBC residue, on the other hand, proved to be scarce in soluble alumina and was not considered suitable for ettringite-based applications.

It is important to note that the phase assemblage of the final solid as well as the composition of the pore solution play a key role in maintaining ettringite stability, as equilibrium requires sufficient activities of three components: calcium, aluminum and sulfate (or oxyanion). If the activities of calcium and aluminum are controlled by another phase at too low a value, then ettringite will dissolve [10].

Overall, the following physicochemical and geotechnical properties and conditions have to be considered during the design of an S/S system, in which the formation of ettringite is possible.

2.1.1. pH

There is a variety of pH intervals reported in the literature, in which the stability domain for sulfate ettringite generally lies between 10.5 and 13 [16,17,26]. Myneni et al. [27] reported that ettringite may still be present down to a pH of 9.5, dissolving partially to gypsum and aluminum hydroxide. It seems, however, that the most widely reported favorable pH conditions for ettringite formation are between 11 and 12.5, at which its solubility is congruent and independent of pH [10]. There is limited reference to the relative stability of sulfate tri- and monophase with pH. Damidot and Glasser [16,17] concluded on the basis of thermodynamic calculations that monosulfate was metastable with respect to either ettringite or hydrogarnet at all pH values, as noted previously. Clark and Brown [28] observed that the monophases became increasingly stable in an alkaline solution, without reporting a specific pH threshold over which monosulfate prevails over ettringite.

The pH influence is similar for oxyanionic species, for which more specific data are available. Perkins and Palmer [29] found during synthesis experiments of chromate ettringite that chromate hydrocalumite (monophase) co-precipitated at pH values close to and above 12, while it was the only precipitate at pH 12.5. Perkins and Palmer [30] further investigated the precipitation reactions of the chromate mono- and triphases and provided pH-dependent stability domains, which show that the triphase prevails at lower pH (around 11). The stability domain of each phase is, however, largely dependent on the free calcium concentration, i.e. excess calcium favors chromate hydrocalumite, expanding its stability domain to lower pH values.

Similarly, Baur and Johnson [31] found in their study of selenate tri- and monophase that the monophase was the stable phase above pH 12.0.

The pH of saturated lime water is 12.4 [23], while the pH of the cement mixture is also highly alkaline [6]. Depending on the treated waste it is therefore possible that the pH of the resulting solid favors the formation of monophases over ettringite. An exception to this are CSA cements, in which the pH of the pore solution if lower, around 10–11, as ettringite is the main hydration product, instead of portlandite [32].

The pH stability domain of ettringite is important not only during the formation process, but also with regard to its stability over time and possible dissolution, if the pH of the solid drops below 10.5. Exposure scenarios to acid rain and carbon dioxide should be evaluated, along with performance of Acid Neutralization Capacity (ANC) tests. The pH regime of the S/S solid is one of the most important parameters and concerns for the success of the treatment, both at the initial stage and over time. Monophases formed at the highly alkaline pH of cement could be replaced by ettringite with the pH dropping to around 11 over time, which would, in turn, also dissolve with further pH decrease. These conversions would have very significant implications both with regard to the geochemical (leaching) properties of the system, as well as its geotechnical behavior and physical integrity, as will be discussed in a subsequent paragraph.

2.1.2. Temperature

Sulfate ettringite formation is generally favored over monosulfate at low temperatures, below 50 °C [16]. More specifically, Damidot and Glasser [16] calculated that monosulfate becomes stable in a small area of the stability diagram of the $CaO–Al_2O_3–CaSO_4–H_2O$ system at 50 °C. The calculations showed that this area expands over a larger range of sulfate concentrations when the temperature is 85 °C; ettringite is, however, still the more stable phase at high sulfate concentrations. Clark and Brown [28,33] confirmed this conclusion experimentally by investigating the hydration of tricalcium aluminate/gypsum mixtures. Ettringite was the only phase formed over a temperature range of 30–90 °C, when the molar ratio of sulfate-to-alumina was 3. Conversely, the rise in temperature favored the formation of monosulfoaluminate, when the sulfate-to-alumina ratio was 1. Temperature may play a role in S/S during the early stages of application: in both unhydrated lime (quicklime) and cement-based applications, CaO hydration elevates the temperature of the medium to high levels. Application of quicklime in soil piles in the field has elevated ground temperature up to 240 °C [23]. The effect of high temperatures would be the initial formation of monophases, which could later convert to triphase, as the temperature of the solid drops. The same observation holds, as in the case of pH, with regard to the geochemical and geotechnical properties of the system, which are significantly affected by the mono- to triphase conversion.

2.1.3. Competing ion effects

Apart from the issue of ettringite stability versus the monophase, another important question to consider in S/S is the degree of oxyanion incorporation into the ettringite structure, which depends largely on competing effects between oxyanions. Klemm and Bhatty [8] studied the degree of incorporation of chromate, arsenate and selenate into the ettringite structure, by conducting synthesis experiments and using one, two or three of these oxyanions in solution. They found that chromate ettringite formed with 2.5 mol of chromate in the crystal, compared to 3 mol of sulfate in the standard ettringite crystal. Charge balance was maintained by extra hydroxyls that fit into the ettringite channels. Similarly, selenate formed ettringite with 1.75 mol and arsenate with 1.25 mol of oxyanion in the channels. The stoichiometry of incorporated oxyanions changed, however, when different combinations of oxyanions were used in the

synthesis solution: arsenate showed higher affinity to form ettringite, when selenate and/or chromate were competing for the available sites, while selenate and chromate entered the ettringite structure in equal molar ratios. When sulfate was present in the solution, it was always preferentially incorporated in ettringite. Sulfate proved to have the ability to displace part of the oxyanions, when the substituted ettringite was placed in a sulfate solution; 7% Cr, 10% As and up to 20% Se leached out as a result of ettringite exposure to sulfate over a period of 28 days.

Zhang and Reardon [34] studied the precipitation of B, Cr, Se and Mo-substituted ettringite and hydrocalumite (monophase with hydroxyls in the interlayer) at conditions relevant to lime-leaching of fly ash as well as to fly ash-containing concrete. They found that the uptake of the oxyanions in ettringite followed the order $B(OH)_4^- > SeO_4^{2-} > CrO_4^{2-} > MoO_4^{2-}$. The reverse order was observed in the case of the monophase.

