

# Assessment of calcium polysulfide for the remediation of hexavalent chromium in chromite ore processing residue (COPR)

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## Abstract

Bench scale and pilot scale treatability studies were conducted to evaluate the remediation of hexavalent chromium [Cr(VI)] in chromite ore processing residue (COPR) using calcium polysulfide. The results from the bench scale study indicated that a calcium polysulfide dosage twice the molar stoichiometric requirement ( $2\times$ ) proved effective in meeting the New Jersey Department of Environmental Protection (NJDEP) total Cr(VI) and the Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP) regulatory standards. The treatment results were more effective at pH 12 than at pH 9.5. X-ray powder diffraction (XRPD) and X-ray absorption near edge structure (XANES) spectroscopy were also used to assess the treatment performance. Based on the bench scale results, an ex-situ pugmill pilot program was implemented to evaluate the applicability of the calcium polysulfide treatment on a larger scale (1000-lb batch test). The pugmill treatment results met Cr(VI) and TCLP regulatory standards over a period of 15 months. XANES analysis indicated that approximately 62% of Cr(VI) was reduced by calcium polysulfide at stoichiometric ratio of  $2\times$  after a curing period of 10 months.

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## 1. Introduction

Millions of tons of chromite ore processing residue (COPR) were deposited at numerous urban areas in the USA, the UK, and elsewhere in the world during the first half of the last century [1–5]. There are currently over 200 active COPR sites in Hudson County, New Jersey. COPR was beneficially used as structural fill because of its favorable structural quality as a granulated material. The deposited COPR was produced by the high lime process where the chromite ore was roasted at approximately 1200 °C to oxidize the chromium in the ore from the trivalent to the hexavalent state. Hexavalent chromium [Cr(VI)] was then chemically combined with the sodium in the added soda ash to form sodium chromate,  $\text{Na}_2\text{CrO}_4$  [6]. Lime was added during the roasting process to act as a mechanical separator allowing oxygen to react with the chromite and sodium carbonate. Lime also served as a sequestering agent combining with various ore impurities to form insoluble compounds. The sodium chromate

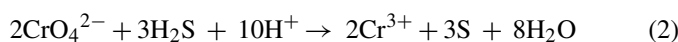
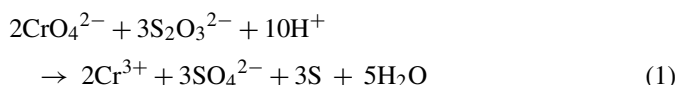
formed during the roasting process was extracted with hot water as a weak yellow liquor solution. The sodium chromate was then converted into sodium dichromate by reaction with sulfuric acid. After draining, the residue was discarded. The disposed COPR contains unreacted chromite ore and un-extracted chromate. Even though the high lime process has ceased in the US and the UK, it is still being used in China, Russia, Kazakhstan, India and Pakistan [7].

In the environment, chromium exists mainly in two oxidation states; hexavalent [Cr(VI)] and trivalent [Cr(III)] chromium. Cr(VI) is highly mobile, severely toxic at moderate doses, and classified as a respiratory carcinogen in humans. In contrast, Cr(III) is used as a dietary element at low doses, and in most environmental systems is immobile [8]. COPR, which contains both Cr(III) and Cr(VI), is not as benign as initially thought; yellow chromate solution was observed to leach from locations where COPR was deposited and elevated Cr(VI) concentrations were measured in ground water, surface water, and water bodies in the proximity of these sites [9]. In consequence, COPR has become a major contamination source of Cr(VI) in many urban areas. Reduction of Cr(VI) combined with pH adjustment is used to minimize potential health hazards and chromium mobil-

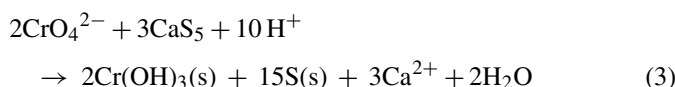
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ity in soil–water systems. The reducing agents commonly used are elemental iron, pyrite, ferrous iron [Fe(II)], sulfites, sulfides, and organic compounds.

Calcium polysulfide (CaS<sub>5</sub>) has been used for the reduction of Cr(VI) in groundwater. The highly soluble Cr(VI) was reduced by CaS<sub>5</sub> to the insoluble, and non-toxic Cr(III), which was then precipitated as chromium hydroxide. The highest reduction rate (70%) occurred during the first 6 months and the reductant continued to react with Cr(VI) for a total of about 18 months, reducing Cr(VI) in groundwater by 99% [10]. CaS<sub>5</sub> had also been used for the removal of heavy metals from wastewater [11,12]. This solution decomposes rapidly to calcium thiosulfate, hydrogen sulfide and solid sulfur by blowing a decomposing gas (air or carbon dioxide) in water; heavy metals react with calcium thiosulfate (CaS<sub>2</sub>O<sub>3</sub>) or hydrogen sulfide (H<sub>2</sub>S) and are precipitated as metal sulfides or hydroxides. The kinetics of this process was studied to design continuous removal process for commercial applications. The reduction of Cr(VI) to Cr(III) by CaS<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>S is shown in the following reactions [13].



