

Long-term treatment issues with chromite ore processing residue (COPR): Cr⁶⁺ reduction and heave

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Abstract

A pugmill treatability study was conducted to remediate chromite ore processing residue (COPR) using ferrous sulfate heptahydrate (FeSO₄·7H₂O) as a reductant. Two different types of COPR, with respect to particle size and mineralogy, were tested in this study. Two different stoichiometric ratios of FeSO₄·7H₂O to Cr⁶⁺ (5× and 8×) were applied to reduce Cr⁶⁺ to Cr³⁺. The effectiveness of FeSO₄·7H₂O treatment was assessed using the toxicity characteristic leaching procedure (TCLP) tests and X-ray absorption near edge structure (XANES) analyses. TCLP results obtained from the pugmill treatability study showed that TCLP Cr concentrations were less than the TCLP regulatory limit of 5 mg/L upon 8× FeSO₄·7H₂O treatment for up to 420 days but may fail to meet this regulatory limit in the long-term. XANES results obtained from samples cured for 300 days showed that all of the treated samples failed the New Jersey Department of Environmental Protection (NJDEP) clean up level for Cr⁶⁺ of 240 mg/kg. However, the Cr⁶⁺ concentration from the sample with the smaller particle size approached 240 mg/kg (338 mg/kg), suggesting that particle size reduction prior to the addition of reductant may improve the effectiveness of the treatment. COPR heaving was investigated with unconfined swell tests upon 5× and 8× FeSO₄·7H₂O treatment. The formation of ettringite, an expansive material, was investigated following the swell tests using X-ray powder diffraction (XRPD). Significant heaving (>50 vol%) was observed at curing times of 138 days for the 5× treatment and the ettringite formation was identified by XRPD analyses.

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1. Introduction

Alkaline (pH > 12) chromite ore processing residue (COPR) is derived from the roasting of chromite ore mixed with soda ash and slaked lime at ~1200 °C to oxidize Cr³⁺ and sequester impurities. The end products are soluble sodium chromate and the solid COPR that mainly consists of brownmillerite (Ca₂FeAlO₅), periclase (MgO) and excess of hydrated lime (Ca(OH)₂) [1]. COPR was widely used as structural fill material in the USA, and major COPR deposition sites are located in Maryland, New Jersey, Ohio and New York [2].

About 1.5 million tonnes of COPR were deposited over a span of 50 years as a fill at various sites in Hudson Country, NJ. In this study, COPR samples obtained from Study Area 7 (SA7)

and COPR materials from NJ deposition sites have shown Cr contents of up to 5% with Cr⁶⁺ concentrations up to 2%. Cr⁶⁺ is mobile in groundwater and is acutely toxic, mutagenic and carcinogenic while Cr³⁺ is much less toxic and immobile under normal groundwater conditions [3–5]. Furthermore, extensive heaving was observed over time at this site, resulting in no site use at all. Details about COPR origin and history of the SA7 site were reported in Dermatas et al. [6]. It has been reported that ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O, AFt) formation is strongly associated with heaving phenomena upon the influx of sulfate in COPR materials [7]. Commonly used to reduce Cr⁶⁺ to Cr³⁺, ferrous sulfate heptahydrate (FeSO₄·7H₂O) also provides a sulfate source for the potential formation of ettringite in COPR materials. Formation of ettringite in COPR materials can take as little as 1 h upon addition of very small amounts of sulfate (<0.1%, w/w) [8]. It should be noted that monosulfate (monophase, AFm) and gypsum (CaSO₄·2H₂O) do not favor the development of swell pressures adequate to provide

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volumetric expansion. In addition, the transformation of ettringite into gypsum is mainly dependant on the system pH. Hunter [9] has reported that when the pH > 10.5, ettringite formation is favored in lime-treated soils. Therefore, Cr⁶⁺ contamination and heaving at COPR deposition sites need to be jointly addressed.

