

Chromium Remediation or Release? Effect of Iron(II) Sulfate Addition on Chromium(VI) Leaching from Columns of Chromite Ore Processing Residue

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Chromite ore processing residue (COPR), derived from the so-called high lime processing of chromite ore, contains high levels of Cr(III) and Cr(VI) and has a pH between 11 and 12. Ferrous sulfate, which is used for remediation of Cr(VI) contamination in wastewater and soils via reduction to Cr(III) and subsequent precipitation of iron(III)/chromium(III) hydroxide, has also been proposed for remediation of Cr(VI) in COPR. Instead, however, addition of FeSO₄ to the infiltrating solution in column experiments with COPR greatly increased leaching of Cr(VI). Leached Cr(VI) increased from 3.8 to 12.3 mmol kg⁻¹ COPR in 25 pore volumes with 20 mM FeSO₄, reaching solution concentrations as high as 1.6 mM. Fe(II) was ineffective in reducing Cr(VI) to Cr(III) because it precipitated when it entered the column due to the high pH of COPR, while Cr(VI) in solution was transported away with the infiltrating solution. The large increase in leaching of Cr(VI) upon infiltration of sulfate, either as FeSO₄ or Na₂SO₄, was caused by anion exchange of sulfate for chromate in the layered double hydroxide mineral hydrocalumite, a process for which scanning electron microscopy with energy-dispersive X-ray microanalysis provided direct evidence.

Introduction

Millions of tons of high pH–chromite ore processing residue (COPR) have in the past been deposited in urban areas (e.g., Hudson County, New Jersey, USA, and Glasgow, Scotland) and continue to leach Cr(VI) at very high concentrations

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(1–4). The so-called high lime process responsible for the generation of this high pH waste was largely abandoned in the Western World by the late 1960s, but it is still being used for Cr processing in countries such as China, Russia, India, and Pakistan (5). In the high lime process, chromite ore is mixed with alkali carbonate and lime or dolomite, which is added to allow a better penetration of air into the mixture. This mixture is heated to 1150 °C to oxidize Cr(III) to Cr(VI), and the soluble Cr(VI) is subsequently extracted by leaching with water (6, 7).

The COPR has a pH of between 11 and 12 and typically contains 3–7% total chromium, present as both Cr(III) and Cr(VI). The majority of chromium is present as Cr(III), partly as unreacted chromite, but Cr(VI) contents ranging from 1 to 30% of total Cr have been reported (4, 8, 9). These two oxidation states of chromium show great contrast in their chemical behavior. In the environment, Cr(VI) is present in anionic form and is relatively mobile, whereas Cr(III) is in general strongly retained in the solid phase. Cr(VI) is carcinogenic, mutagenic, and toxic through dermal and oral exposure, whereas Cr(III) is an essential dietary micronutrient (10).

This study focuses on sites in the southeast of Glasgow where COPR from a local chromium works was deposited (3, 4, 7, 11–13). Concentrations of Cr(VI) found in pore water and groundwater are up to 1.6 mM (3), and there is a risk of migration of Cr(VI) and contamination of nearby soils, groundwaters, and surface waters (3, 11). Batch studies of Cr(VI) release from COPR by Geelhoed et al. (4) indicated that the key process responsible for the release of Cr(VI) is mineral dissolution. The chemistry of COPR is dominated by the dissolution and secondary precipitation of calcium aluminate phases, which is also responsible for the high pH of COPR. Solid phases in COPR that contain Cr(VI) are chromium(VI) hydrocalumite (Ca₄Al₂(OH)₁₂CrO₄·6H₂O) and Cr(VI)-substituted hydrogarnet (Ca₃Al₂(H₄O₄)₃). When the pH decreases below 11.2, chromium(VI) ettringite (Ca₆Al₂(OH)₁₂·(CrO₄)₃·26H₂O) is likely to be present. Other minerals that were identified in COPR are chromite ((Mg,Fe)(Cr,Al)₂O₄) from the original ore; periclase (MgO), brucite (Mg(OH)₂), and calcite (CaCO₃) derived from the addition of lime and dolomite; and brownmillerite (Ca₂(Al,Fe,Cr)₂O₅), which is associated with Cr(III). In addition, there was a large fraction (about 35%) of amorphous material (4, 12, 13). The mineral composition and chemistry of COPR shows important similarities with cement and municipal solid waste incinerator bottom ash (4).

One approach to decrease the release of Cr(VI) is by conversion of Cr(VI) to Cr(III), either by microbial or chemical reduction. On a number of sites in Hudson County where COPR was deposited on top of an organic-rich layer of decayed vegetation, reduction appeared to occur naturally. The organic-rich layer was shown to act as a natural barrier to the migration of Cr(VI) by sustaining microbial reduction of Cr(VI) to Cr(III) (9). However, in other cases Cr(VI) may drain to groundwaters and surface waters (3, 11), and the introduction of microorganisms and/or chemicals to bring about reduction of Cr(VI) to Cr(III) may be a method to reduce the risk of the Cr(VI) spreading into the wider environment.