McCarthy et al. [10] confirmed that boron shows a greater affinity to form ettringite compared to other oxyanions. Borate seems to be an oxyanion that is particularly prone to incorporation in ettringite, an observation that is validated by the existence of two naturally occurring, borate-containing ettringites, sturmanite $(Ca_6Fe_2(SO_4)_2[B(OH)_4]\cdot26H_2O)$ and charlesite $(Ca_6(Al, Si)_2(SO_4)_2[B(OH)_4](OH, O)_{12}\cdot26H_2O)$.

The same authors applied synthesis reactions to remove borate and selenate from solution at a range of concentrations from 1 to 1000 mg/L and were successful to remove 95% of the initial quantity for both anions.

Kumarathasan et al. [35] also observed only minor substitution of arsenate, vanadate and molybdate for sulfate in cementitious matrices from coal combustion by-products.

When multiple oxyanions are present in an engineered system (in contrast to designed precipitation experiments), it is more likely that the dominant anion (primarily sulfate) will form ettringite, while other oxyanions will either form a monophase or interact in another way (sorption and physical inclusion) with the solid phase. Klemm and Bhatty [8] studied the formation of ettringite in artificially contaminated cement pastes. They found that sulfate ettringite formed when gypsum was present in the original mixture. Moreover, the ettringite peak intensity in the XRPD pattern increased in the presence of oxyanions, indicating that substituted ettringite may have formed. From the results of the leaching experiments on the final solids they concluded, however, that Cr and Se immobilization was primarily due to sorption and inclusion in CSH, as their solubility curve followed the characteristic pH values of CSH dissolution, not those of ettringite. Similarly, As and Pb leaching behavior could also not be directly linked to ettringite dissolution. No direct evidence was provided that substituted ettringite had actually formed in the cement pastes.

Substitution in ettringite is not only possible for oxyanions, but also for divalent and trivalent metals, that can compete with Al^{3+} in the octahedra. A naturally occurring ettringite, bentorite $(Ca_6(Cr(OH)_6)_2(SO_4)_3\cdot26H_2O)$ is an example of Cr^{3+} substitution. Albino et al. [36] conducted synthesis experiments to incorporate Cu, Cr, Cd, Fe, Pb and Zn in the ettringite structure. They provided XRPD and SEM/EDX data that proved incorporation of Cr^{3+} and Cd^{2+} in ettringite; it is however, uncertain, whether this reaction is likely to occur to a significant extent in a field cementitious system.

When a large-scale application of S/S is considered, the issue of variability of the materials and the environmental conditions over space and time is especially important with regard to the above discussion. Even if bench scale studies indicate that the incorporation of hazardous oxyanions into mono- or triphases is successful, it is possible that the in situ conditions will prohibit the substitution of occurring over smaller or larger areas. This applies especially to ettringite, for which the presence of sulfate, even in moderate amounts, can completely turn the system around and leave oxyanions in solution.

2.1.4. Carbonation effects

Carbon dioxide dissolves ettringite not only due to the pH decrease it causes, but also through direct carbonation reactions. Nishikawa et al. [37] studied ettringite decomposition due to carbonation under wet and dry conditions, finding that the presence of excess water decelerated carbonation reactions. On the other hand, excess water eventually lead to complete dissolution of ettringite to gypsum, vaterite $(CaCo_3)$ and alumina gel. Under dry conditions, ettringite remained essentially stable, with fine gypsum and vaterite crystals forming rapidly on the surface. The basic structure and composition of ettringite remained essentially intact in the latter case. Zhou and Glasser [14] studied ettringite stability under controlled relative humidities at 68 and 88% in different solid forms, as powder and in pellets. Ettringite completely transformed to gypsum and vaterite, when it was in powder form, while only the exposed surface presented complete dissolution in pellets. In the exposed pellets, the layers beneath revealed partial dissolution and transformation to monophase, while in the deepest layer, ettringite remained intact. This implies that in the case of a monolithic solid, ettringite that is exposed to the pore solution will be vulnerable to carbonation through what appears to be a slow dissolution process. Zhou and Glasser [14] consider, however, that carbonation should not be a serious problem in commercial sulfoaluminate cements, as they achieve low permeabilities and they tend to be too dry for rapid carbonation to occur. Conversely, this may not be the case in contaminated soil and sediment applications, where significantly higher values of hydraulic conductivity apply. Overall, the degree to which such conditions actually prevail in the field should be first established before an accurate prediction on the rate of ettringite destruction by carbonation can be made.

It should be stressed, however, that the prediction of the rate of carbonation and pH decrease is critical to S/S involving the presence of ettringite and/or monophases, as it is a process that is thermodynamically driven and will eventually lead to treatment failure upon dissolution of the pozzolanic phases.

2.1.5. Geotechnical implications of ettringite formation

In cement literature, the formation of ettringite is widely associated with expansion and concrete deterioration. Various authors [38–41] have dealt with the phenomenon of Delayed Ettringite Formation (DEF).

When the curing temperature of cement during the initial stages of setting and hardening is high (above 70–90 °C [41]) ettringite is unstable and monosulfate forms from the available sulfate in the clinker (or, in the general case of S/S, from available sulfate and other anions present in the system). When the temperature drops after the hardening is complete, monosulfate converts to ettringite, which is thermodynamically favored at lower temperatures, as stated previously. The needle-like structure of ettringite, compared to the platy morphology of the monophase, leads to an increase in volume, which may create catastrophic expansion, when the swell pressures cannot be suppressed by the confining matrix [41].

The phenomenon of ettringite-induced swelling has not only been observed in cements, but also in lime-stabilized soils [42]. When water gains access to a cementitious system, the expansion of the ettringite crystal by water adsorption may lead to swelling. In other words, there are two mechanisms responsible for expansion in the presence or ettringite: crystal formation, when sulfate becomes available and thermodynamic conditions are favorable, and crystal growth due to water adsorption [42]. Based on the pertinent literature, it is still unresolved which mechanism is predominant or if both contribute to build up the necessary swell pressures for expansion to occur.

The curing temperature is therefore critical in S/S. It influences the relative stability of compounds, which determines the system geochemistry and the solubility of the hazardous compounds in question. The different stability of solid phases at elevated temperatures changes the geotechnical properties of the matrix as well. The formation of monophases in hydrothermal conditions may, on the one hand, lead to low concentrations of oxyanions in solution. The decrease in temperature with time could, however, convert them to ettringite and lead to catastrophic expansion and formation of cracks. The penetration of water in the matrix can then result in significant leaching of oxyanions and possibly other contaminants present.