CaS<sub>5</sub> was also used for in situ geochemical fixation of Cr(VI) in soil and groundwater in alluvial fan sediments at a former metal plating facility in western Arizona by URS Corporation (USA). CaS<sub>5</sub> reduces Cr(VI), commonly in the form of chromate, CrO<sub>4</sub><sup>2-</sup>, to a relatively insoluble form of Cr(III) and tends to fall out of solution and adhere to soil. An example of the aqueous reduction of Cr(VI) by CaS<sub>5</sub> is given as:



This reaction is reported to be theoretically reversible, however, under natural groundwater conditions the equilibrium condition is dominated by the right side of the reaction [14]. CaS<sub>5</sub> has also been used to remediate Cr(VI) from contaminated groundwater and COPR in Glasgow, United Kingdom. The treatment was effective in reducing Cr(VI) to Cr(III) quantitatively and rapidly over a pH range of 8–12.5. A stoichiometric ratio of 5:1 (5×) resulted in excess active polysulfide species to solid Cr(VI), as Cr(VI) was not detected either in solution or in the solid phase [1].

The purpose of this work is to investigate the performance of CaS<sub>5</sub> for the remediation of Cr(VI) in COPR on a bench scale and pilot scale levels.

## 2. Materials and methods

### 2.1. Materials

The COPR samples, used in this investigation, were obtained from a study area in Jersey City, New Jersey. The samples were collected from two stratigraphic layers (B1 and B2) during a

major bulk-sampling event from 14 borings across the site. Layer B1 represents the upper most unsaturated zone and layer B2 lies directly below layer B1. The water table level fluctuates within layer B2 throughout the entire site. A composite sample B1B2 was prepared by mixing equal amounts of all samples from layers B1 and B2 across the borings. The samples were always thoroughly homogenized before any COPR material was used. Calcium polysulfide (CaS<sub>5</sub>, 29% wt.) was supplied by Best Sulfur Products (Fresno, CA). All chemical reagents used were of ACS or higher-grade quality and were obtained from Fisher Scientific (GA, USA). All stock solutions were prepared using deionized (DI) water.

### 2.2. Physical characterization

The samples originating from the two COPR horizons were classified according to ASTM D2488-00 [15]. The water content was measured according to ASTM D2216-98 [16] and the Standard penetration Test (SPT) *N*-values were obtained according to ASTM D1586-99 [17].

### 2.3. Chemical characterization

The elemental composition of the COPR samples was determined by digesting the COPR material according to EPA Method 3051A [18] followed by EPA Method 6010B [19]. Cr(VI) concentration was obtained using EPA Method 3060A [20] and EPA Method 7196A [21] or EPA Method 7199 [22]. EPA Method 1311 [23] and EPA Method 6010B [19] were used to determine the toxicity leaching characteristics of Cr in COPR. Total carbon was measured using ASTM D5291-96 [24] and it was assumed to consist of inorganic carbonates. Silicon concentration was determined by fusing the sample with disodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and precipitating Si as Silicon dioxide (SiO<sub>2</sub>). SiO<sub>2</sub> was measured using the gravimetric method. All sulfur was assumed to be present as sulfate.

### 2.4. X-ray powder diffraction (XRPD) analysis

XRPD analysis was conducted to assess the mineralogical changes upon treatment. Representative samples were air dried for 24 h and then were pulverized using a McCrone micromill for 5 min with cyclohexane. The resulting slurry was air dried and mixed with 20% mass based corundum (α-Al<sub>2</sub>O<sub>3</sub>) as internal standard and the resulting solids were subjected to XRPD analysis. Step-scanned X-ray diffraction data were collected by the Rigaku DXR 3000 computer-automated diffractometer using Bragg-Brentano geometry. The diffractometry was conducted at 40 kV and 40 mA using diffracted beam graphite-monochromator with Cu radiation. The data were collected in the range of 5–65° 2θ with a step size of 0.02° and a count time of 3 s per step. The qualitative and quantitative analyses of the XRPD patterns was performed using the Jade software [25], version 7.0 and the Whole Pattern Fitting function of Jade, which is based on the Rietveld method [26]. The reference databases for powder diffraction and crystal structure data were the International Center for Diffraction Data database [27] and the Inorganic Crystal Structure Database [28], respectively.

## 2.5. XANES analyses

XANES analyses were conducted 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 N<sub>2</sub> 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. The quantitative XANES analyses were conducted using the ATHENA program in the IFEFFIT computer package [29].