The purpose of this study was to investigate the optimum dosage of FeSO₄·7H₂O for effective Cr⁶⁺ reduction, and the mitigation of heaving phenomena in COPR materials. The target Cr⁶⁺ concentration for the remediation of COPR materials was 240 mg/kg, the soil cleanup criteria established by the New Jersey Department of Environmental Protection (NJDEP) for residential land use for the inhalation exposure pathway [10]. Toxicity characteristic leaching procedure (TCLP) tests also were performed to evaluate the total Cr leaching upon treatment based on the TCLP regulatory limit of 5 mg/L. X-ray absorption near edge structure (XANES) analyses were conducted to evaluate the Cr⁶⁺ reduction. X-ray powder diffraction (XRPD) analysis was performed to investigate the mineralogical changes in COPR materials and to document the presence of ettringite.

2. Experimental methodology

2.1. COPR materials, reagents and pugmill mixer

COPR materials were collected (about 1000 lb based on dry weight) from zones B1, B2 and C. The vertical profile of COPR stratigraphy and physical description at SA 7 were reported in Dermatas et al. [6]. Zone B1 and B2 materials consist of coarse sand with some silt and gravel, while Zone C consists mainly of fine-grained, gray, brown, green yellow fine sand/silt with some clay. The particle size distribution of COPR materials are presented in Table 1. Composite B1B2 samples and Zone C sample were used in this study. Specifically, the composite B1B2 samples were prepared by mixing equal amounts of composite B1 and composite B2. The average Cr⁶⁺ concentration in composite B1B2 and C materials, based on alkaline digestion tests, was 4000 mg/kg and 6000 mg/kg, respectively. Composite B1B2 and Zone C samples were sieved through a 3/8 in. sieve to minimize sample variability. All the larger sam-

ple fractions which remained on the sieve were crushed down to pass through the 3/8 in. sieve, and were homogenized with the remaining COPR materials. To simplify nomenclature, the composite B1B2 sample was designated as “I”, and Zone C as “II”.

Ferrous sulfate heptahydrate (FeSO₄·7H₂O) obtained from Fisher Scientific (Suwanee, GA) was used as a reductant. The stoichiometric ratios of FeSO₄·7H₂O to Cr⁶⁺ (5× and 8×) were calculated based on the number of electrons transferred during oxidation and reduction reactions based on an average Cr⁶⁺ of 4000 mg/kg and 6000 mg/kg for samples I and II, respectively. The sample designations upon treatment are I-5×, I-8×, II-5× and II-8×.

A two cubic yard capacity batch-type pugmill mixer (Maxon Industries, Milwaukee, WI) featuring a dual directional mixing capabilities and an eight-paddle agitator shaft was used.

2.2. Methods

Excavated COPR I and II materials at their “as excavated” moisture content were introduced to the mixer. Extra water was added and pugmilling for 5 min was undertaken to provide a homogenous material before addition of the reductant (Table 2). FeSO₄·7H₂O was then added based on the stoichiometric ratios (illustrated in Table 2) and mixing was performed for an additional 5 min. After the FeSO₄·7H₂O treatment the COPR materials were removed from the mixer and cured.

2.3. Swell test

Unconfined swell tests were performed for 138 days by placing the treated COPR samples into clear cylindrical plastic molds with an internal diameter of 3.79 in. and a height of 4 in. The molds were fully open at the top and closed at the bottom. A 2-in. travel dial gauge was used to monitor height changes. Height change measurements reported in this study were taken in the center of sample’s surface. The percent heave (swelling) was calculated as the ratio of the change in vertical height to the original height of COPR multiplied by 100.