Conversely, if the curing temperature of the binding agent is low (20–50 °C), ettringite formation is favored. Ettringite is a significant strength agent, as its needle-like structure leads to crystal interlocking [2], enhancing thus the geotechnical properties of the matrix when it forms at the early stages of application.

In order to evaluate ettringite stability with regard to the aforementioned physicochemical parameters for a specific system, a geochemical model that reflects system chemistry and simulates different field conditions can be used. The geochemical model requires the input of thermodynamic constants for ettringite and its oxyanion analogs, as well for the respective monophases. A summary of thermodynamic constants available in the literature is presented in the following.

## 2.2. Available thermodynamic data for ettringite and monophases

Sulfate ettringite has been extensively studied in the cement literature and there is a variety of reported solubility product (log K_{sp}) values. A summary of representative values is presented in Perkins and Palmer [26]. These values vary between −35 and −45, most of them lie, however, in the range −43.9 to −45.1, based on the reaction

$$Ca_6[Al(OH)_6]_2(SO_4)_3 \cdot 26H_2O$$
$$= 6Ca^{2+} + 2Al(OH)_4^- + 3SO_4^{2-} + 4OH^- + 26H_2O \quad (1)$$
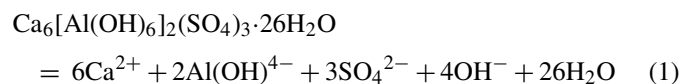
Reported values −111.3 [43] and −111.6 [27] refer to a dissolution reaction based on $\{Al^{3+}\}$ rather than $\{Al(OH)_4^-\}$. Perkins and Palmer [26] calculated the charge imbalance from the available experimental data and found that it was 30% in Atkins et al. [43] and 20% in Myneni et al. [27], while the use of $\{Al(OH)_4^-\}$ in other studies resulted in charge imbalances less than 10%. They note that many of the studies suffer from incomplete data sets, minimal data points and high charge balance errors. Generally, caution is warranted when considering thermodynamic constants from the literature for the purpose of obtaining a coherent and dependable set of values. This also applies to values that are already entries to thermodynamic databases in geochemical modeling software. Visual MINTEQ ver. 2.30 [44] uses a log K_{sp} value of 56.85 for sulfate ettringite, which results by transforming reaction (1) with log $K_{sp} = -44.9$ reported by Perkins and Palmer [26] in terms of Al^{3+} and H^+ instead of $Al(OH)_4^-$ and OH^-. EQ3/6 [45] uses a value of 62.53 for the same reaction, reported by Sarkar et al. [46]. The two values differ by almost six orders of magnitude, which may prove to yield significant differences in modeling results. The thermodynamic constants of substituted ettringites are in the same range of values, so that a discrepancy of a few orders of magnitude may change the relative stability of sulfate and substituted ettringite in the model.

Table 1 presents a summary of reported values for sulfate, chromate and selenate ettringite and the respective monophases. No values could be found in the literature for other species, such as arsenate or molybdate. The solubility products for the selenate phases were transformed to match the reactions for the sulfate and chromate species by using the reactions

$$Al^{3+} + 4H_2O = Al(OH)_4^- + 4H^+, \quad \log K_{sp} = -23.00 \quad (2)$$

$$H_2O = H^+ + OH^-, \quad \log K_{sp} = -13.997 \quad (3)$$
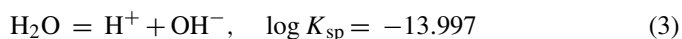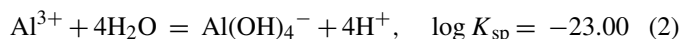
from the MINTEQ [44] thermodynamic database.

Comparing the triphases in Table 1, it is apparent that sulfate ettringite is the more stable phase, as its solubility product is three orders of magnitude lower. The log K_{sp} values for the chromate and the selenate species are very close, which concurs with the findings of Klemm and Bhatty [8] that chromate and selenate entered the ettringite structure in equal molar ratios when they were competing for the available sites. These values also endorse the generally accepted observation that sulfate ettringite is the most stable of the triphases.

Similar comparison between the monophases shows that the chromate species is more insoluble, followed by the sulfate and the selenate monophase.

All phases listed in the table attain very low solubilities. In order to provide a basis for comparison, insoluble hydroxides that are widely considered as viable mechanisms for heavy

Table 1
Thermodynamic properties of sulfate, chromate and selenate mono- and triphases at 25 °C

	$\log K_{sp}$	ΔG_f° (kJ/mol)	ΔH_f° (kJ/mol)	pH
Sulfate ettringite [26]	$Ca_6[Al(OH)_6]_2(SO_4)_3 \cdot 26H_2O = 6Ca^{2+} + 2Al(OH)_4^- + 3SO_4^{2-} + 4OH^- + 26H_2O$			
	-44.90 ± 0.32	$-15,211 \pm 20$	$-17,550 \pm 16$	10.5–13
Chromate ettringite [29]	$Ca_6[Al(OH)_6]_2(CrO_4)_3 \cdot 26H_2O = 6Ca^{2+} + 2Al(OH)_4^- + 3CrO_4^{2-} + 4OH^- + 26H_2O$			
	-41.46 ± 0.30	$-15,131 \pm 19$	$-17,330 \pm 8.6$	10.5–12.15
Selenate ettringite [31]	$Ca_6[Al(OH)_6]_2(SeO_4)_3 \cdot 31.5H_2O + 12H^+ = 6Ca^{2+} + 2Al^{3+} + 3SeO_4^{2-} + 43.5H_2O$			
	61.29 ± 0.60	n.a.	n.a.	11.37–11.61
Selenate ettringite (transformed)	$Ca_6[Al(OH)_6]_2(SeO_4)_3 \cdot 31.5H_2O = 6Ca^{2+} + 2Al(OH)_4^- + 3SeO_4^{2-} + 4OH^- + 31.5H_2O$			
	-40.70	n.a.	n.a.	11.37–11.61
Sulfate monophase [16]	$3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O = 4Ca^{2+} + 2Al(OH)_4^- + SO_4^{2-} + 4OH^- + 6H_2O$			
	-29.43	n.a.	n.a.	n.a.
Chromate monophase [30]	$3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot 15H_2O = 4Ca^{2+} + 2Al(OH)_4^- + CrO_4^{2-} + 4OH^- + 9H_2O$			
	-30.38 ± 0.28	-9905 ± 16	$-11,303 \pm 8.3$	10.5–12.5
Selenate monophase [31]	$3CaO \cdot Al_2O_3 \cdot CaSeO_4 \cdot xH_2O + 12H^+ = 4Ca^{2+} + 2Al^{3+} + SeO_4^{2-} + (x+6)H_2O$			
	73.40 ± 0.22	n.a.	n.a.	11.75–11.90
Selenate monophase (transformed)	$3CaO \cdot Al_2O_3 \cdot CaSeO_4 \cdot xH_2O = 4Ca^{2+} + 2Al(OH)_4^- + SeO_4^{2-} + 4OH^- + xH_2O$			
	-28.59	n.a.	n.a.	11.75–11.90