Inorganic chemical reagents that have been proposed for the reduction of Cr(VI) are ferrous iron (Fe(II)), zero-valent iron (Fe(0)), and sulfide (S(–II)) (14–19). Of these, reduction by Fe(II) in solution has been most intensively studied. Following reduction of Cr(VI) to Cr(III) with Fe(II), a mixed iron(III)/chromium(III) hydroxide is formed. The stoichiometry and kinetics of Cr(VI) reduction by Fe(II) has been

TABLE 1. Elemental Contents of COPR^a

element	content (mol kg ⁻¹ dry COPR)	element	content (mol kg ⁻¹ dry COPR)
Mg	5.20	Al	1.46
Ca	4.52	Cr	0.77 (30 ± 5% as Cr(VI))
Si	1.64	S	0.137
Fe	1.49	Na	0.087

^a Data from Geelhoed et al. (4).

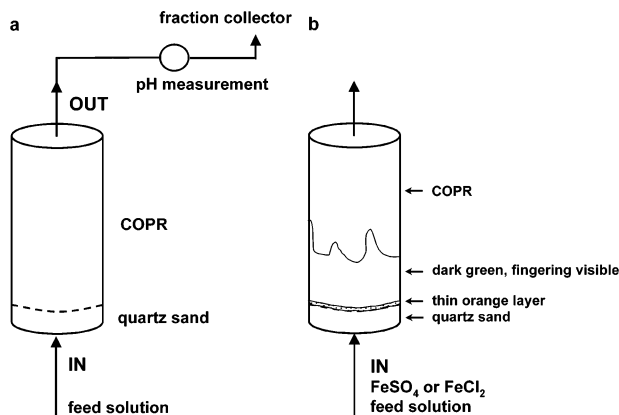


FIGURE 1. (a) Schematic representation of the setup of a column experiment and (b) visualization of Fe precipitation in the columns treated with Fe(II)-containing feed solution.

examined in laboratory studies in the pH range from 1 to 8.5 (14–16, 20), and the effectiveness of Fe(II) in converting Cr(VI) to Cr(III) in Cr(VI)-contaminated soils has been demonstrated in both batch (21, 22) and column systems (23). The use of FeSO₄ as a reducing agent for Cr(VI) in COPR has been suggested by Higgins et al. (9) and tested in a pilot study on one of the sites in Glasgow (24). In this field experiment, an apparent decrease in the Cr(VI) concentration of COPR was observed. However, the variation between the replicates was very large, and because the experiment was carried out in an open system, it is not clear whether the decrease in Cr(VI) was caused by conversion to Cr(III) or by leaching.

The aim of this study is to assess the extent of leaching of Cr(VI) from COPR and to investigate the effectiveness of FeSO₄ addition on Cr(VI) conversion and leaching from COPR in column experiments. To help explain the obtained results, additional experiments were set up in which columns of COPR were leached with FeCl₂ and Na₂SO₄. Scanning electron microscopy–energy-dispersive X-ray microanalysis (SEM-EDX) was carried out to determine the elemental composition of Cr(VI)-containing solid phases.

Experimental Section

Chromite Ore Processing Residue. COPR was sampled at a former playing field in the southeast of Glasgow, where COPR that had been used to backfill an old quarry was covered with a 5–10 cm thick layer of topsoil vegetated with grass (site 2 in ref 7). The COPR contains 4% total Cr of which 30 ± 5% is Cr(VI) (Table 1 (4)).

Column Experiments. All column experiments were carried out with field-moist material, from which aggregates larger than approximately 6 mm were removed. For each experiment, a 2.5 cm diameter column was filled with 10.0 g of acid-washed sand and, above that, a 5-cm layer of field-moist COPR (Figure 1a). Small quantities of COPR were incrementally added to the column, while 1 mM NaCl solution was slowly pumped (3 mL h⁻¹) into the lower end of the column. The pore volume, defined as the volume of solution present in the 5-cm layer of COPR, was approximately 15 mL

in each of the experiments. The amount of COPR per column was approximately 23 g dry weight.

After 3 d, leaching of the column was started. The feed solution was pumped into the lower end of the column at a rate of approximately 6 mL h⁻¹. Leachate pH was measured in-line using a flat-surface pH electrode and a flow cell with an internal volume of 200 μL. The leachate was collected in aliquots of 5 mL during the first 12–16 pore volumes and later in 10-mL aliquots. Total element concentrations were determined by ICP–OES analysis of acidified samples. Aqueous S was assumed to be sulfate in solution. Cr(VI) concentrations were determined in non-acidified samples by colorimetry using diphenylcarbazide (25). Carbonate in solution was not determined because, during the time it took to collect the samples, the solutions would have attracted CO₂ from the atmosphere due to their high pH.

Fresh 20 mM Fe(II) solutions were prepared daily. NaCl solutions (1 mM) were acidified with 1 M HCl to pH 3, after which FeSO₄ (Merck, p.a.) or FeCl₂ (Fisher Chemicals, pure grade) was added. During the experiment, the Fe(II) feed solution was continuously bubbled with N₂. FeCl₂ is relatively unstable and contained a small amount of iron(III) hydroxide. Therefore, the FeCl₂ solutions were filtered (Whatman 540 filter paper), and the Fe(II) concentration was checked by colorimetric analysis using 2,4,6-tri-(2'-pyridyl)-s-triazine (26) with Fe(NO₃)₃ reduced by hydroxylamine hydrochloride as a standard. Measured Fe(II) concentrations were 20 mM within 1% deviation. Other feed solutions used for leaching were 1 mM NaCl and 1 mM NaCl + 20 mM Na₂SO₄.