Table 1
Particle size distribution for samples I and II

Samples	Percent passing (dry weight basis)									
	3/2 in.	3/4 in.	3/8 in.	#4	#10	#20	#40	#60	#100	#200
I	100	94.6	86.9	82.4	77.6	69.5	57.6	45.5	33.7	24.3
II	100	100	98.7	93.5	87.8	81.5	75.5	69.2	62.1	52.4

Table 2
Ferrous sulfate-COPR pugmill mixing matrix

Samples	Dosage	Initial moist weight of COPR sample (lb)	Moisture content of COPR (%)	Target moisture content of COPR sample (%)	Ferrous sulfate heptahydrate (lb)
I-5×	5×	1230	21.8	30	323
I-8×	5×	1257	22.9	40	522
II-5×	5×	1723	101.5	As is	410
II-8×	8×	1892	115.8	As is	675

Table 3
Swell test matrices and testing conditions

Samples	Treatment	Initial water content (%)	Initial pH	Weight of sample (lb)	Diameter (in.)	Height (in.)	D/H ratio	Wet density (lb/ft ³)	Dry density (lb/ft ³)
I	Untreated	20	12.05	–	–	–	–	–	–
I-5×	5×	27	8.12	1.45	3.79	1.72	2.2	128.9	101.5
I-8×	8×	23	4.78	1.47	3.79	1.72	2.2	130.2	105.9
I-5×-c	5× control	20	8.2	–	–	–	–	–	–
I-8×-c	8× control	26	5.63	–	–	–	–	–	–

Two treatment levels (5× and 8×) of FeSO₄·7H₂O were tested (Table 3). COPR samples were mixed with FeSO₄·7H₂O and then placed into the molds by manual kneading using a rubber pestle to achieve the field density. A 5× and 8× control sample each were prepared to monitor pH without disturbing the actual swell samples during the testing period. About 10 mL of deionized (DI) water was added to each sample daily in order to accelerate the reaction (Table 3).

2.4. Physicochemical analyses

pH and water content were measured according to ASTM methods D 4980-89 and D 2216-98 [11], respectively. Total Cr concentrations in TCLP leachate were measured by Inductive Coupled Plasma/Atomic Emission Spectrometry (ICP/AES). Total Cr content in the untreated sample was determined by digesting 1 g of COPR material using 1:1 HNO₃, concentrated HNO₃ and 30% H₂O₂ on a hot plate [12]. After the cooling process, the digested sample was diluted to 100 mL with deionized water for analysis of Cr using ICP/AES. TCLP tests were performed according to the EPA method 1311 using extraction fluid no. 2 (pH 2.88) [13]. TCLP tests were conducted on the COPR samples before treatment, immediately after treatment, and after 30, 120 and 420 days of curing. Total Cr⁶⁺ was measured by the U.S. EPA methods 3060A [14] and 7196A [15]. All sample analyses were conducted with duplicates and averaged values were reported, using two different quality control standards, as well as the method of standard addition (spiking).

2.5. X-ray absorption near edge structure (XANES) analyses

XANES analyses were conducted for treated COPR samples cured for 300 days using a BL7C1 (Electrochemistry) beamline in a storage ring of 2.5 GeV with a ring current of 130–185 mA at the Pohang Accelerator Laboratory (PAL), South Korea. A Si (111) double crystal monochromator was used to monochromatize the X-ray photon energy. High order harmonic contamination was eliminated by detuning the monochromator to reduce the incident X-ray intensity by approximately 30%. All spectroscopic data were collected in the fluorescence mode using pure N₂ gas-filled ionization chambers as gas detectors. Energy calibration was simultaneously performed for each measurement using a reference Cr foil placed in front of the third ion chamber, and assigning the first inflection point to 5989 eV. Two standard reference chromium

compounds, K₂CrO₄ (Cr⁶⁺) and Cr(NO₃)₃·9H₂O (Cr³⁺) were also analyzed. Quantitative XANES analyses were conducted using the ATHENA program in the IFEFFIT computer package [16].