metal immobilization, have solubility products in the range 10^{-15} (cadmium hydroxide) to 10^{-20} (lead hydroxide) [47]. Consequently, monophases and ettringite, which are by 10 and 25 orders of magnitude more insoluble, are significantly more favorable species to control solubilities at low levels. It should be noted, however, that the solubility of hazardous compounds is not solely controlled by pH, as is the case with hydroxides. The concentrations of calcium and aluminum, which may be controlled by other phases in the cementitious matrix, also play an important role in the solubility of sulfate, chromate or selenate. It is therefore necessary to conduct geochemical modeling in the specific system in order to evaluate the concentration of hazardous oxyanions in the pore solution.

Baur and Johnson [31] modeled the solubility of selenate in the presence of monosulfate and selenate triphase, as well as in the presence of monosulfate and selenate monophase against pH. Their model showed that selenate monophase controlled selenate solubility to lower levels than ettringite at high pH values (>11.5). The influence of sulfate presence was significant, increasing selenate solubility by one order of magnitude (from 10^{-4} to 10^{-3} mol/L as sulfate increased from 10^{-5} to 10^{-4} mol/L).

van der Sloot [5] conducted geochemical modeling to predict the leaching behavior of concrete mortars and cement-stabilized waste. The model could not predict the low concentrations of Cr and Mo above pH 11, as the thermodynamic database probably did not contain entries for substituted ettringite and hydrocalumite. The author points, however, at the capacity of ettringite-type phases to accommodate hazardous oxyanions in order to explain the discrepancy at high pH values.

To better illustrate the role of modeling, an example of the application of geochemical modeling to assess the immobilization of chromate in ettringite and/or monochromate is presented in Section 3.

2.3. Application examples

Ettringite formation has been directly applied as an immobilization mechanism to remove heavy metals from solution, i.e. as an alternative wastewater treatment, in a research project of the Portland Cement Association [48]. The authors of that project proposed two alternatives for the implementation of boron and selenium removal, one involving the production of small amounts of solid ettringite and metal-free solution and the other the formation of a monolith, solidifying the entire mass. The latter is recommended only in cases with very high concentrations of oxyanions, since the volume of the resulting solid increases dramatically, thus raising the associated disposal costs. The authors of the study acknowledged that disposal of the solid is an issue, since the pH stability at high values is essential to ensure immobilization and cannot be guaranteed at most disposal sites. Zhang and Reardon [34] also studied removal of boron, chromium, selenium and molybdenum from wastewater by incorporation in ettringite and hydrocalumite. Hydrocalumite proved to be more suitable to remove oxyanions from solution to below the drinking water standards. No commercial application of this approach has thus far being reported in the literature.

Ettringite formation in cementitious systems has, on the other hand, been proposed by several authors as a mechanism that can explain experimental leaching patterns, as in the case of the discrepancy of experimental and modeling results by van der Sloot [5].

Serclerat et al. [49] studied leaching of zinc, lead and chromium, both trivalent and hexavalent, in Portland cement clinkers. They found that the concentration of hexavalent chromium in the leachate was low (below 5 ppm) in the pH region 11–13 and point to the stability of ettringite in this domain, without providing direct evidence for its presence or the inclusion of chromium in its structure.

Cioffi et al. [50] proposed a stabilization process for galvanic sludge containing cadmium, nickel and chromium, which entailed the use of a binder made of calcium silicate and sulfoaluminate. Ettringite and CSH were the primary phases in the resulting matrix. The authors proposed that chromium was partially bound in ettringite, as it was the primary phase in the X-ray powder diffraction (XRPD) pattern of the stabilized material. They did not provide, however, direct evidence to support their hypothesis.

Lecuyer et al. [51] studied desulfurization processes of fly ash and proposed that the formation of ettringite in wetted fly ash, treated in a conventional pulverized coal boiler equipped with lime injection, lead to the entrapment of As, Se and Cr in the resulting monolith. Their hypothesis is, however, solely based on previous literature that referred to the potential of ettringite to immobilize oxyanions.

Duchesne and Reardon [52] studied the leaching behavior of lime-treated fly ash. They found that the reduction in Cr and Mo was more pronounced in class F fly ash, in which the formation of monophases was pronounced, as evidenced by XRPD. The authors did not provide, however, evidence that hydrocalumite was the solubility-controlling phase for oxyanions in class F fly ash. Hydrogarnet and ettringite formed in class C fly ash upon lime treatment, which did not control the solubility of Cr and Mo, when the liquid-to-solid (L:S) ratio of leaching tests was varied.

Mollah et al. [53] investigated the speciation of As(V) in Portland cement type V by means of XRPD and Fourier transform infrared spectroscopy (FTIR). XRPD revealed the presence of ettringite with a significant shift in the first reflection from 9.76 Å (the standard value for sulfate ettringite) to 9.65 Å, which the authors attribute to arsenate substitution for sulfate. Ettringite was, however, not the sole immobilization mechanism, as arsenate was shown to exist in different forms of calcium arsenate in the cement matrix.

Dermatas and Moon [54] identified a hydrocalumite species with both sulfate and chromate in the interlayer $(3CaO \cdot Al_2O_3 \cdot 0.5CaCrO_4 \cdot 0.5CaSO_4 \cdot nH_2O)$ by performing XRPD of soil treated with a combination of quicklime and fly ash. The formation of this compound at high pH ($\sim$12) restricted leaching of hexavalent chromium to concentrations below 5 ppm.