SEM-EDX. Samples of dried COPR were embedded in a low-viscosity epoxy resin, polished to produce a smooth flat surface, and coated with a thin layer (20 nm) of vacuum-evaporated carbon. Specimens prepared in this way are suitable for backscatter imaging and X-ray microprobe analysis. The samples were examined in a Philips XL20 SEM using a beam operating voltage of 20 kV. Quantitative elemental analysis was performed with an energy-dispersive X-ray spectrometer fitted with a Li drifted Si detector and a Be window, allowing detection of all elements with an atomic number ≥ 11. The spectra for quantitative analysis were collected in the spot analysis mode for periods of 100 s using count rates of 4000–5000 counts s⁻¹ while maintaining the deadtime below 30%. The data were subsequently processed by a standards-based ZAF correction program to take account of effects of atomic number (Z), absorption (A), and fluorescence (F).

Anion-Exchange Experiment. A sample stub from SEM analysis was immersed in a solution with the following composition (mM): Al, 0.65; Ca, 3.5; Cl, 21.2; K, 0.15; Mg, 0.01; Na, 2.74; SO₄, 3.0; Si, 0.02; OH, 3.7. The total treatment time was 30 min in a N₂ atmosphere, after which the sample stub was dried at 30 °C. Hydrogarnet and hydrocalumite minerals in the specimen were analyzed using SEM-EDX before and after the treatment. Because of damage by the X-ray beam to these hydrated minerals, the second analysis was not performed at exactly the same location but at a distance of about 1–2 μm from the first analysis on the same crystal.

Results and Discussion

Leaching of Cr(VI) from COPR. The column was saturated with a 1 mM NaCl solution, and after 3 d, leaching with a feed solution of 1 mM NaCl was started. The Cr(VI) concentration in the leachate decreased from 0.62 to 0.09 mM during 70 pore volumes (Figure 2). These measured concentrations are 3 orders of magnitude greater than the environmental quality standard used in the U.K. for total Cr in groundwaters and surface waters, which is 0.1–1 μM Cr depending on the hardness of the solution (27). The U.S.

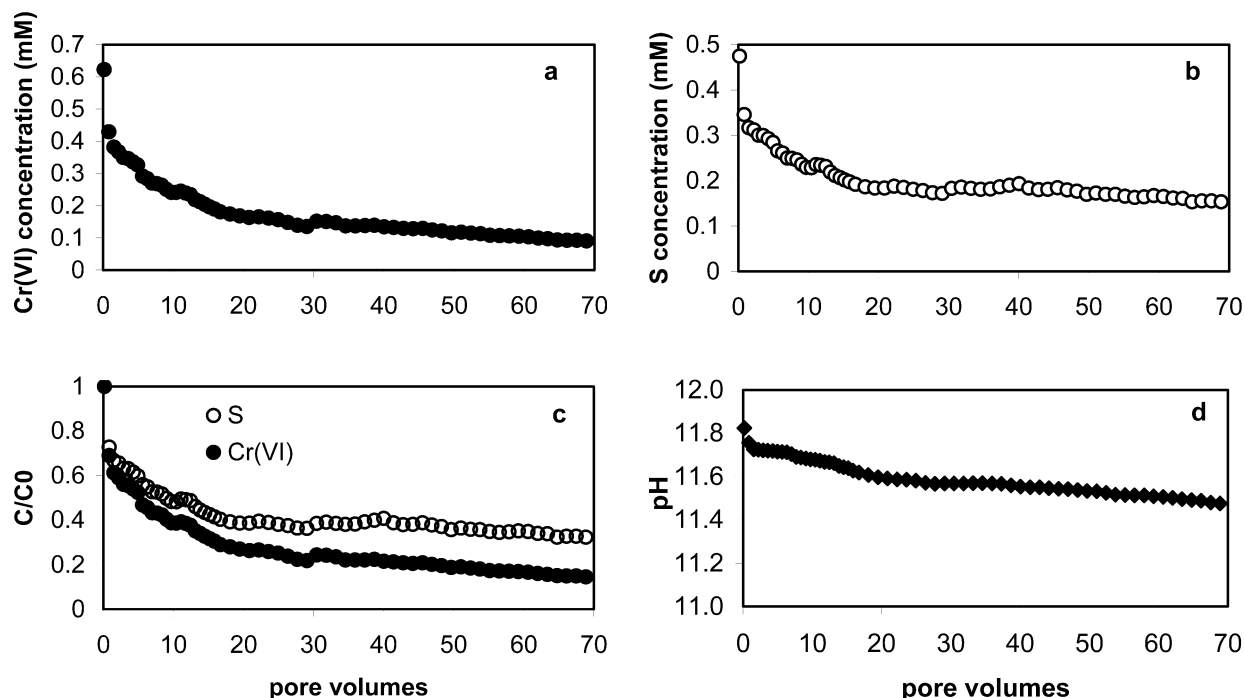


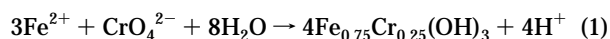
FIGURE 2. Aqueous concentrations of (a) Cr(VI) and (b) S in leachate, also (c) plotted as relative concentrations, and (d) pH of leachate. Column of COPR leached with 1 mM NaCl feed solution.

