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Remediation of chromite ore processing residue using ferrous sulfate and calcium polysulfide

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ABSTRACT: Batch tests were conducted to assess the potential use of ferrous sulfate and calcium polysulfide for the remediation of chromite ore processing residue (COPR). The remediation process entails addition of ferrous sulfate or calcium polysulfide to chemically reduce hexavalent chromium [Cr(VI)] to trivalent chromium [Cr(III)] in slurry form and pH adjustment to precipitate Cr(III) as chromium hydroxide. The present study investigates the effects of COPR particle size, treatment pH, and chemical dosage on the performance of the treatment. Smaller particle size resulted in increases in alkaline digestion and Toxicity Characteristic Leaching Procedure (TCLP) Cr(VI) concentrations for the untreated samples. The chemical reduction of Cr(VI) with ferrous iron and sulfides was non-stoichiometric. Four times the stoichiometric amount of ferrous iron or two times the stoichiometric amount of polysulfide were needed to meet both the New Jersey Department of Environmental Protection (NJDEP) regulatory limit of 240 mg/kg for Cr(VI) and EPA TCLP regulatory limit of 5 mg/L for chromium [Cr]. pH adjustment was necessary to prevent the formation of ettringite, a swell causing mineral, upon the introduction of sulfate to the COPR material via ferrous sulfate or calcium polysulfide. The slow hydration of some COPR minerals caused the pH of the treated COPR to creep upward during the curing period. However, when sufficient acid was added, the pH value was controlled at less than 9.27 for a curing period of 1.5 years, which prevented the formation of ettringite.

Key words: chromite, COPR, ettringite, ferrous, polysulfide

1. INTRODUCTION

Chromite ore processing residue (COPR) is an industrial refuse that was used as fill material at various sites in the United States. It was produced during the extraction of chromium from its chromite ore using the high lime process (Allied Signal, 1982). This COPR is highly alkaline and it contains unreacted chromite ore and un-extracted chromate. Chromium concentrations are present up to 5% including hexavalent chromium with concentration up to 2%. Chromium exists mainly in two oxidation states: hexavalent – Cr(VI) and trivalent – Cr(III). 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 supplement, and in most environmental systems is immobile (Higgins et al., 1998). The COPR material that was deposited at various locations in Hudson County was discovered not to be benign as initially thought; yellow chromate solution was observed to leach from locations where COPR was deposited, and structures built on sites where COPR was used as fill material experienced catastrophic failures due to heave and uncontrolled expansion of the COPR. The COPR minerals, which were formed at high temperature, are not stable under normal atmospheric conditions. These minerals undergo compositional changes due to their interaction with water. This compositional change manifests in Cr(VI) leaching and COPR matrix expansion.

Most remediation methods for Cr(VI) contaminated soils and water involve the chemical reduction of Cr(VI) to Cr(III) and adjustment of the pH to precipitate Cr(III) as chromium hydroxide, $Cr(OH)_3$. A survey of the reducing agents used includes elemental iron, pyrite, ferrous iron, sulfites, sulfides, and organic compounds.

Ferrous iron, Fe(II) is the most investigated reductant for the remediation of Cr(VI) contaminated soils and water (James, 1994; Buerge and Hug, 1999; Seaman et al., 1999; Geelhoed et al., 2003; Su and Ludwig, 2005). Buerge and Hug (1999) concluded that in-situ remediation of Cr(VI) contaminated soils by addition of soluble Fe(II) salts may be a cheaper alternative to other treatment technologies based on their investigation on the influence of mineral surfaces on the reduction of Cr(VI) by Fe(II). On the other hand, the precipitation of Fe(II) out of solution as ferrous hydroxides or ferrous carbonates at alkaline pH values was found to impede the effectiveness of the chemical treatment of COPR in column infiltration tests due to the high alkalinity and buffering capacity of COPR (Geelhoed et al., 2003). Su and Ludwig (2005) had reported that a mixed reductant solution of Fe(II) and sodium dithionite was used to overcome the

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problem of ferrous precipitation in the infiltration treatment of chromite ore processing waste.