Palmer [55] examined the speciation of Cr(VI) in contaminated concrete by means of electron diffraction and microscopy. Palmer identified both Cr-substituted ettringite and hydrocalumite; the pH of the system is, however, not mentioned in the report, nor the nature of the contamination.

In summary, most of the references on the application of ettringite and monophases to oxyanion stabilization with cement or cementitious binders do not provide direct evidence to support the hypothesis that oxyanions are substituted in the mineral channels or interlayer, respectively. They mostly refer to previous studies conducted as synthesis experiments, such as Poellmann et al. [11] and Kumarathasan et al. [35]. A few authors provide, however, X-ray diffraction data for the existence of ettringite and monophases in S/S-treated media. The immobilization mechanism seems to play a role in actual matrices, whereby ettringite

does not seem to be more suitable to immobilize oxyanions than the monophase. The presence of sulfate ettringite may imply partial accommodation of an oxyanion, while monophases may occur in the pure oxyanionic form and lead to lower concentrations in solution.

3. Experimental findings

3.1. Materials and methods

The formation of Cr(VI)-ettringite was investigated for the specific case of Chromite Ore Processing Residue. COPR is a hazardous waste as defined by the U.S. Environmental Protection Agency criteria. It is generated by the extraction of chromium as soluble sodium chromate from chromite ore of the general formula $(Mg, Fe)(Cr, Al, Fe)_2O_4$ by means of a high-temperature roasting process. Addition of lime at 1200 °C leads to formation of oxides such as brownmillerite $(Ca_4(Fe, Al)_2O_{10})$ and periclase (MgO), which may incorporate trace compounds, such as Si and Cr. The resulting solid contains residual chromium in concentrations 3–5%, up to 30% of which is in its hexavalent form [56]. In order to determine the speciation of Cr(VI) in the solid, COPR samples were obtained from a deposition site in NJ, USA, where extensive investigation is taking place with regard to chromium presence and treatment [57]. A total of 96 discrete disturbed samples were obtained from different depths in 38 soil borings, while a further 27 relatively undisturbed samples were obtained from tube samplers. Composite samples were prepared by mixing material from five discrete soil borings at three depth intervals, in order to obtain a representative sample of the COPR matrix. The analyses included:

- *pH*: Method ASTM D4980-89 [58] was used to measure the pH of the solid.
- *XRPD*: Samples were air-dried for 24 h and pulverized to pass a USA standard #400 sieve (38 μm). Step-scanned XRPD data were collected using a Rigaku DXR 3000 computer-automated diffractometer using Bragg–Brentano geometry. The diffractometry was conducted at 40 kV and 30 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 0.05° and a count time of 5 s per step. XRPD patterns were analyzed by the Jade software Version 7.0 [59] and reference to the patterns of the International Centre for Diffraction Data database [60], Version 1998, as well as the Inorganic Crystal Structure Database [61], release 2004 (1).
- *Scanning electron microscopy/energy dispersive X-ray (SEM/EDX)*: Air-dried samples were mounted on carbon coating and analyzed by SEM/EDX using a LEO 982 field emission scanning electron microscope with an Oxford energy dispersive X-ray analyzer.
- *Toxicity characteristic leaching procedure (TCLP)*: The EPA regulatory test TCLP, method EPA 1311 [62] was employed to investigate Cr(VI) leaching.
- *Total analyses*: The total content of individual metals was measured by acid digestion (EPA method 3015A [63]) and

inductively coupled plasma/atomic emission spectrometry (ICP/AES—EPA method 6010B [64]). The Cr(VI) content was measured by alkaline digestion and colorimetric analysis (EPA method 3060A [65] and 7196A [66]).

3.2. Results and discussion

COPR is a highly alkaline waste; the pH of most samples was between 12.4 and 12.7; it was lower only in the cases where the presence of soil admixture was detected.

The mineralogy of COPR consists mainly of the following phases: brownmillerite (Ca_2FeAlO_5), periclase (MgO), portlandite ($Ca(OH)_2$), brucite ($Mg(OH)_2$), hydrogarnets (katoite $(CaO)_3Al_2O_3(H_2O)_6$ being the main phase), calcite, hydrotalcites or double-layered hydroxides ($Al_2Mg_4(OH)_{12}(CO_3)(H_2O)_3$ is a representative compound), ettringite in many cases, depending on sulfate availability, and chromate hydrocalumite in different hydration states ($Ca_4Al_2O_6(CrO_4)\cdot nH_2O$, $n = 9, 12, 14$). All of these phases are also encountered in cements and S/S-treated soils in different stoichiometries. The pH regime and the mineralogy of COPR are analogous to those of a cementitious system; the experimental and modeling investigation of this chromate-contaminated system will, therefore, provide some insight into the ability of mono- and triphases to incorporate chromate in their structure.

Fig. 1 shows a detail of a COPR XRPD pattern, in the *d*-spacing interval of 12.62–5.21 Å. This is the region in which triphases (ettringite) and monophases (hydrocalumite) present their primary peak position. The lines in the figure show the strongest reflections (1 0 0) for sulfate ettringite (Powder Diffraction File (PDF) 41-1451) and chromate ettringite (PDF 41-0218). The lines show that complete substitution of chromate for sulfate in the channels of the ettringite crystal results in a shift of the *d*-spacing from 9.82 to 9.87 Å, due to the slightly larger radius of the chromate anion compared to sulfate. McCarthy et al. [10], provide an XRPD pattern for chromate ettringite that shows a reversal in the relative intensities of the first and second reflection compared to the pattern of sulfate ettringite. Such a pattern is, however, not available in the ICDD database.
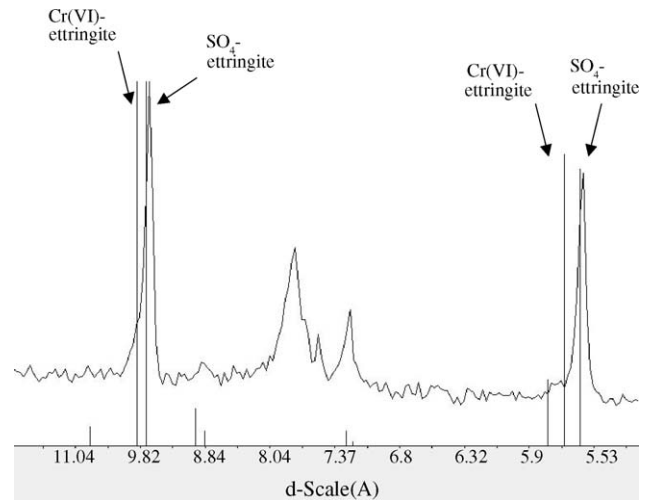

Fig. 1. Detail of COPR XRPD pattern. The lines show the first and second peak position of sulfate and chromate ettringite according to their PDFs (41-1451 and 41-0218).