## 2.6. Bench scale study

The bench scale treatability study was conducted using 100 g COPR samples with two CaS<sub>5</sub> dosages (1× and 2×; 10.3% and 20.6%, w/w of 29% CaS<sub>5</sub> solution) and two pH values (free drift, represented as N and 9.5). For the stoichiometric calculations, the sulfide species was assumed to oxidize to elemental sulfur by Cr(VI). The target pH 9.5 was selected because of the instability of Cr(VI) bearing minerals and swell causing minerals such as ettringite in the pH range 8.5–10.5 [9]. The COPR samples were passed through 4.75 mm (mesh 4) sieve. The water content was adjusted to one for all samples. For the samples with target treatment pH 9.5 the calculated quantity of acid was diluted into the required water and allowed to cool to room temperature. The diluted acid was then slowly added to the COPR sample ensuring no steep rise in temperature. The selected CaS<sub>5</sub> dosage was added to the acidified sample after 2 days to prevent the reaction between CaS<sub>5</sub> and the acid. The samples were prepared in triplicates and allowed to cure for a period of 1 month. After the curing period, the samples were homogenized and analyzed for Cr(VI), Toxicity Characteristic Leaching Procedure (TCLP) Cr, TCLP Cr(VI) and pH. The reported results are the average of three replicates. The amount of acid required to attain the target pH of 9.5 was calculated based on the Acid Neutralization Capacity (ANC) test [30]. Briefly, representative air dried COPR samples were pulverized to finer than 150 μm (mesh 100) to accelerate the equilibration of the COPR samples with the acid dosages. The pulverized COPR samples were mixed with DI water using a liquid-to-solid ratio of 20. Incremental amounts of concentrated HCl were added to cover a wide range of pH values. The mixtures were left on an end-over-end mixer for 1 week before the pH values of the mixtures were recorded.

## 2.7. Pilot scale study

Based on the preliminary bench scale results, an ex situ pugmill pilot program was implemented to evaluate the applicability of CaS<sub>5</sub> for the treatment of Cr(VI) in COPR on a larger scale (1000-kg batch test). The pilot program involved excavating



Fig. 1. Picture of the pugmill equipment used in the pilot program during pilot program execution.

large quantities of COPR from layers B1 and B2 and placing them in a roll off-box. The COPR was then transferred from the roll-off box to 55-gallon (208.17 L) drums. The drums simplified the process of transferring of COPR to the pugmill. The pugmill equipment used in the pilot program was a 2-cy (1.52 m<sup>3</sup>) capacity batch-type pugmill mixer (Maxon Industries, Milwaukee, WI). This pugmill has dual directional mixing capabilities (forward and reverse action) and an eight paddle agitator shaft to promote mixing. The pugmill equipment is shown in Fig. 1. After the COPR was placed in the pugmill, it was mixed for few minutes to spread the material over the length of the pugmill and evaluate the consistency of the COPR. The required amount of CaS<sub>5</sub> (2×; 18%, w/w of 29% CaS<sub>5</sub> solution) was metered directly from a 35-gallon (132.47 L) CaS<sub>5</sub> drum into the pugmill from the top using an electric pump. Following addition of all required chemical and moisture, the pugmill was operated for a minimum of 12 min switching the mixing direction (forward and reverse) every 2 min to promote complete mixing of the COPR and reagents.

Following mixing/treatment, the contents of the pugmill were transferred into containers via the discharge gate. The treated material was monitored for Cr(VI), TCLP Cr, total Cr, and pH over long-term interval. The reported results are the average of two replicates.

Table 1  
Elemental composition of composite COPR sample B1B2

Element	% mass basis
Al	4.60
Ca	23.90
CO <sub>3</sub> <sup>2-</sup>	11.50
Cr(VI)	0.52
Cr	2.71
Fe	11.80
K	0.03
Mg	6.10
Mn	0.12
Na	0.37
Si	1.98
SO <sub>4</sub> <sup>2-</sup>	0.34