Conversely, calcium polysulfide had been used as a reductant for the removal of heavy metals from waste water (Yahikozawa et al., 1978). Messer et al. (2003) had reported that calcium polysulfide is a more stable and persistent reductant in subsurface environments than sodium dithionite and ferrous sulfate. Calcium polysulfide was used for the geochemical fixation of Cr(VI) in soil and groundwater in alluvial fan sediments at Arizona by URS Corporation. Calcium polysulfide reduces Cr(VI), commonly in the form of chromate, CrO_4^{2-}, to a relatively insoluble form of Cr(III) and tends to fall out of solution and adhere to soil. The fixation of Cr(VI) by calcium polysulfide is considered to be a rather permanent technique under most ground water conditions.

The remediation of the COPR material is complicated by the high alkaline content of the COPR matrix, the slow release of chromium and alkalinity from the COPR minerals, and the potential swell of COPR pre- and post-treatment. The delayed alkalinity release, in the presence of sulfate, may prove detrimental to the remediation process due to the potential for future swell of the treated COPR material caused by the formation of swell causing minerals such as ettringite.

In this study, an experiment was conducted to investigate the capacities of ferrous sulfate and calcium polysulfide to remediate COPR. In addition, the resultant treated COPR matrix was investigated for mineralogical changes to check for the formation ettringite, a swell causing mineral.

2. EXPERIMENTAL METHODOLOGY

2.1. Materials

The COPR material that was used in this study is a composite sample made of 10 homogenized samples that were collected from an unsaturated COPR zone. The samples were collected during a major bulk-sampling event in Jersey City, NJ. The pH of the COPR material is 12.5 and its initial characterization is shown in Table 1. Iron (II) sulfate heptahydrate ($FeSO_47H_2O$), acids, and bases were obtained from Alfa Aesar (MA, USA). Calcium polysulfide solution, 29% CaS_5, was donated by Best Sulfur Products (CA, USA). All stock solutions were prepared using ACS or higher-grade reagents and deionized (DI) water.

2.2. Treatability Design

The treatment target pH was free drift (denoted by N) or set to 9, the particle size was selected as mesh 4 (4.75 mm) and mesh 200 (0.075 mm), and the molar stoichiometric ratios of the reductant to hexavalent chromium [X] were set to 2 or 4 for ferrous sulfate, and 1 or 2 for calcium polysulfide. The experimental design is presented in Table 2. All the samples were prepared in triplicates. The reported treatability results are the averages of three replicates.

Table 2. Experimental design for the treatability study

Test No.	Particle Size (Mesh #)	Chemical Reagent	Dosage	Target pH
1	4	$FeSO_4$	2X	N
2	4	$FeSO_4$	4X	N
3	4	$FeSO_4$	2X	9
4	4	$FeSO_4$	4X	9
5	200	$FeSO_4$	2X	N
6	200	$FeSO_4$	4X	N
7	200	$FeSO_4$	2X	9
8	200	$FeSO_4$	4X	9
9	4	CaS_x	1X	N
10	4	CaS_x	2X	N
11	4	CaS_x	1X	9
12	4	CaS_x	2X	9
13	200	CaS_x	1X	N
14	200	CaS_x	2X	N
15	200	CaS_x	1X	9
16	200	CaS_x	2X	9

2.3. Sample Preparation

Representative 100 g of air-dried COPR samples were pulverized to the predetermined particle sizes and introduced into 250 mL plastic bottles. The amount of HCl needed to reach the target pH values was calculated from Acid Neutralizing Capacity (ANC) tests (Isenburg et al., 1992). The dosage of the chemical reductant needed was calculated based on the amount of Cr(VI) present in the COPR sample. Cr(VI) was assumed to oxidize ferrous iron and sulfide to ferric iron and elemental sulfur, respectively (Eary and Rai, 1988; Kim et al., 2001). The stoichiometric ratios of reductant to Cr(VI) were calculated based on the number of electrons transferred during the oxidation-reduction reactions. DI water was added to maintain a liquid-to-solid ratio of one in all samples. Sub-samples were withdrawn from the sealed plastic bottles at set time intervals and were analyzed for total Cr(VI), TCLP Cr(VI), pH and mineralogy.