No pure chromate ettringite could be identified in any of the 120 XRPD patterns analyzed. When ettringite was present, the peak positions matched the sulfate species, while chromate was bound in the monophase in 80% of the patterns [67]. No other chromate precipitate could be identified in the XRPD patterns; the speciation of chromate remained inconclusive in the 20% of the remaining patterns, where chromate hydrocalumite was not detected.

SEM/EDX analyses were also performed on several samples in which sulfate ettringite was identified, in order to investigate the existence of solid solution with chromate that could not be detected by XRPD. The analyses revealed very limited Cr substitution in the ettringite crystal, in isolated cases. Fig. 2 shows the SEM image and EDX spectrum of ettringite in the sample corresponding to the XRPD pattern of Fig. 1. The EDX spectrum shows some minor Cr substitution. However, the XRPD pattern did not reveal any detectable change in the ettringite peaks due to this partial Cr substitution. It should also be stressed that EDX cannot identify the valence of the metals, so that the Cr detected
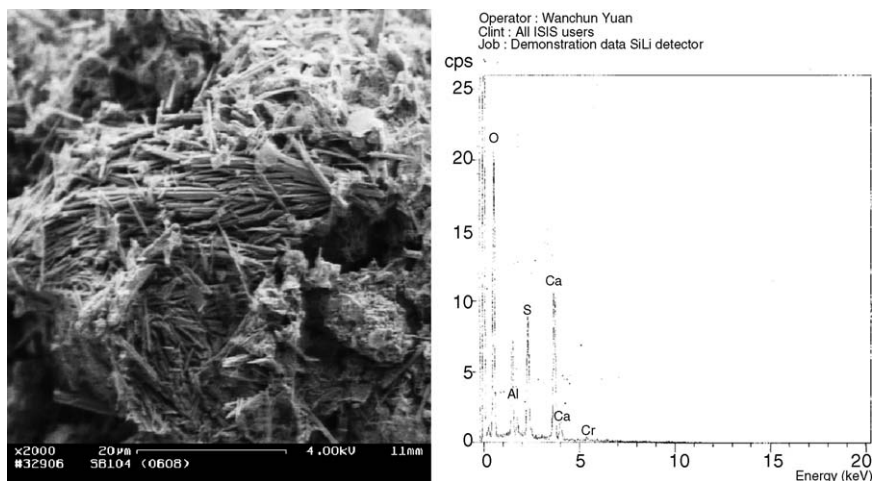

Fig. 2. SEM image and EDX spectrum of ettringite in COPR.

Table 2
Quantification of ettringite EDX spectrum (in mol%)

	Ca	Al	S	Cr
Theoretical	54.55	18.18	27.27	–
EDX	56.65	16.51	25.16	1.68

Table 3
Input data for geochemical modeling, obtained from total analyses on sample composite B1

Element	mg/kg
Ca	260100
Al	42400
Fe	149900
Mg	52900
Cr(VI)	5739
S	1600
Na	4000
Cl	10000
Si	4000
CO_3^{2-}	80000

could, instead of being in its oxyanion form, be in its trivalent form and substitute for Al^{3+} in the octahedra. This is probable, as the Al source in COPR is brownmillerite ($Ca_2(Fe, Al)_2O_5$), which contains Cr(III) as an impurity. The simultaneous release of Al and Cr through brownmillerite dissolution could result in the uptake of both metals in the ettringite crystal during formation.

The quantification of the EDX spectrum is presented in Table 2, along with the theoretical composition of ettringite. There is good agreement between the element percentages; a slight deficiency of ~2% on a molar basis is observed in both Al and S. This could be compensated by Cr(III) in the case of Al and by Cr(VI) in the case of S. EDX is only a semi-quantitative method; it therefore remains inconclusive in this case, whether the detected Cr is in its trivalent or hexavalent form (or both). Overall, SEM/EDX from 25 samples containing ettringite revealed the presence of minor amounts of Cr in 9 samples, with mostly very small peaks compared to the S peak, as is the case in Fig. 2. Therefore, the only reliable conclusion to draw is that Cr substitution, whether in its tri- or hexavalent form, is very limited and thus insignificant in terms of an ettringite-based Cr immobilization mechanism.

Both XRPD and SEM/EDX analyses showed that Cr(VI) is mainly bound in the chromate monophase. None or only limited solution with sulfate was found in the platy crystals of the monophase. It seems that sulfate preferentially incorporates in ettringite, while chromate goes into the monophase in the COPR system. This observation agrees with the theoretical background and the findings of other studies, as these were presented in the literature review. In summary, the pH dependence between the sulfate tri- and monophase is much less pronounced compared to the oxyanionic species; sulfate ettringite prevails, although the pH of the system is highly alkaline. Conversely, chromate hydrocalumite is favored over chromate ettringite, as predicted by the thermodynamic study of Perkins and Palmer [30] and the findings of other authors [34,52].

This finding was further investigated by conducting geochemical modeling using the Visual MINTEQ ver. 2.30 software package [44]. The database for solid phases was expanded by adding the phases katoite (data obtained from the Common Thermodynamic Database Project [68]), Cr(VI)-hydrocalumite (data obtained from Perkins and Palmer [30]) and afwillite (data obtained from the EQ3/6 cmp database [45]), since all of these phases were observed in the COPR XRPD patterns. The input for the model was obtained by conducting total analyses on composite sample B1 (see Table 3), with the exception of chloride and carbonate. Chloride was estimated and only serves as a tracer element for charge balance, as it does not participate in precipitation reactions.

The carbonate concentration was set at a high level, as the sequestration effect causes constant consumption of CO_2 to form calcite, which was observed in high amounts in the COPR XRPD patterns. Cr(III) was not included in the model, as it is mostly present as impurity in the various phases and has not been observed to precipitate in a pure form in any of the XRPD patterns. The L:S ratio was set to 20 to simulate TCLP conditions and the model runs were performed at a range of pH values in the interval from 9 to 13.7 with each run at a constant value within that range, in order to evaluate mineral stability, as well as the aqueous concentrations at equilibrium. Calculation of activity coefficients was performed by using the Davies equation and the temperature was assumed constant at 25 °C.