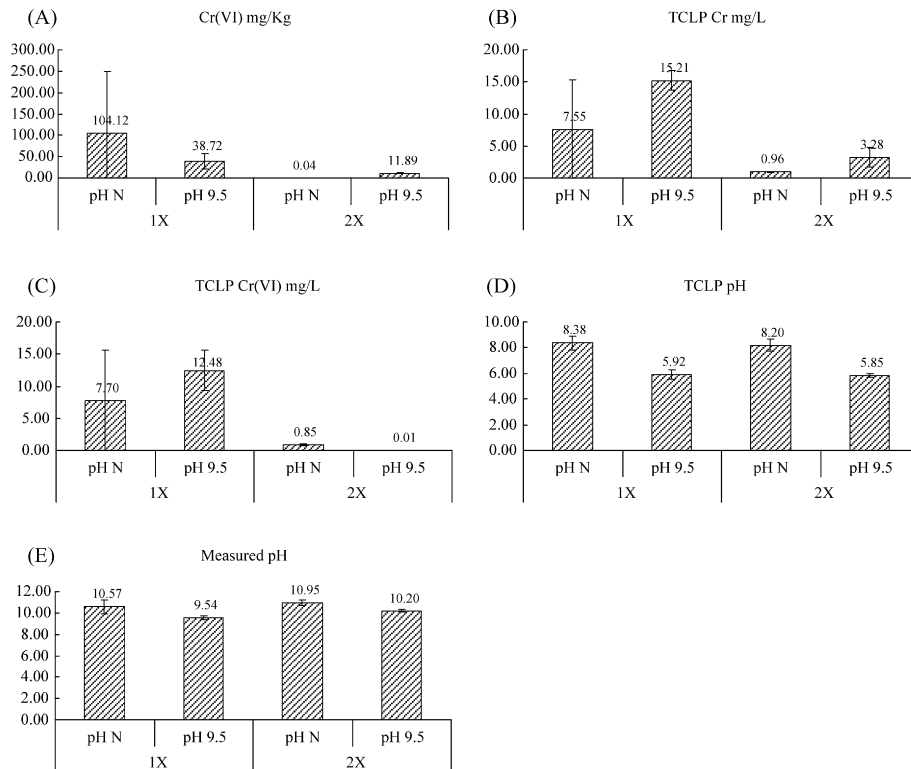


Fig. 2. (A) The Cr(VI) results for the bench scale study; (B) the TCLP Cr results for the bench scale study; (C) the TCLP Cr(VI) results for the bench scale study; (D) the TCLP pH results for the bench scale study; (E) the treatment pH results for the bench scale study.

Air monitoring was conducted throughout the pugmill program as per a health and safety plan. Two particulate air monitoring meters (DataRams) were maintained within the work zone area (one upwind and another downwind of the pugmill). Additionally, a 4-gas meter was used to monitor hydrogen sulfide, carbon monoxide, combustible gas, and oxygen. The monitoring equipments were calibrated daily. Time weighted daily average particulate levels were below the  $380 \mu\text{g}/\text{m}^3$  action level throughout the pugmill pilot program. Hydrogen sulfide, carbon monoxide, and combustible gas were non-detect in the breathing zone.

### 3. Results and discussion

#### 3.1. Sample characterization

##### 3.1.1. Physical characterization

The COPR material originating from layer B1 is black to grey, fine to coarse sand sized with trace silt, silty sand, and sandy silt particles. The B1 layer was encountered from the ground surface to approximately 7–9 ft (2.13–2.74 m) below ground surface (bgs). Standard Penetration Test (SPT) *N*-values ranged from 23 to 111 blows per foot (bpf) with an average of 42 bpf. The samples in this horizon contained material that appeared to have amounts of cementation. The measured water content ranged from approximately 4–23% with an average value of approximately 18%. Conversely, the COPR material in B2 layer is gray, fine to coarse sand sized with seams of silt and sandy silt particles trace gravel size particles. The B2 layer was encoun-

tered beginning from approximately 7–9 ft (2.13–2.74 m) bgs to approximately 12–15 ft (3.65–4.57 m) bgs with thickness ranging from approximately 3.5 to 6.5 ft. SPT *N*-values ranged from 11 to 41 bpf with an average value of 23 bpf. Samples in this layer also appeared to have some amounts of cementation. Moisture contents ranged from approximately 20–38% with an average value of approximately 28%.

##### 3.1.2. Chemical characterization

The elemental composition of the COPR sample is shown in Table 1. The relatively high calcium concentration at approximately 24% is due to the addition of lime during the extraction process. The carbonate most likely was absorbed as  $\text{CO}_2$  by the COPR material after the roasting process due to its alkaline nature. The sulfate may have entered the system from the oxidation of sulfur in the kiln fuel oil (Bunker C fuel oil) during the roasting process, or from the sodium sulfate operations at the site [6]. The presence of sulfate is known to cause expansion in cement and cement-like material such as COPR.

#### 3.2. Bench scale study results

##### 3.2.1. Chemical analyses

The results from bench scale study indicated that a  $\text{CaS}_5$  dosage of 1× was sufficient to meet total Cr(VI) regulatory standards at 240 mg/kg (Fig. 2A); however, it was not sufficient to meet TCLP Cr regulatory standards of 5 mg/L (Fig. 2B). The measured average Cr(VI) and TCLP Cr concentrations at