Table 1. Characterization of the COPR material

Element	Al	Ca	CO_3^{2-}	Cr(VI)	Cr	Fe	K	Mg	Mn	Na
Percent	4.6	23.9	6.8	0.48	2.1	11.8	0.03	6.1	0.12	0.37

2.4. Physicochemical Analyses

The elemental composition of the COPR samples was obtained by EPA Method 3051A (Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils). The total hexavalent chromium concentration was obtained using EPA Method 3060 (Alkaline Digestion For Hexavalent Chromium) and the colorimetric method (EPA Method 7196A). TCLP tests were conducted according to EPA method 1311. Carbonate concentration was obtained using ASTM D5291.

ANC tests were conducted by mixing representative 1.0 g of pulverized air-dried COPR samples of particle size mesh 100 (0.15 mm) with 20 mL of DI water in 50 mL plastic centrifuge tubes. Different amounts of concentrated HCl were added to each centrifuge tube to cover a wide range of pH values. The mixtures were left on an end-over-end mixer where the pH values, Cr(VI), and Cr concentrations in the leachates were measured at set time intervals.

2.5. X–Ray Powder Diffraction (XRPD) Analyses

Representative samples were air dried for 24 hours and pulverized using mortar and pestle and then passed through mesh 400 (0.038 mm) sieve. The resulting samples were subjected to XRPD analyses. 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 2θ range of 5° to 65° with a step size of 0.02° and a count time of 3 seconds per step. The XRPD patterns were analyzed using the JADE software package (version 6.5). JADE software was used to quantify the identified crystalline mineral phases. JADE uses "Whole Pattern Fitting" which is based on the Rietveld method (Rietveld, 1969).

3. RESULTS AND DISCUSSION

3.1. Untreated Samples

The results in Table 3 indicated that greater Cr(VI) concentrations were obtained for the reduced particle size samples, for both alkaline digestion and TCLP analyses. The values increased almost by 1.5 times; Cr(VI) concentrations increased from 4575 mg/kg and 103 mg/L to 6313 mg/kg and 165 mg/L for alkaline digestion and TCLP, respectively.

Table 3. The effects of particle size on Cr(VI) concentration for untreated samples

Mesh #	Particle Size (mm)	Alkaline Digestion	TCLP	
		Cr(VI) (mg/kg)	Cr(VI) (mg/L)	pH
4	4.750	4575	103	9.7
100	0.150	4974	132	9.4
200	0.075	6313	165	9.5

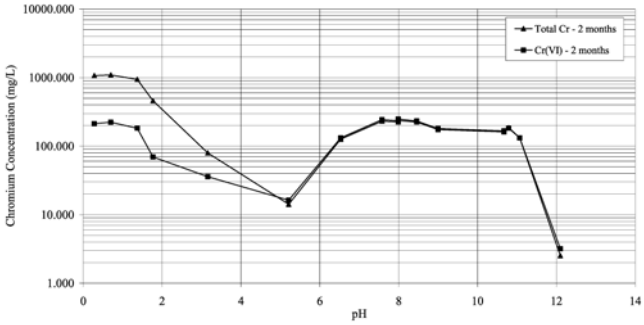

Fig. 1. ANC results of untreated samples.

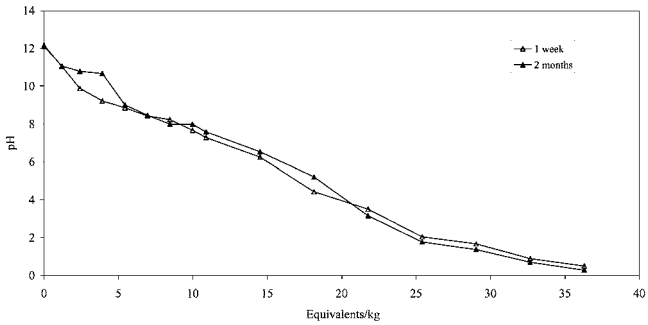

Fig. 2. Variation of COPR alkalinity upon the addition of HCl.