Fig. 3 presents the results for Cr(VI) speciation, i.e. its distribution between the aqueous phase and the precipitated solids (chromate monophase and ettringite). The results show that all the available chromate is free in solution when the pH is below 10.9 or above 13.0, as there is no stable solubility-controlling phase in these regions. Chromate hydrocalumite precipitates when the pH is between 11.19 and 12.96, while chromate ettringite is stable between 10.9 and 11.18, which is an extremely narrow window for ettringite stability. Other authors have reported stability regions for Cr(VI)-ettringite at 10.5–12.5 [29] and 9.1–11.2 [69]. There is a significant discrepancy between these results. It is noted that the pH range of 10.5–12.5 was obtained by synthesis and dissolution experiments, with subsequent modeling of the results; the values
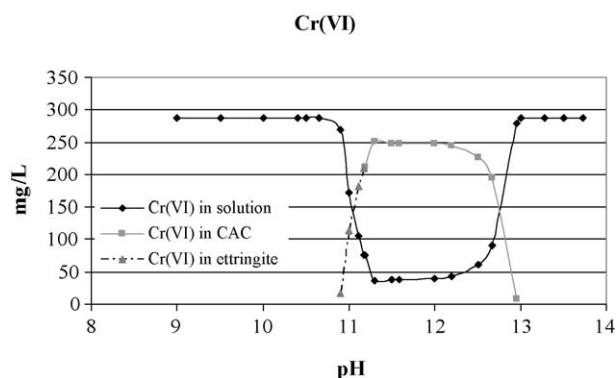

Fig. 3. Cr(VI) distribution in the aqueous and solid phase in mg/L according to geochemical modeling.

9.1–11.2 were obtained by performing leaching tests on COPR samples and modeling the aqueous concentrations. No evidence was provided that Cr(VI)-ettringite precipitated under these low-pH conditions; the authors attribute the low-pH threshold to the use of a lower log K for Cr(VI)-ettringite. An optimum pH of 11 is, however, generally accepted in the literature to form chromate ettringite, although, as a practical matter, it is extremely difficult to maintain field conditions at a pH environment that is constant at 11.0 through space and time.

Fig. 3 shows that there is a pH region between approximately 11.3 and 12.4, in which the amount of chromate bound in hydrocalumite is constant and the solubility of chromate is consistently below 50 ppm. Conversely, the amount of chromate bound in chromate ettringite varies greatly with pH. This indicates that control of chromate solubility may be more reliable when hydrocalumite forms, while substituted ettringite is more sensitive to environmental changes. The ettringite stability field is in the pH area, in which the solubilities of calcium and aluminum increase, as other phases dissolve and precipitate. Fig. 4 shows the amount of precipitated monophase and ettringite according to the model. The lower amount of ettringite (in mol/L) translates to less calcium and aluminum required to immobilize the same amount of Cr(VI) compared to the monophase. In other words, the stoichiometries of Ca and Al versus Cr(VI) in the chemical formula of the tri- and the monophases favor ettringite in the area where the increased solubility of these compounds leaves less amount available to form pozzolanic phases. The importance of solubility-controlling phases for other constituents besides chromate is thus illustrated in the example of COPR. It would be very difficult to control the amount of any precipitate in a pH domain, where multiple geochemical shifts take place in the system. Controlling the pH in a narrow area around 11 would be also difficult to accomplish. In field applications it is technically feasible to control the pH of a solid to above 12 by means of lime addition (the pH of saturated lime solution is 12.4 [23]). CSA cements that have ettringite as main hydration product present a lower pH (∼10–11) in the pore solution due to the absence of portlandite [32]; their use could, potentially, be a means of controlling the pH to lower pH values in the field. The application of CSA cements in S/S is still, however, in the developmental stage.
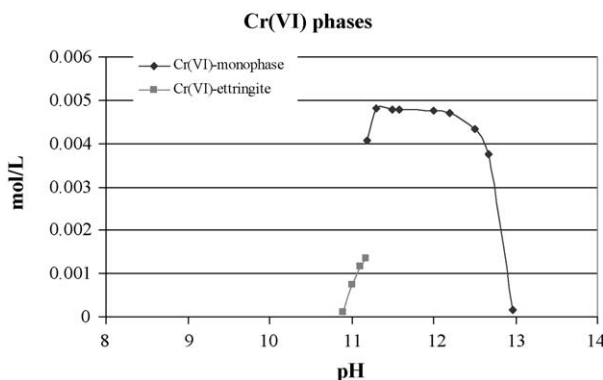
With regard to the Cr concentrations as predicted by geochemical modeling, neither hydrocalumite nor ettringite can control its solubility below the EPA regulatory limit of 5 ppm. The lowest concentrations produced by the geochemical model are approximately 40 and 75 ppm for hydrocalumite and ettringite, respectively. TCLP analysis was performed on the same sample (composite B1) for purpose of comparison to the modeling results. Analyses of duplicate samples yielded an average TCLP concentration of 182 mg/L at leachate pH 9.7, which is significantly lower than the 287 mg/L predicted by the model at the same pH.

XRPD was performed on the TCLP residue to investigate the speciation of residual chromate in the solid, but no chromate compounds could be identified. It is possible however, that residual monophase below the detection limit was still present in the solid. The authors believe that the lower concentration can either be explained by kinetic limitations, or by sample variability, which is significant even in samples obtained from the same location. Ongoing investigations also explore the possibility of chromate adsorption at pH values 7–9.

In order to investigate whether the high concentration of Cr(VI) even in the presence of hydrocalumite was due to limited availability of calcium and aluminum that were scavenged by other phases such as sulfate ettringite and calcite, the model was repeated omitting the sulfate and carbonate input. The results remained the same with regard to chromate solubility. It is, therefore, hypothesized that the calcium and aluminum concentrations are controlled by other phases in COPR, namely portlandite and hydrogarnet, so that the equilibrium concentrations of these species do not allow for lower chromate concentrations.