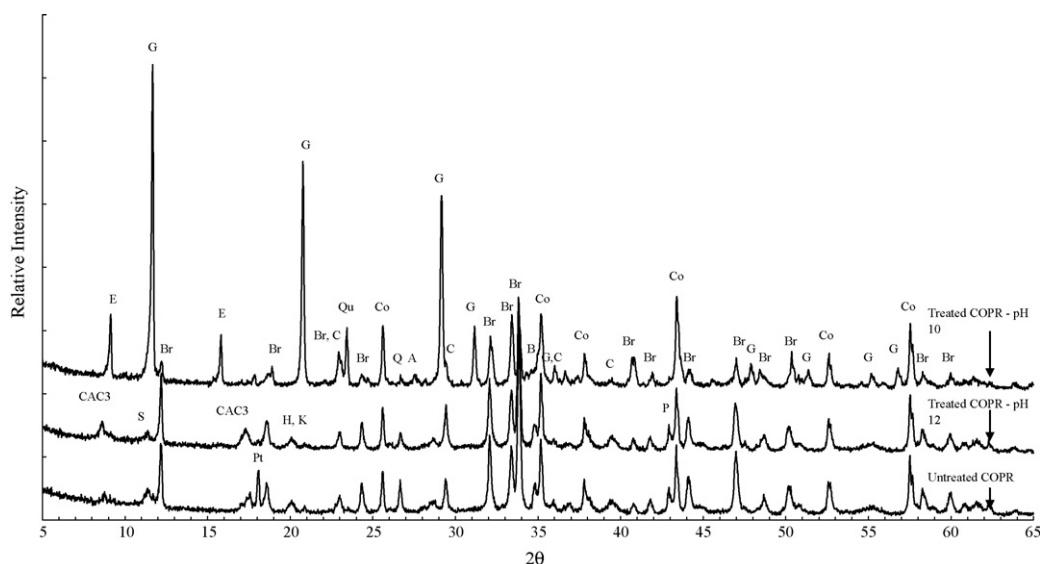


Fig. 3. The XRPD patterns for the untreated and treated COPR samples—bench scale study. A: albite, B: brucite, Br: brownmillerite, C: calcite, CAC3: calcium aluminum chromium hydrate, Co: corundum, E: ettringite, G: gypsum, H: hydroandradite, K: katoite, P: periclase, Pt: portlandite, Q: quartz, Qu: quintinite, and S: sjogernite.

dosage  $1\times$  were 104.12 mg/kg and 7.55 mg/L, respectively, at target pH N whereas these concentrations were 38.72 mg/kg and 15.21 mg/L, respectively, at target pH 9.5. Better treatment results were obtained when the dosage value was increased to  $2\times$ . The measured average Cr(VI) and TCLP Cr results were  $<2$  mg/kg and 0.96 mg/L, respectively for target pH N whereas these values were 38.72 mg/kg and 3.28 mg/L at target pH 9.5. It is interesting to note that even though the  $1\times$  dosage treatment met the Cr(VI) regulatory standards it did not meet TCLP Cr standards. For example, the measured total Cr(VI) and TCLP Cr(VI) values at target pH 9.5 were 38.72 mg/kg and 12.48 mg/L, respectively. The TCLP test has a liquid to solid ratio of 20, which indicates that during TCLP test, 249.6 mg/kg Cr(VI) was extracted from a sample that is supposed to contain only 38.72 mg/kg according to the alkaline digestion procedure. This could be due to the different conditions that exist during the two testing procedures indicating that testing interferes with the test results. It seems that the chemical reduction of Cr(VI) by  $\text{CaS}_5$  is more favorable during the alkaline digestion than during TCLP. Inherent to this conclusion is that partial treatment occurs during both analytical tests.

The difference between TCLP Cr and TCLP Cr(VI) concentrations is attributed to Cr(III) (Fig. 2B and C). For example, TCLP Cr and TCLP Cr(VI) concentrations are 15.21 mg/L and 12.48 mg/L, respectively for testing condition of  $1\times$  and target pH 9.5. The difference between TCLP Cr and TCLP Cr(VI) is not significant for testing condition at target pH N; i.e., the TCLP Cr and TCLP Cr(VI) concentrations were 0.96 mg/L and 0.85 mg/L for dosage of  $1\times$ . The difference in Cr(VI) and Cr concentrations is probably due to the different TCLP pH values as shown in Fig. 2D since Cr(III) is sparingly soluble at  $\text{pH} > 6$ , whereas it has greater solubility at  $\text{pH} < 6$  [9]. The TCLP pH values for dosage of  $1\times$ , and target pH N and 9.5 were 8.38 and 5.85, respectively.

### 3.2.2. XRPD analyses

The XRPD patterns for the untreated and treated COPR samples are shown in Fig. 3. The major mineral phase in the untreated COPR sample is brownmillerite which is present at approximately 32% of the crystalline phases. The amorphous content as determined by the corundum internal standard was approximately 34%. All other mineral phases were present at less than approximately 5% (Table 2). The only known Cr(VI) bearing mineral identified was calcium aluminum oxide chromium hydrates (CAC) also known as Cr(VI)-hydrocalumite, with molecular formula  $(\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{CrO}_4 \cdot n\text{H}_2\text{O})$ . Cr(VI)-hydrocalumite is a layered double hydroxide (LDH) mineral with chromate anions held in the interlayers. A Cr(VI)-hydrocalumite content of 1.12% indicate a Cr(VI) concentration of approximately 567 mg/kg. This indicates that the majority of Cr(VI) is not encapsulated in the Cr(VI)-hydrocalumite phase. Cr(VI) could be present in other mineral phases such as hydrogarnet (katoite) [9] and hydrotalcites (data not presented) through anionic substitution.

No significant changes occurred upon the calcium polysulfide treatment at target pH N except for the slight increase in the amorphous content from approximately 34% to approximately 41%. Moreover, Cr(VI)-hydrocalumite content did not decrease upon the calcium polysulfide treatment. The Cr(VI)-hydrocalumite content increased from 1.12% to 1.72% of the crystalline phases upon treatment (pH N condition). The slight increase could be due to the dilution effect upon the addition of the calcium polysulfide reagent and due to sample variability. However, upon the  $\text{CaS}_5$  treatment at target pH 9.5, many phases were destabilized such as CAC3, SCASH, hydroandradite, katoite, periclase, and portlandite. Also, brownmillerite content decreased from approximately 32% to approximately 9%. The treatment triggered the formation of ettringite at approximately 13%. This could be due to localized pH conditions with values higher than those measured since ettringite is reported to be