EPA maximum contaminant level for total chromium in drinking water is 0.1 mg L^{-1} ($\sim 2 \text{ }\mu\text{M}$) (28). The amount of Cr(VI) leached from the column was 7.0 mmol kg^{-1} COPR, which is however only 3.0% of the total Cr(VI) present in COPR. Together with the shape of the leaching curve, this small fraction suggests that leaching of these high concentrations of Cr(VI) can continue for a much longer period of time.

The concentration of sulfate in the leachate is similar to the Cr(VI) concentration, although sulfate concentrations are maintained at higher concentrations after the first few pore volumes (Figure 2). During leaching for 70 pore volumes, the pH decreased only slightly from 11.8 to 11.5.

The concentrations in the leachate decreased strongly within 1 pore volume (Figure 2). This indicates heterogeneous flow conditions due to preferential flow channels in the column or along the glass wall of the column, probably caused by the large variation in aggregate size of COPR. If the flow in the column was homogeneous, the concentration in the leachate should remain constant for at least 1 pore volume, also in systems that are not buffered by release from the solid phase. The fact that the pH of the leachate remains very high during leaching is an indication that despite the presence of preferential flow channels there is a strong interaction of the feed solution with COPR.

FeSO₄ Feed Solution. A column of COPR was leached with a feed solution containing ferrous sulfate to assess whether this treatment results in a decrease in Cr(VI) leaching from COPR. Remediation of Cr(VI) contamination in soils and waters using FeSO₄ is based on the reduction of Cr(VI) with Fe(II) and the subsequent precipitation of a mixed iron(III)/chromium(III) hydroxide:



Leaching a column of COPR with 1 mM NaCl + 20 mM FeSO₄ (pH 3) solution resulted in precipitation in the column. At the inlet of the column, just above the layer of sand, a thin layer of orange-colored precipitate developed, indicating the formation of the mixed iron(III)/chromium(III) hydroxide

(Figure 1b). However, further into the column a dark green precipitate formed, which appeared to be an Fe(II) precipitate because its color changed from dark green to brown upon exposure to air. Some fingering in the pattern of Fe(II) precipitation was observed, indicating heterogeneous flow.

Most studies of Cr(VI) remediation with Fe(II) have been carried out using Fe(II) solutions, but Fe(II)-containing minerals such as green rust have also been shown to be effective in reducing Cr(VI) to Cr(III) (29, 30). However, in our experiment, a much larger amount of Cr(VI) was leached out with a feed solution containing FeSO₄ as compared to leaching with NaCl solution (Figure 3). This result shows that the beneficial effect of Fe(II) addition in decreasing Cr(VI) leaching as observed in soils (21–23, 31) does not occur with COPR. In the first 25 pore volumes, FeSO₄ solution leached out three times more Cr(VI) than the NaCl solution (Table 2). After these 25 pore volumes, Cr(VI) in the FeSO₄-treated column decreased to lower concentrations than in the NaCl-leached column.

Another important difference between the leachate composition of the columns leached with FeSO₄ and NaCl solution was the occurrence of high concentrations ($\sim 18 \text{ mM}$) of Ca in the leachate of the column treated with FeSO₄ (Figure 3). The breakthrough concentration of sulfate was also approximately 18 mM. The decrease in sulfate concentration below the feed concentration of 20 mM was caused by precipitation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in the column, as can be concluded from the calculated ion activity product (IAP) of the leachate for gypsum (Figure 4). To elucidate the observed effect of FeSO₄ on Cr(VI) leaching, two additional column experiments were carried out with feed solutions containing FeCl₂ and Na₂SO₄.

FeCl₂ Feed Solution. Leaching a column of COPR with 1 mM NaCl + 20 mM FeCl₂ (pH 3) solution had visibly the same effect as leaching with FeSO₄ solution. At the inlet of the column, a thin layer of orange precipitate formed and just above that a dark green precipitate. In the FeCl₂ treatment, slightly more Cr(VI) leached from the COPR column than with NaCl but much less than with FeSO₄ in the feed solution (Figure 3, Table 2). Similar to leaching with