2.6. X-ray powder diffraction (XRPD) analyses

XRPD samples were collected from the inside of the swell samples upon completion of the study. All samples were air dried for 24 h and then pulverized to pass through a US standard #400 sieve (38 μm). The resulting powder was mixed with 20% (w/w) of internal standard (α-corundum, Al₂O₃) (Sawyer, Lot. No. C04-AO-41). Step-scanned X-ray diffraction patterns were collected by the Rigaku DXR-3000 computer-automated diffractometer. XRPD analyses were performed at 40 kV and 40 mA using a diffracted beam graphite-monochromator with Cu radiation. The XRPD patterns were collected in the 2θ range of 5–65° with a step size of 0.02° and a count time of 3 s per step. The qualitative analyses of the XRPD patterns were performed using Jade software version 7.1 [17] and the PDF-2 reference database from the International Center for Diffraction Data database [18].

3. Results and discussion

3.1. Physicochemical analyses

The TCLP results, treatment pH values and water contents obtained from the pugmilling and cured samples are presented in Table 4. The change in TCLP Cr concentrations upon curing along with the TCLP regulatory limit of 5 mg/L are presented in Fig. 1. TCLP results indicated that total Cr concentrations from

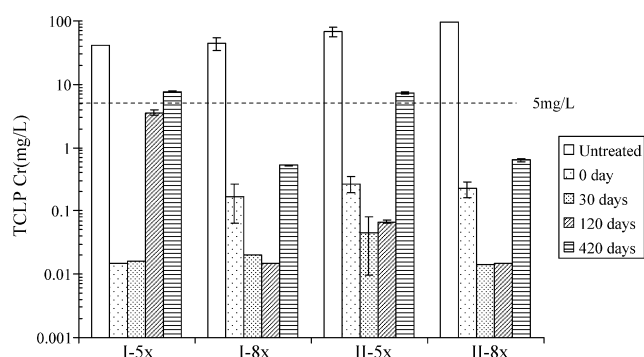


Fig. 1. TCLP Cr concentration (mg/L) for untreated and treated I and II samples.

Table 4
TCLP, water content and pH data for untreated and treated I and II samples

Samples	Total Cr (mg/kg)					TCLP Cr (mg/L)					Water content (%)					pH				
	Untreated	0 day	30 days	120 days	420 days	Untreated	0 day	30 days	120 days	420 days	Untreated	0 day	30 days	120 days	420 days	Untreated	0 day	30 days	120 days	420 days
I-5×	27,350	20,950	22,150	21,250	–	41.35	0.02	0.02	3.55	7.68	19.85	18.55	33.325	33.3	25.52	12.4	6.5	9.95	10.24	11.33
I-8×	24,050	13,300	17,450	18,300	–	44.15	0.17	0.02	0.02	0.64	19.95	8.45	36.1	41	31.07	12.65	5.75	6.35	9.38	10.17
II-5×	21,050	18,700	19,150	18,900	–	68.20	0.077	7.95	0.07	5.311	57.95	65.3	11.3	84.15	87.11	13.1	11.6	11.3	10.53	10.49
II-8×	20,900	15,750	16,000	17,800	–	95.40	0.23	0.01	0.02	0.8583	92	77.9	10.85	83.35	78.39	12.75	9.4	10.85	10.27	9.39