Table 2

The Rietveld quantification of the minerals phases for the untreated and treated COPR samples (after a curing period of 11 months)—bench scale study

Mineral phase	Untreated	pH N	pH 9.5
Calcium aluminum oxide chromium hydrate (CAC3), $\text{Ca}_4\text{Al}_2\text{O}_6(\text{CrO}_4)\cdot 14\text{H}_2\text{O}$	1.12%	1.72%	NA
Sodium calcium aluminum sulfate hydrate, $\text{NaCa}_4\text{Al}_2\text{O}_6(\text{SO}_4)_{1.5}\cdot 15\text{H}_2\text{O}$ (SCASH)	2.44%	2.25%	NA
Brownmillerite, $\text{Ca}_2(\text{Al, Fe}^{3+})_2\text{O}_5$	31.90%	30.48%	9.29%
Brucite, $\text{Mg}(\text{OH})_2$	3.76%	3.91%	1.27%
Calcite, $\text{CaCO}_3$	5.01%	6.81%	3.80%
Hydroandradite, $\text{Ca}_3\text{Fe}_2(\text{SiO}_4(\text{OH})_4)_3$	3.95%	3.73%	NA
Katoite, $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$	3.76%	0.30%	NA
Periclase, $\text{MgO}$	2.50%	2.37%	NA
Portlandite, $\text{Ca}(\text{OH})_2$	1.58%	NA	NA
Quartz, $\text{SiO}_2$	2.11%	1.78%	0.84%
Quintinite, $\text{Mg}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3)\cdot 3\text{H}_2\text{O}$	1.91%	NA	3.68%
Ettringite, $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$	NA	NA	13.15%
Sjogrenite, $\text{Mg}_6\text{Fe}^{2+}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$	2.18%	1.54%	0.24%
Albite, $\text{NaAlSi}_3\text{O}_8$	3.69%	4.32%	2.05%
Gypsum, $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$	NA	NA	26.00%
Amorphous	34.09%	40.82%	39.68%
Total	100.00%	100.00%	100.00%

NA: not applicable.

stable at  $\text{pH} > 10.5$  [31]. This meta-stable phase may undergo incongruent dissolution upon pH equilibration. It is interesting to note that other researchers observed ettringite in the COPR material at pH values less than 10.5 [9]. The treatment also caused the formation of gypsum at 26%. The sulfate needed for the formation gypsum and ettringite must have been produced from the oxidation of the sulfide species. A gypsum and ettringite contents of 26% and 13%, respectively of the crystalline phases indicates that approximately 82% of the sulfide species was oxidized to sulfate.

### 3.3. Pilot scale study results

#### 3.3.1. Chemical analyses

Based on the results of the bench scale treatability study, the pilot scale study was conducted at a dosage of  $2\times$  and target pH N since these conditions gave satisfactory results. The treatment results were monitored over a period of 15 months. These results proved satisfactory based on Cr(VI) and TCLP regulatory levels (Fig. 4A and 4B). The measured average Cr(VI) and TCLP Cr were 8.63 mg/kg and 0.9 mg/L, respectively over a curing period of 15 months. The measured treatment pH values showed a decreasing trend as the samples aged. The measured pH values decreased from 12.4 to 12.25, 11.9, 11.6, and 11 after a curing period of 1 week, 1 month, 2 months, 4 months, and 15 months, respectively (Fig. 4C). The pugmill sample pH value after a curing period of 15 months equilibrated at approximately the same pH value to the bench scale tests after a curing period of 1 month, for the same testing conditions (Figs. 4C and 2E).

#### 3.3.2. XRPD analyses

The XRPD patterns and the Rietveld quantification of the mineral phases for the treated pugmill sample are shown in Fig. 5 and Table 3, respectively. The results were similar to

bench scale ones for similar testing conditions. The amorphous content increased upon treatment from approximately 34% to approximately 43%, and the Cr(VI)-hydrocalumite content at 1.69% was similar to the value obtained during the bench scale test at 1.72%.