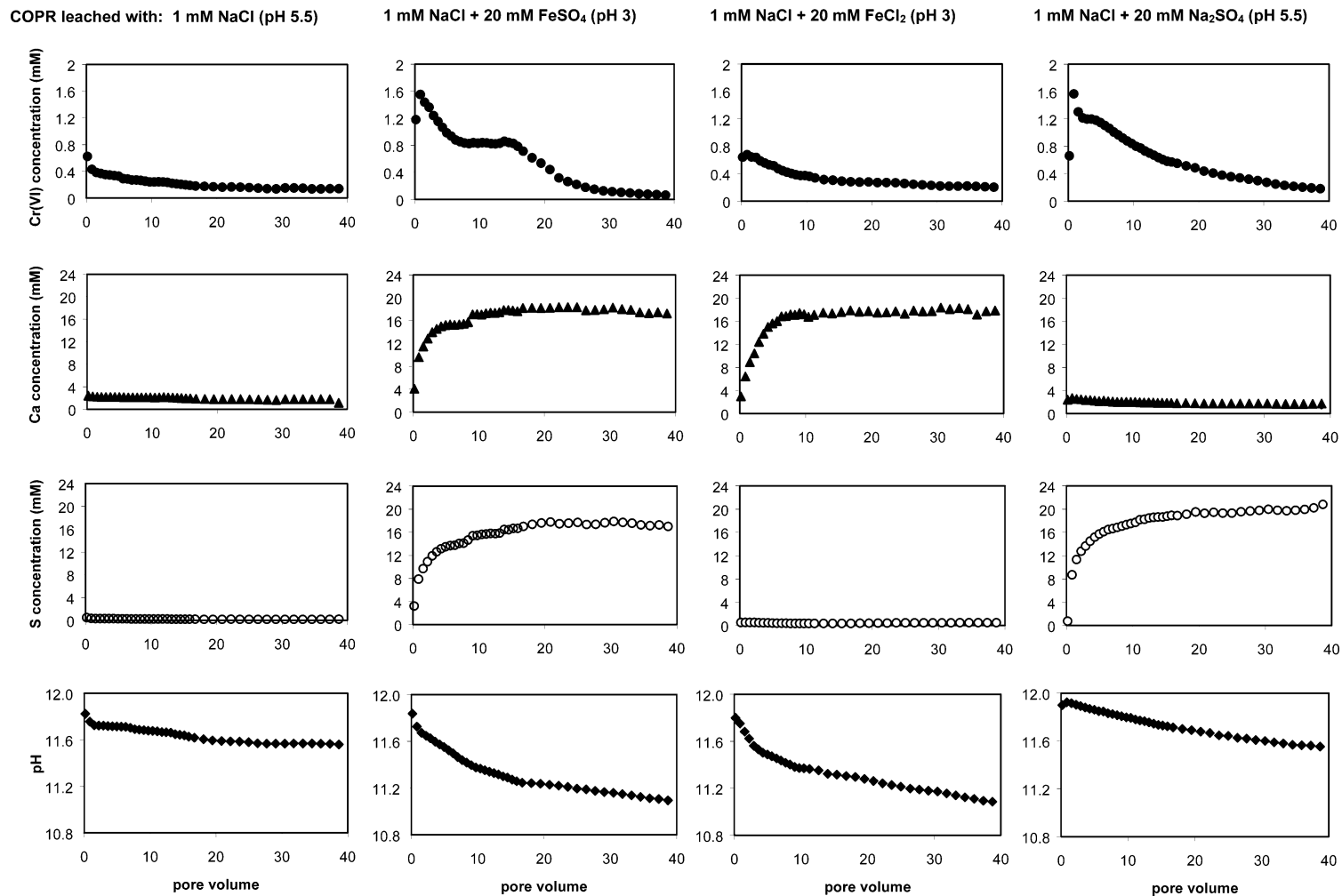


FIGURE 3. Aqueous concentrations of Cr(VI), Ca and S, and pH of leachate (top to bottom) in four column experiments with COPR (left to right).

TABLE 2. Amounts of Cr(VI) and Ca Leached from COPR in the Column Experiments

infiltrating solution		1 mM NaCl, pH 5.5	1 mM NaCl + 20 mM FeSO ₄ , pH 3	1 mM NaCl + 20 mM FeCl ₂ , pH 3	1 mM NaCl + 20 mM Na ₂ SO ₄ , pH 5.5
Cr(VI) leached ^a	(mmol kg ⁻¹) ^b	3.8	12.3	5.8	12.5
	(%)	1.6	5.3	2.5	5.4
Ca leached ^a	(mmol kg ⁻¹) ^b	46	267	253	32
	(%)	1.0	5.9	5.6	0.7

^a In 25 pore volumes. ^b mmol kg⁻¹ dry COPR.

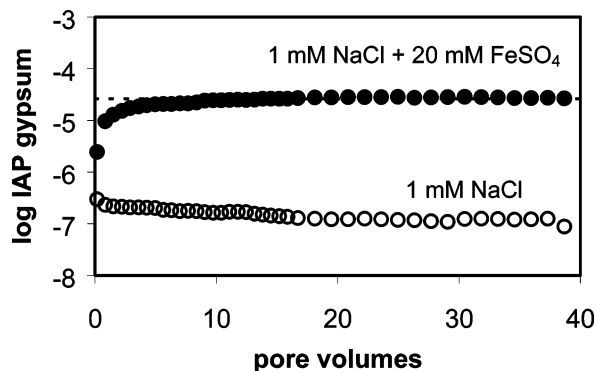


FIGURE 4. Log IAP for gypsum in the leachate of columns of COPR leached with 1 mM NaCl and with 1 mM NaCl + 20 mM FeSO₄ (pH 3). The log *K* for gypsum is -4.58 (32).

FeSO₄, however, high concentrations of Ca were leached from the column and the pH decreased. The sulfate concentration in the leachate was comparable for leaching with FeCl₂ and NaCl solution.

Na₂SO₄ Feed Solution. Leaching with 1 mM NaCl + 20 mM Na₂SO₄ solution did not show visible effects of precipitation in the column. It did, however, result in a large increase in the concentration of Cr(VI) in the leachate (Figure 3). A plateau occurred in the Cr(VI) leachate concentration, but at a different time (pore volume) and concentration than for leaching with FeSO₄. The total amount of Cr(VI) that was leached in 25 pore volumes was 12.5 mmol kg⁻¹ COPR, which is very similar to the amount leached in the FeSO₄ treatment (Table 2).