In summary, the formation of chromate hydrocalumite seems to be the controlling mechanism for chromate immobilization in COPR under the highly alkaline conditions prevailing in the field. Chromate substitution in ettringite is very limited, while no pure chromate ettringite could be identified in any COPR sample. Geochemical modeling predicted that the pH stability domain of chromate ettringite in COPR is very narrow (10.9–11.2) and confirmed that hydrocalumite is stable under the prevailing pH conditions in COPR (>12).

4. Summary and conclusions

The immobilization of heavy metal oxyanions such as chromate, arsenate, selenate, molybdate, etc., poses a challenge, as they are mobile in neutral and alkaline environments. When S/S is applied, an effective precipitation mechanism is necessary in order to minimize their leaching, as sorption is generally minimal at the alkaline pH environment caused by S/S binders.

The mineral ettringite often occurs in concrete and S/S cementitious systems, such as lime-treated soils, when sulfate is available. Such systems provide a favorable environment for ettringite formation, as the pH is between 11 and 13 and there is a calcium and aluminum source in the pore solution. Sulfate ions in ettringite may easily be replaced by anions of similar geometry and charge, as these can be accommodated in the channels along the axis of the needle-like structure of ettringite. Several authors

Fig. 4. Cr(VI) monophase and ettringite stability according to geochemical modeling.

have proposed this substitution as a possible immobilization mechanism in S/S systems and have studied substituted ettringites in synthesis reactions. The comparative study of different oxyanion-substituted ettringites showed that the sulfate species is the most stable and that sulfate can displace other oxyanions, even after formation of substituted ettringite is complete. Moreover, the coexistence of different oxyanions in solution results in varying uptake of each anion, depending on its affinity to ettringite and its concentration in solution.

Ettringite exists in equilibrium with monosulfate in cementitious systems, depending on sulfate concentration and temperature. Monosulfate is a pozzolanic product with one sulfate group in the interlayer of a platy structure. Similar to ettringite, sulfate in the interlayer may be replaced by oxyanions and immobilize them. Studies on the chromate and selenate monophases showed that they prevail over substituted ettringite when the pH is above 12, i.e. there is strong pH dependence between substituted mono- and triphase that has not been reported for sulfate ettringite and monosulfate systems.

Monophases may control the solubility of oxyanions to lower levels than substituted ettringite. This was demonstrated in several cases in the literature [30,34,48] and was also the conclusion of the experimental and modeling investigation of Chromite Ore Processing Residue in the present study. Chromate hydrocalumite prevailed when the pH was above 11.2 and controlled the solubility of chromate to lower levels than chromate ettringite. The pH stability domain for chromate ettringite in COPR was very narrow (10.9–11.2) according to geochemical modeling and the precipitated quantities dropped very quickly with decreasing pH. This indicates that ettringite is not a viable chromate immobilization mechanism in COPR without further treatment. In general, it may be easier to control the pH of cementitious systems to high levels by means of lime addition, favoring the formation of monophases. The use of calcium sulfoaluminate cements in S/S may be a way of keeping the pH of the treated waste at lower levels (∼11) that favor ettringite formation; more research is, however, deemed necessary to establish the technical and economical feasibility of CAS application in waste immobilization.

The presence of either mono- or triphases does not ensure that the solubility of the oxyanions will be below regulatory limits, as it depends on the overall system chemistry and the solubility-controlling phases for other constituents, namely calcium and aluminum. Geochemical modeling in COPR showed that the soluble chromate concentration was one order of magnitude above the regulatory limit in the chromate monophase stability domain, as calcium and aluminum concentrations were apparently controlled by other phases, keeping the chromate concentration at high levels.

Conducting geochemical modeling in the specific system is therefore essential to evaluate the final assemblage of the solid and the solution composition. There are published values for the solubility products of substituted ettringite and monophases, which may be used as additional entries to existing thermodynamic databases; the user should, however, be cautious to use a coherent set of data, as the differences in K_{sp} values between substituted ettringites are small compared to those reported for sulfate ettringite and misleading results may thus be generated. Geochemical modeling should also be conducted at higher temperatures, if the curing temperature of the binder is not 25 °C. Temperature plays an important role in the relative stability of monophases and ettringite and a temperature gradient may lead to complete conversion of a tri- to a monophase and vice versa.

The conversion of monophases to ettringite has significant geotechnical implications, as the structural change form plate to needle may lead to volume increase and catastrophic expansion, when the cementitious matrix cannot accommodate the developing swell pressures. Conversely, when ettringite forms at the early stages of binder application, it serves as a significant strength agent.

In summary, both ettringite and hydrocalumite may serve as viable mechanisms for the immobilization of oxyanions, since there are limited options for their treatment in an alkaline environment. The authors are aware of only a few cases, when the sole contaminant present is one oxyanion, such as the case of COPR. Heavy metal contamination usually involves the presence of multiple species, which need to be effectively addressed by S/S treatment. When a treatment feasibility study results in the conclusion that S/S is the most cost-effective solution, then heavy metal oxyanions have to be addressed in a context where competitive oxyanion effects are carefully evaluated. Both mono- and triphases form in cementitious systems, in which the formation environment is favorable and provides the necessary building blocks, i.e. calcium and aluminum. In that sense, their role should be considered during the planning and bench scale testing phases of treatment.

Several factors have to be considered, however, when the formation of these pozzolanic phases is proposed as the main immobilization scheme of hazardous oxyanions. The interplay between the mono- and the triphase is intricate and depends on several physicochemical conditions, such as pH, temperature, presence of sulfate and other competing anions and influx of carbon dioxide. It is important to predict the speciation and stability of oxyanions, as these dictate the leaching as well as the geotechnical properties of the system to a great extent. The phenomenon of Delayed Ettringite Formation, i.e. the conversion of monosulfate to ettringite after the pozzolanic reactions in cement are complete and the temperature drops, is a scenario that may also take effect in any S/S application. Concrete expansion and failure has widely been attributed to DEF. Such a failure would have severe consequences in S/S matrices, as it would result in rapid leaching of oxyanions that are not otherwise retained in the matrix.

Caution is warranted when references to the immobilization potential of ettringite are postulated as evidence that this occurs in a cementitious system. There is a large tendency to refer to synthesis studies that have proven the theoretical basis of this potential, while there is limited evidence that extensive substitution in ettringite actually occurs in stabilized media. X-ray diffraction and micromorphological studies are strongly recommended to verify the nature and extent of the immobilization mechanism and evaluate the reversibility in the case of a decrease in pH or some other environmental change.

Acknowledgements

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