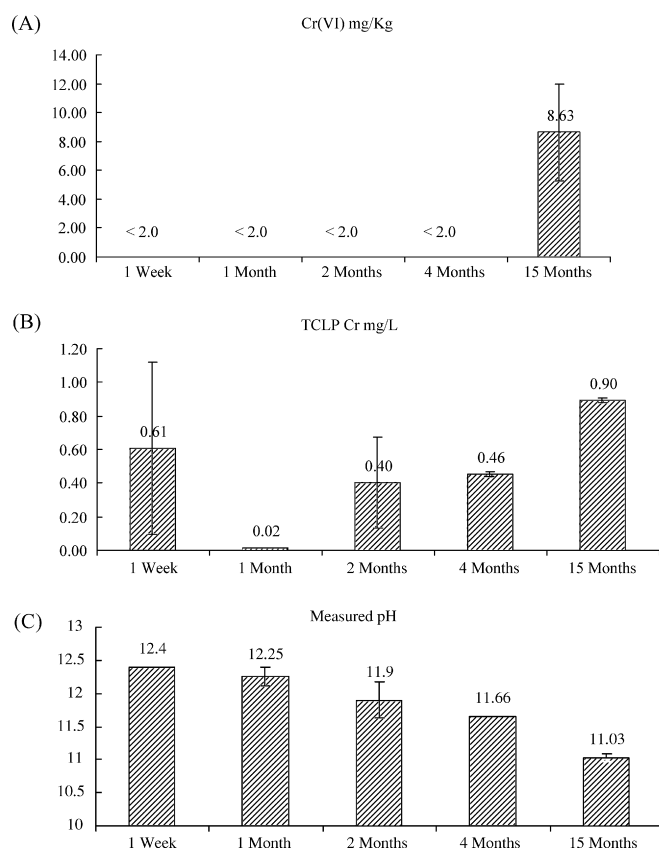


Fig. 4. (A) The Cr(VI) results for the pilot scale study; (B) the TCLP Cr results for the pilot scale study; (C) the treatment pH results for the pilot scale study.

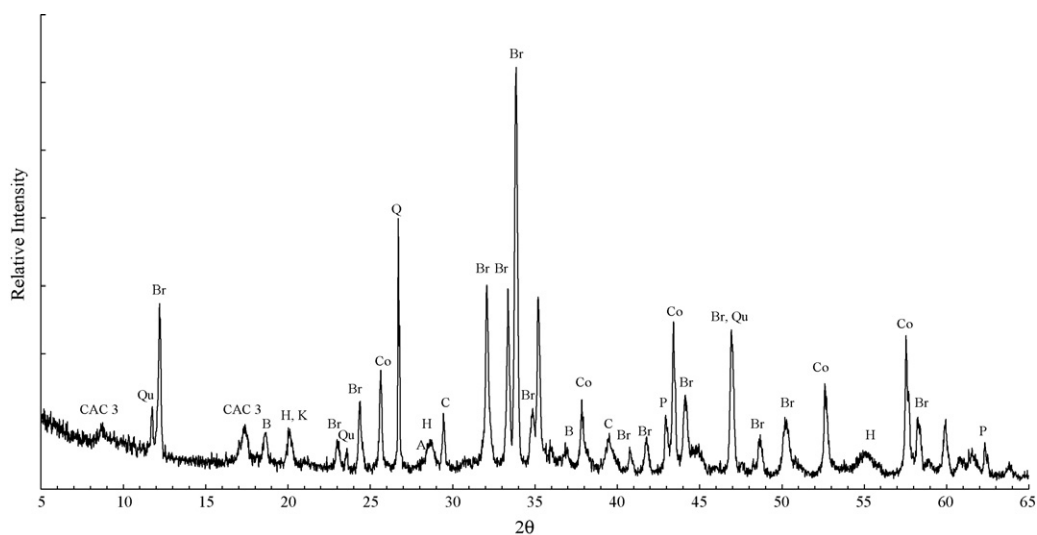


Fig. 5. The XRPD patterns for the treated COPR samples—pilot scale study. A: albite, B: brucite, Br: brownmillerite, C: calcite, CAC3: calcium aluminium chromium hydrate, Co: corundum, H: hydroandradite, K: katoite, P: periclase, Q: quartz, and Qu: quintinite.

Table 3

The Rietveld quantification of the minerals phases for the treated COPR sample after a curing period of 15 months—pilot scale study

Mineral phase	Treated COPR (%)
Calcium aluminium oxide chromium hydrate (CAC3), $\text{Ca}_4\text{Al}_2\text{O}_6(\text{CrO}_4) \cdot 14\text{H}_2\text{O}$	1.69
Brownmillerite, $\text{Ca}_2(\text{Al}, \text{Fe}^{3+})_2\text{O}_5$	29.18
Brucite, $\text{Mg}(\text{OH})_2$	2.31
Calcite, $\text{CaCO}_3$	3.39
Hydroandradite, $\text{Ca}_3\text{Fe}_2(\text{SiO}_4(\text{OH})_4)_3$	6.32
Katoite, $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$	1.24
Periclase, $\text{MgO}$	2.48
Quartz, $\text{SiO}_2$	3.61
Quintinite, $\text{Mg}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3) \cdot 3\text{H}_2\text{O}$	3.33
Albite, $\text{NaAlSi}_3\text{O}_8$	2.82
Amorphous	43.57
Total	99.95

### 3.3.3. XANES analyses

To further assess the treatment results of the pilot scale program, XANES analyses was conducted on untreated and treated samples after a curing period of 10 months. Chromium K-edge XANES spectra for the untreated and treated samples and the quantification data are presented in Fig. 6 and Table 4. The XANES spectrum for Cr(VI) 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 Cr(VI) concentration [32,33]. The XANES spectrum for the

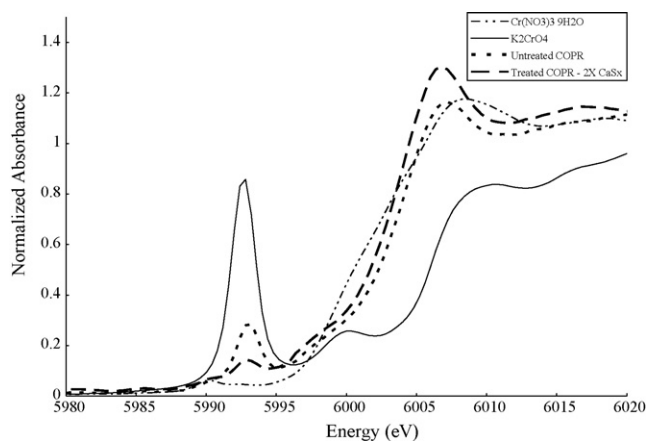


Fig. 6. Chromium K-edge XANES spectra for untreated and treated COPR samples—pilot scale study.

treated sample showed a significant pre-edge peak reduction. The Cr(VI) concentration was reduced from 7588 mg/kg to 2910 mg/kg as shown in Table 4.