Effect of Fe(II). For both column experiments where Fe(II) was added to the feed solution, leaching of Cr(VI) was larger than in the control treatment with NaCl (Figure 3, Table 2). This shows that Fe(II) was not effective in converting Cr(VI) to Cr(III) and hence not suitable for decreasing the leaching of Cr(VI) in a column of COPR.

The large pH buffering capacity of COPR (4) results in a rapid increase in the pH of the feed solution from 3 to approximately 11.8 when it enters the column. Solubility calculations for 20 mM Fe(II) at *I* = 0.01 M show that Fe(II) precipitates as Fe(OH)₂ at pH > 8 for the FeCl₂ solution and at pH > 8.25 for the FeSO₄ solution. Carbonate in COPR is present in the form of calcite (4, 13), and the equilibrium aqueous carbonate concentration is too low for precipitation of siderite (FeCO₃). These solubility calculations are in agreement with the color of precipitates formed in the column; siderite has a light gray color, whereas Fe(OH)₂ is dark green.

Only at the inlet of the column, when the pH is still below 8 and Fe(OH)₂ is not precipitated, Cr(VI) will be reduced by Fe(II), resulting in the precipitation of the orange iron(III)/chromium(III) hydroxide. Aqueous Fe(II) in equilibrium with Fe(OH)₂ is in the micromolar range, which results in insignificant reduction of Cr(VI) of which the aqueous concentration is in the range of 0.1–1 mM. Hence, because of the very high pH and resulting precipitation of Fe(II), Cr(VI)

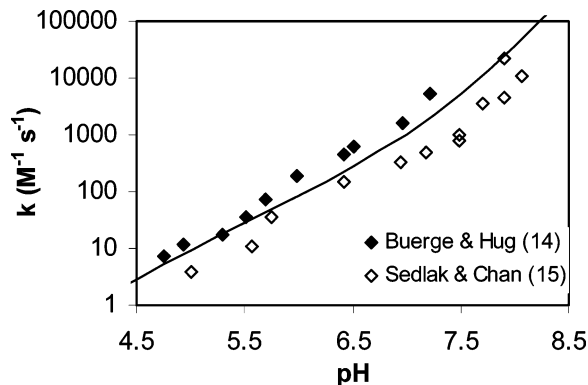


FIGURE 5. pH-dependent rate constant for oxidation of Fe(II) by Cr(VI), defined as $k = (d[Fe(II)]/dt)/([Fe(II)][Cr(VI)])$, where [] denotes the total concentration of a component. Markers indicate data from the literature for *T* = 23–25 °C and *I* ~ 0.01 M (14, 15). The line represents the fitted equation (eq 3).

was not reduced but leached from the column by the infiltrating solution.

Kinetics of Fe(II) Oxidation by Cr(VI) and O₂. It is well-known that the rate of Fe(II) oxidation by O₂ increases strongly with increasing pH (33). It is important to determine whether this process contributes to the ineffectiveness of Fe(II) in reducing Cr(VI) in columns with COPR. Kinetic studies of Fe(II) oxidation by oxygen showed that the rate of oxidation is first order in O₂ and in Fe(II) (33). Literature data for Fe(II) oxidation by oxygen are available up to pH 8.5, and this is the pH range where Fe(II) in the COPR columns is still in solution. In the pH range 4.5–8.5, the kinetics of Fe(II) oxidation by oxygen can be represented by the following equation (34):

$$d[Fe(II)]/dt = 4 \times 10^2 (O_2)(FeOH^+) + 5 \times 10^7 (O_2)(Fe(OH)_2^0) \quad (2)$$

where [Fe(II)] denotes the total iron concentration and () denotes the activity of a species. The rate constants in this equation were calculated using the formation constants for Fe(II) species from Baes and Mesmer (35).

We used kinetic data for Fe(II) oxidation by Cr(VI) available in the literature (14, 15) to describe the oxidation rate in terms of the Fe(II) and Cr(VI) speciation (Figure 5). In the pH range 4.5–8.5, the rate of Fe(II) oxidation by Cr(VI) can be described using the activity of the species FeOH⁺ and Fe(OH)₂⁰, as is the case for Fe(II) oxidation by O₂ (14). This makes a direct comparison of the rate of oxidation by the two oxidants possible. The rate equation fitted to the data, using formation constants for Cr(VI) from the MinteqA2 database (36) and for Fe(II) from (35), expressed for oxidation of Fe(II) by Cr(VI), is

$$d[Fe(II)]/dt = 5 \times 10^5 \{ (HCrO_4^-) + (CrO_4^{2-}) \} (FeOH^+) + 3 \times 10^9 \{ (HCrO_4^-) + (CrO_4^{2-}) \} (Fe(OH)_2^0) \quad (3)$$