all treated COPR samples cured for 120 days were less than the TCLP regulatory level of 5 mg/L (Fig. 1). Even though Sample II showed high Cr leachability prior to treatment (>68 mg/L) it exhibited better treatment than Sample I (Table 4). Specifically, the TCLP Cr values were 68.2 mg/L and 0.07 after 120 days of curing upon the 5× treatment for the untreated and treated Sample II, respectively. Conversely, these values were 95.4 mg/L and 0.02 mg/L upon the 8× treatments, respectively. On the other hand, the TCLP Cr values were 41.35 mg/L and 3.55 within the same time frame for the untreated and treated Sample I upon 5× treatment, respectively whereas the corresponding values were 44.15 mg/L and 0.02 mg/L for the 8× treatment. Overall, Sample II materials have a greater percentage of fines and higher surface area than Sample I materials, which may play significant role in facilitating reactions. However, at 420 days all 5× treatments failed to meet the TCLP criteria (Table 4 and Fig. 1), whereas, the 8× treatments were able to meet the regulatory criteria. The measured TCLP Cr values for the 8× treatment were 0.64 mg/L and 0.53 mg/L for Samples I and II, respectively. Even though the 8× treatment gave satisfactory results after a curing period of 420 days, the TCLP data for 5× treatment showed an increase in Cr concentration in the TCLP leachate for longer curing periods. This suggests that the 8× treatment may fail to meet the regulatory limit of 5 mg/L in the long-term. Long-term compliance with the TCLP leaching criteria is likely associated with the availability of Fe²⁺ ion to reduce Cr⁶⁺. Therefore, if Fe²⁺ is scavenged by competing reactions, as it was initially in excess quantities, then the treatment may fail. It has been reported that ferrous sulfate treatment of COPR may have failed due to the scavenging of Fe²⁺ by molecular oxygen [19]. This may have contributed ultimately to the failure of the 5× treatment at 420 days.

The reduction Cr⁶⁺ to Cr³⁺ in slurry form and pH adjustment enables Cr³⁺ precipitation as Cr(OH)₃. Dermatas and Moon [20] reported that Cr³⁺ immobilization was mainly controlled by the precipitation of the sparingly soluble Cr³⁺ hydroxides under the alkaline conditions.

The pH values for all samples were higher than 9.95 after 30 days of curing, except for the Sample I-8× which was 6.35 (Table 4). This indicated that even though Sample II showed better treatment with respect to Cr reduction, pH conditions were potentially more favorable for ettringite formation. Even though the Sample II TCLP Cr and the heavy results were satisfactory at 30 days the long-term outlook must account for potential formation of ettringite due to the buffering capacity of COPR and alkalinity produced by mineralogical transformations.

3.2. XANES analyses

Chromium K-edge XANES spectra and the quantification data for selected samples after 300 days of curing are presented in Fig. 2 and Table 5, respectively.

The XANES spectrum for Cr⁶⁺ showed a well-defined pre-edge peak starting at approximately 5990 eV. The height and area of this pre-edge peak is quantitatively proportional to the Cr⁶⁺ concentration [21,22]. The XANES spectrum of Samples I and II showed a significant pre-edge peak reduction following

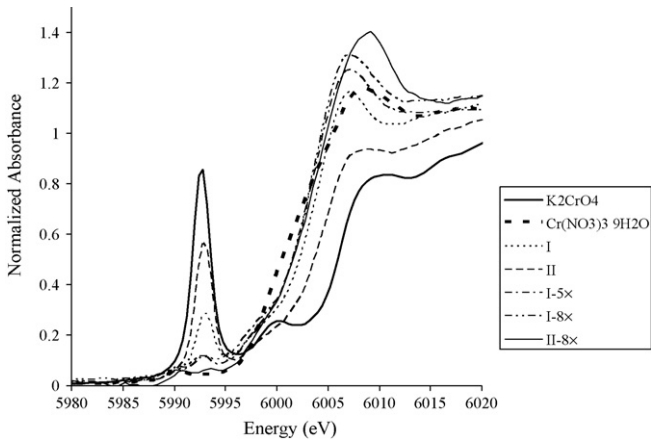


Fig. 2. Chromium K-edge XANES spectra for untreated and treated samples I and II.

the reductive treatment. The measured XANES Cr⁶⁺ concentration for samples I-5× and II-8× were 1672 and 338 mg/kg, respectively, whereas, the Cr⁶⁺ concentration for sample I-8× was reported earlier at 1656 mg/kg [19].