Even though total Cr(VI) and TCLP Cr results indicated satisfactory results with Cr(VI) and TCLP Cr values of 8.63 mg/kg and 0.9 mg/L, respectively, the XANES analysis indicated that only about 62% of the Cr(VI) content was reduced upon treatment as shown in Table 4. The residual Cr(VI) concentration in the treated samples 10 months after treatment was 11.5% of the measured total chromium, which amounted to approximately

Table 4

Quantitative XANES analyses of untreated and treated COPR samples

Sample i.d.	Total Cr (mg/kg)	Alkaline digestion Cr(VI) (mg/kg)	XANES analyses			
			Cr(VI) %	Cr(III) %	Cr(VI) (mg/kg)	Cr(III) (mg/kg)
Untreated COPR	27,100	4575	28.0	72.0	7588	19,512
Treated COPR (2× CaS <sub>5</sub> )	25,300	2.4	11.5	88.5	2910	22,391

2910 mg/kg, much higher than the NJDEP regulatory standard of 240 mg/kg. It is worth mentioning that the total Cr(VI) concentration for the untreated sample as measured by alkaline digestion was much lower than the one measured by XANES. The measured Cr(VI) concentration for the untreated COPR sample by alkaline digestion and by XANES were 4575 mg/kg and 7588 mg/kg, respectively. This may indicate that alkaline digestion may have underestimated Cr(VI) concentration. Similar results were reported recently by Dermatas et al. [34].

Cr(VI) reduction by CaS<sub>5</sub> is expected to proceed during curing until the exhaustion of the sulfide species. Mass transfer limitation may impede the reaction between Cr(VI) and the sulfide species; however, factors such as particle size reduction and aggressive mixing may accelerate the reduction of Cr(VI). In the presence of excess sulfide species, Cr(VI) leached during the alkaline digestion or the TCLP tests will react with sulfide and the leached Cr(VI) will be reduced indicating satisfactory results. During the initial curing period, most of the reductant reagents will be intact in the treated matrix and upon regulatory testing, whether by TCLP or alkaline digestion, there is sufficient residual reductant in the treated COPR to reduce the majority of the Cr(VI) leached during the test. Consequently, the test results indicate a successful treatment. However, upon aging, the reductant can be consumed by competing reactions within the COPR matrix or from dissolved oxygen. Hence, as Cr(VI) is released over time the availability of reductant is less and the measured Cr(VI) concentration increases. Therefore, the satisfactory treatment results obtained by regulatory tests should not conclusively indicate that all Cr(VI) in the treated samples has been reduced. Furthermore, the discrepancy between the alkaline digestion and TCLP Cr(VI) concentration results encountered earlier during the bench scale tests could be due to the different conditions that exist during each test. For example the pH and the temperature during the alkaline digestion are approximately 13 and 95 °C, respectively whereas these values are room temperature and approximately pH 8 (for treatment with target pH N) during the TCLP test. These different testing conditions may accelerate or slow down the reaction between the Cr(VI) and the sulfide species, hence reaching at different conclusions. Overall, the results indicate that current regulatory testing may not be suitable to assess treatment results in the presence of excess reductant or reducing environments. Both the TCLP and alkaline digestion are destructive tests and part of the chemical reduction of Cr(VI) may occur during chemical analysis.

#### 4. Conclusions

The bench scale and the pugmill pilot scale treatability results indicated that a CaS<sub>5</sub> dosage of twice the stoichiometric requirement (2×) was sufficient to meet total Cr(VI) and TCLP Cr(VI) regulatory limits. The CaS<sub>5</sub> pugmill treatment gave satisfactory results over a period of 15 months. However, the XANES analyses indicated that Cr(VI) reduction was not complete, even though satisfactory results were obtained using alkaline digestion and TCLP analyses. The XRPD analyses indicated that Cr(VI) is partially encapsulated in the Cr(VI)-hydrocalumite. Moreover, this phase was not destabilized upon the calcium

polysulfide treatment at target pH (N) even though alkaline digestion results indicated Cr(VI) concentration of 8.63 mg/kg. The XANES analyses, the XRPD results, and the discrepancy between the alkaline digestions and the TCLP results warrant further investigation into the applicability of alkaline digestion and TCLP to ascertain whether the aforementioned methods provide true indication about residual Cr(VI) concentration in the CaS<sub>5</sub> treated COPR samples.

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