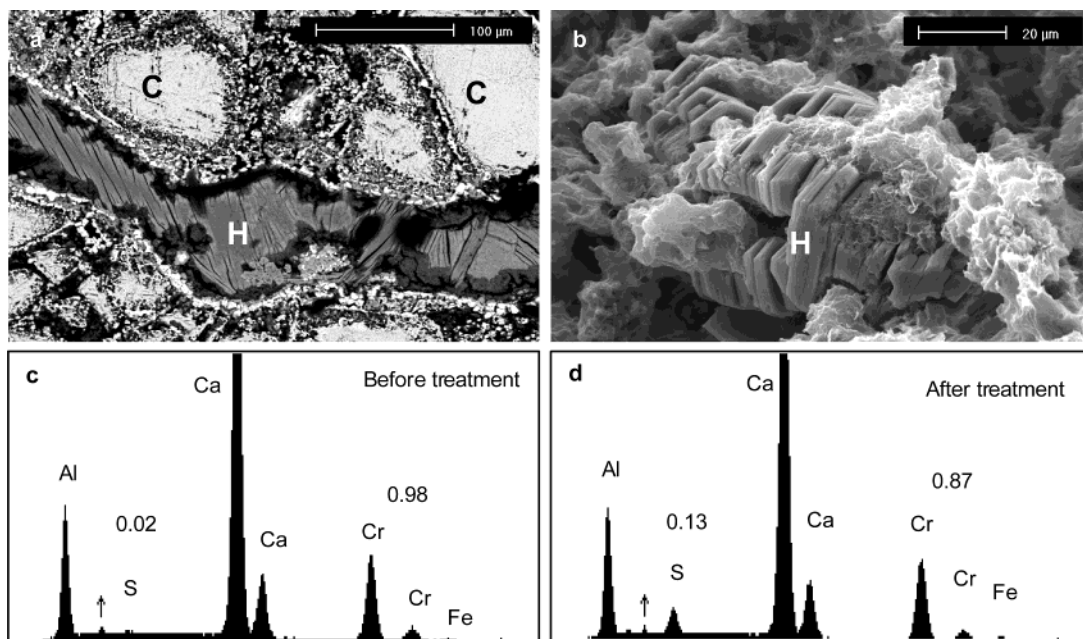


FIGURE 6. SEM backscattered image of hydrocalumite (H) in (a) polished sample and (b) fractured sample of COPR. C denotes relict chromite particles. SEM-EDX analysis of a hydrocalumite crystal (c) before and (d) after submersion for 30 min in artificial pore water containing 3 mM sulfate but no Cr(VI). Normalized Cr and S contents are expressed in atoms per unit of hydrocalumite ($\text{Ca}_4(\text{Fe}/\text{Al})_2(\text{OH})_{12}(\text{CrO}_4/\text{SO}_4) \cdot 6\text{H}_2\text{O}$).

Comparison of the Fe(II) oxidation kinetics shows that, at equal concentrations of Cr(VI) and O_2 , oxidation of Fe(II) by Cr(VI) is 100–1000 times faster than by O_2 . Since the O_2 concentration in solution in the column at air saturation (~ 0.25 mM) and the initial Cr(VI) concentration in solution (~ 0.62 mM) are of the same order of magnitude, oxidation of Fe(II) by Cr(VI) is the dominant process. The Fe(II)-containing feed solutions were purged with N_2 and hence devoid of O_2 .

Effect of pH. The leachate pH of columns leached with feed solution containing NaCl or NaCl + Na_2SO_4 decreased from 11.8 to about 11.6 in 40 pore volumes. Leaching with Fe(II) feed solutions resulted in a pH of 11.1 after 40 pore volumes. Precipitation of Fe(II) as $\text{Fe}(\text{OH})_2$ results in the release of 2 mol of H^+ /mol of Fe(II). The Fe(II) feed solutions also contained 1 mM H^+ as HCl, so in total 41 mM H^+ is added or released in the column, resulting in the observed pH decrease from 11.8 to 11.1 (Figure 3). Buffering of the pH by COPR is dominated by the dissolution of Ca-containing phases, which explains the release of high concentrations of Ca in the Fe(II)-treated columns.

Results from previous experiments (4) show that a decrease in pH from 11.7 to 11 resulted in an increase in the aqueous Cr(VI) concentration from 0.45 to 0.73 mM in batch systems. Speciation calculations for these experiments show that this is due to the partial dissolution of chromium(VI) hydrocalumite and Cr(VI)-substituted hydrogarnet (4). For the column experiment with FeCl_2 in the feed solution, the partial dissolution of Cr(VI)-containing phases with decreasing pH can explain the observed increase in Cr(VI) leaching. However, this explanation is not sufficient to account for the much larger increase in Cr(VI) leaching when COPR is leached with FeSO_4 solution.

Effect of Sulfate. In the column experiment with NaCl as feed solution, leaching of Cr(VI) and sulfate was similar (Figure 2), which suggests that chromate and sulfate are present in the same mineral forms in COPR. Cr(VI) in COPR is present in the minerals hydrogarnet ($\text{Ca}_3\text{Al}_2(\text{H}_4\text{O}_4/\text{SiO}_4/\text{CrO}_4)_3$) and chromium(VI) hydrocalumite. SEM-EDX analysis of these minerals showed that hydrogarnet did not contain sulfate. However, sulfate was present in hydrocalumite, at

5.4% (± 2.4 , $n = 14$) of anion content in the formula unit $\text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{anion}) \cdot 6\text{H}_2\text{O}$ (4). In a number of subsamples of COPR, traces of ettringite were found. These contained both chromate and sulfate, but the sulfate content was much higher, ranging from 53 to 96% of anion content in $\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{anion})_3 \cdot 26\text{H}_2\text{O}$ (13). X-ray diffraction analysis and calculation of the IAP of the liquid in batch experiments showed that no gypsum is present (4, 13).