Specifically, 77.97% and 78.18% reductions in Samples I-5× and I-8× treatments were observed, respectively, while 97.7% reduction was obtained for the II-8× treatment. There were no significant differences with respect to Cr⁶⁺ concentrations in the I-5× and I-8× treatments, indicating no significant dosage effects on the treatment. Even though the Cr⁶⁺ concentration in Sample II was twice that in Sample I, the pre-edge peak reduction was more pronounced compared than Sample I-8×. These results also coincide with TCLP Cr leachability results, indicating that particle size (Sample II finer than the Sample I) may be the key to enhance the effectiveness of the treatment.

Overall, even though the TCLP Cr (mg/L) concentrations in both I and II samples were less than the regulatory limit of 5 mg/L, the target Cr⁶⁺ concentration of 240 mg/kg was not achieved upon 8× treatments after 300 days of curing. Moreover, the I-5× treatment showed similar Cr⁶⁺ results compared to I-8× treatment, suggesting particle size reduction prior to FeSO₄·7H₂O addition may yield improved results.

It should be also noted that XANES quantification results showed that the initial content of Cr⁶⁺ was 7588 mg/kg and 14,763 mg/kg in untreated Samples I and II, respectively. These Cr⁶⁺ concentrations were much greater than the 4000 mg/kg and 6000 mg/kg obtained from the alkaline digestion (AD) method

Table 5
Quantitative XANES analyses of untreated and treated I and II samples

Samples	Total Cr (mg/kg)	XANES	
		Cr ⁶⁺ (mg/kg)	Cr ³⁺ (mg/kg)
I	27,100	7,588	19,512
II	23,433	14,763	8,670
I-5×	20,900	1,672	19,228
I-8×	18,400	1,656	16,744
II-8×	14,700	338	

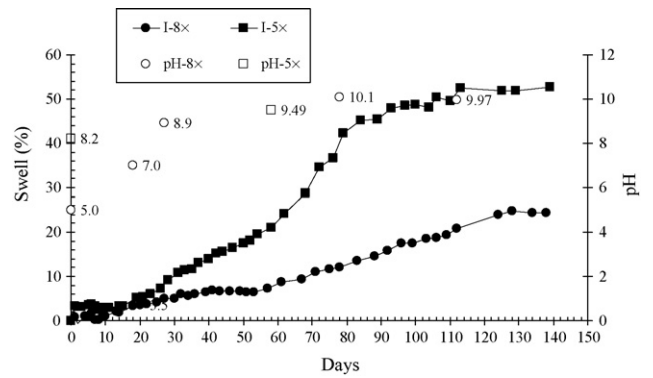


Fig. 3. Height changes (%) for treated I samples.

[14], suggesting that the AD method is unreliable for Cr⁶⁺ estimates in COPR materials [19].

3.3. Unconfined swell tests

Sample I materials were used in the swell tests. Height changes, in percent, and corresponding pH values of the controls are presented in Fig. 3. The I-5× treatment showed more than 50% swell after 138 days, while I-8× swelled 24.4% (Fig. 3). For perspective, Fig. 4 shows Sample I-5× at 84 days with a measured heave of 45.2%.

The pH rebound toward alkaline conditions occurred faster in the I-5× treatment than in the I-8× treatment. According to separate slurry experiments (not presented here), ettringite formation in COPR materials is favorable when pH is greater than approximately 9. This pH condition in COPR systems is low compared to soil and cement systems where ettringite is stable at pH > 10.5 [9]. The initial pH value of the I-5× treatment was 8.2. This indicated that the higher initial pH of the I-5× likely enabled ettringite formation at earlier times. On the other hand, the I-8× treatment showed a low initial pH of 5.0, indicating that ettringite formation was not favored. The sudden increase in swell for the I-5× treatment at about 28 days (9.1%) is likely the result of the ettringite reactions becoming favorable after the pH ≥ 9. Within the timeframe of this study, this pH shift was not observed in the I-8× treatment. However, again, the long-term outlook must account for the potential formation of ettringite owing to the ample buffering capacity

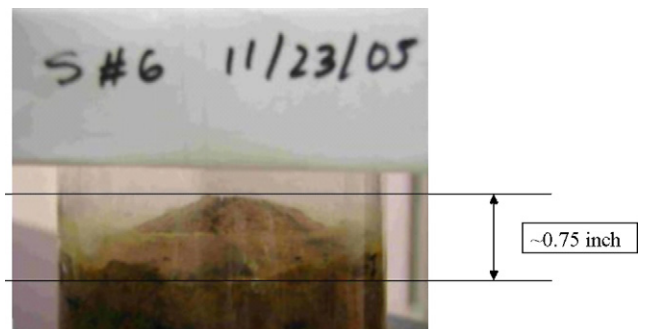


Fig. 4. Heaving (45.2%) of Sample I-5× at 84 days of curing.

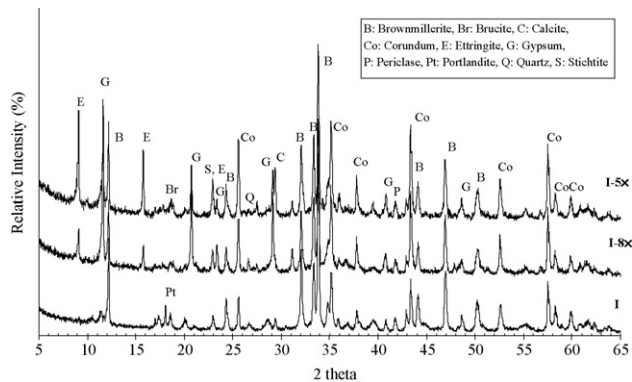


Fig. 5. XRPD patterns for untreated, I-5× and I-8× samples.

of COPR and alkalinity produced by mineralogical transformations.

3.4. XRPD analyses

XRPD patterns obtained from untreated, I-5× and I-8× samples following the swell test after 130 days are presented in Fig. 5. Ettringite formation was more pronounced in the I-5× treatment. Conversely, gypsum formation was more pronounced in the I-8× sample, illustrating the importance of pH on the predominance of reactions and end product formation, i.e., the conversion of gypsum to ettringite.

All treatments ultimately failed the NJDEP clean up standard of 240 mg/kg, and no significant treatment effects were observed between 5× and 8× treatments with respect to Cr⁶⁺ reduction. It is clear that particle size reduction plays a greater role in treatment effectiveness, as demonstrated by the favorable leaching performance of sample II over Sample I. Particle size reduction coupled with addition of acid to COPR materials therefore emerges as a potential approach to improve the 5× treatment and to avoid ettringite formation. The quantity of acid needed to reduce the pH below 9 in COPR was estimated to be six equivalents per kilogram of dry COPR based on the acid neutralization capacity (ANC) tests [23]. The combination of increased particle fineness and acid addition emerges as a potential approach to affect Cr⁶⁺ reduction and heave mitigation provided that the pH reduction imparted is permanent, i.e., a pH of less than 9 is permanently attained. Otherwise, in the event of a future pH rebound within the ettringite stability field range, delayed ettringite formation may lead to excessive swelling.

4. Conclusions

COPR was pugmilled with FeSO₄·7H₂O at stoichiometric ratios of 5× and 8×. TCLP, XANES and XRPD analyses were performed to evaluate Cr⁶⁺ concentrations and mineralogical changes upon treatment. The TCLP results showed that TCLP Cr concentrations upon 8× treatment were below the EPA regulatory level of 5 mg/L after 420 days of curing, while TCLP Cr concentrations for the 5× treatment exceeded 5 mg/L. XANES results showed that all of the treated samples failed to meet the

NJDEP clean up standard of 240 mg/kg. Moreover, the COPR particle size was strongly linked to the effectiveness of the treatment. Unconfined swell test results showed significant swelling upon the treatment, the presence of ettringite being confirmed by XRPD analyses.

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