In the column experiments with sulfate in the feed solution, as either FeSO_4 or Na_2SO_4 , leaching of Cr(VI) increased dramatically (Table 2, Figure 3). A possible explanation for this increase is the direct exchange of sulfate for chromate in chromium(VI) hydrocalumite. Hydrocalumite belongs to the group of layered double-hydroxide minerals or AF_m phases. It is the Ca analogue of hydrotalcite and has anion-exchange properties (37, 38). Hydrocalumite consists of octahedral layers of $\text{Ca}_2\text{Al}(\text{OH})_6^+$, of which the charge is balanced by exchangeable anions that are present in the interlayer together with water molecules. A range of anions may be present in the interlayer: OH^- , SO_4^{2-} , $\text{Al}(\text{OH})_4^-$, $\text{AlSiO}_8\text{H}_8^-$, CO_3^{2-} , Cl^- (37, 38), CrO_4^{2-} (39, 40), BO_3^{3-} , SeO_4^{2-} , AsO_4^{3-} , and MoO_4^{2-} (41).

Anion Exchange. Using SEM-EDX, we examined a sample of COPR before and after immersing it in a high-pH artificial pore water solution containing 3 mM sulfate but no chromate to study chromate–sulfate exchange. A similar procedure was used earlier to demonstrate direct cation exchange in the clay minerals kaolinite, illite, and smectite (42). Crystals of hydrocalumite were identified using SEM in the backscattered imaging mode (Figure 6), and identification was confirmed by stoichiometric calculations based on elemental contents determined with EDX. The average composition of the 9 crystals that were analyzed was $\text{Ca}_4(\text{Al}_{0.76}\text{Fe}_{0.24})_2(\text{OH})_{12}(\text{Cr}_{0.98}\text{S}_{0.02}\text{O}_4)$, indicating that there was considerable substitution of Fe(III) for Al but that the sulfate content in the examined crystals was very small. After 30-min treatment in the artificial pore water solution, the sulfate content in hydrocalumite had increased to 12% of (Cr + S) content, while the chromate content decreased to 88% (Table 3, Figure 6). We also examined Cr(VI)-substituted hydrogarnet to check whether it remains stable in the presence of sulfate and found

TABLE 3. Cr and S Content of Hydrocalumite^a

	before sulfate treatment			after sulfate treatment		
	average	SD ^b	normalized	average	SD	normalized
Cr	1.016	0.067	0.98	0.921	0.044	0.88
S	0.021	0.015	0.02	0.128	0.059	0.12
Cr + S	1.038			1.049		

^a Contents determined by SEM-EDX analysis of 9 crystals expressed as atoms per formula unit of hydrocalumite (Ca₄(Fe/Al)₂(OH)₁₂(CrO₄/SO₄)·6H₂O) before and after immersion for 30 min in high-pH artificial pore water containing 3 mM sulfate but no chromate. ^b SD, standard deviation.

no change in composition.

In 30 min, sulfate exchanged 10% of Cr(VI) present in the interlayers of hydrocalumite. Chloride may also be present as the interlayer anion in hydrocalumite, in a mineral that is known as Friedel's salt. However, leaching with FeCl₂ solution resulted in only a small increase in Cr(VI) leaching, which could be attributed to a decrease in pH (Figure 3). Thus, sulfate was much more effective than chloride in anion-exchange reactions with chromate, as would be expected from the similarity in the charge and size of sulfate and chromate.

In-situ formation of hydrocalumite by the addition of lime to waste materials such as fly ash has been proposed as a method for decreasing the leaching of potentially hazardous anions. In this process, anions such as borate, selenate, arsenate, chromate, and molybdate are scavenged in the interlayer, thereby decreasing their concentration in solution (41, 43). In samples of COPR from several sites in the Glasgow area, the content of hydrocalumite ranged from 4.3 to 5.8 wt % (12, 13). However, analysis with SEM-EDX has shown that the interlayer of hydrocalumite is almost completely filled with chromate ions, ranging from 67 to 99% (average 92%, *n* = 35). So, instead of having the ability to act as a sink for chromate, hydrocalumite is an important source of leachable Cr(VI) in COPR. Moreover, the leaching process is considerably enhanced in the presence of anions such as sulfate, which can participate effectively in anion-exchange reactions.

Implications for Remediation of COPR. Fe(II) is not effective for remediation of Cr(VI) in COPR by reduction to Cr(III) because of the very high pH of COPR, which causes Fe(II) to precipitate. Because of the very large buffering capacity of COPR, the pH is maintained at very high values despite the production of acidity in the precipitation process. In the case of ferrous sulfate, additional Cr(VI) is released from COPR through anion exchange of sulfate for chromate. In contrast to treatment of COPR, the treatment of Cr(VI)-contaminated surface waters and groundwaters originating from COPR sites with Fe(II) is likely to be effective. These waters generally have a lower pH, between 7 and 9, although values up to 12.5 were also found (3), and virtually no buffering capacity. In addition, the organic C content is generally low (3), and so reduction of Cr(VI) to Cr(III) will not result in the formation of mobile organic-Cr(III) complexes, but Cr(III) will precipitate as mixed iron(III)/chromium(III) hydroxide.

In a wider context, the results presented here show that direct transfer of remediation treatments from one matrix to another needs to be very carefully considered before being deployed at field sites. A thorough understanding of the processes involved is essential in the evaluation of remediation treatments and the assessment of risks from contaminated land.

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