The leaching results in Figure 1 indicated that most of the chromium was released when the pH was approximately 1.5. Approximately 32 equivalents of acid (H^+) per one kilogram of COPR were needed to attain pH 1.5 (Fig. 2). In addition, most Cr(VI) as quantified by alkaline digestion, was leached at approximately pH 8.5. For example, Cr(VI) concentration in the leachate was approximately 250 mg/L at pH of 8.5, and the test has a liquid-to-solid ratio of 20, which means that 5000 mg/kg Cr(VI) was leached from the COPR sample constituting the entire Cr(VI) content. Similarly, chromium concentration in the leachate at pH < 1.5 was approximately 1000 mg/L, which means that 20,000 mg/kg of chromium was released (the entire chromium content within the experimental error). Furthermore, the results in Figure 2 indicated that the leaching of the COPR alkalinity was kinetically controlled, the measured pH increased from approximately 9 to 11 for 4 (H^+) eq/kg, between mixing periods of 1 week and 2 months respectively.

3.2. Treated Samples

A ferrous iron stoichiometric ratio of 4X was needed to reduce Cr(VI) concentration to less than 240 mg/kg, whereas 2X dosage was sufficient to reduce the TCLP Cr(VI) concentration to less than 5 mg/L for the target pH 9 but not

Table 4. Treatment results of COPR using ferrous sulfate after a curing period of 1 month

Test No.	Treatment pH (1:1)	Cr(VI) mg/kg	TCLP Cr mg/L	TCLP Cr(VI) mg/L	TCLP pH
1	11.03	600.56	8.38	7.77	7.40
2	10.92	160.77	ND	ND	7.03
3	7.39	457.81	1.27	ND	5.42
4	5.83	57.51	ND	ND	5.46
5	11.12	682.12	12.38	12.77	8.00
6	10.51	149.60	ND	ND	7.65
7	8.34	709.03	2.6	1.84	5.68
8	8.63	67.53	ND	ND	6.46

Table 5. Treatment results of COPR using calcium polysulfide after a curing period of 1 month

Test No.	Treatment pH (1:1)	Cr(VI) mg/kg	TCLP Cr mg/L	TCLP Cr(VI) mg/L	TCLP pH
9	10.57	104.12	7.54	7.70	8.38
10	10.95	ND	0.96	0.85	8.20
11	9.54	38.72	15.2	12.48	5.92
12	10.20	11.89	3.27	ND	5.85
13	10.80	51.70	2.8	2.91	7.99
14	10.71	ND	0.9	0.83	8.90
15	9.74	14.48	21.77	20.10	6.39
16	10.16	2.51	3.04	ND	6.14

for the free drift pH, for the reported curing periods (Table 4). Also, more alkalinity was released during curing for smaller particle size as evidenced by the treatment pH for target pH of 9 and TCLP pH for the free drift pH condition, N. There was no apparent effect for the particle size for the 4X treatment; however, total Cr(VI) and TCLP Cr(VI) values increased for the smaller particle size and lower chemical dosage.

As shown in Table 5, Cr(VI) results were satisfactory for all treatment conditions (< 240 mg/kg) when calcium polysulfide was used; however, a stoichiometric dosage of 2X was needed for satisfactory Cr(VI) TCLP concentration (< 5 mg/L).

3.3. XRPD Analyses

The XRPD results in Figures 3 and 4, and the Rietveld quantification analyses in Table 6 indicated that no ettringite was detected at pH less than 9.58. Ettringite and monophases were detected upon calcium polysulfide treatment at pH greater than 11.55 whereas ettringite was detected upon ferrous sulfate treatment and its content increased for longer curing periods. It also appears that brownmillerite content decreased upon ferrous sulfate treatment.

3.4. Discussion of the Treatment

Four factors may affect the reaction between Fe(II) and Cr(VI): (1) availability of aqueous Fe(II), (2) availability of aqueous Cr(VI), (3) kinetics of reduction of Cr(VI) by Fe(II), and (4) kinetics of scavenging of Fe(II) by oxygen (Eary

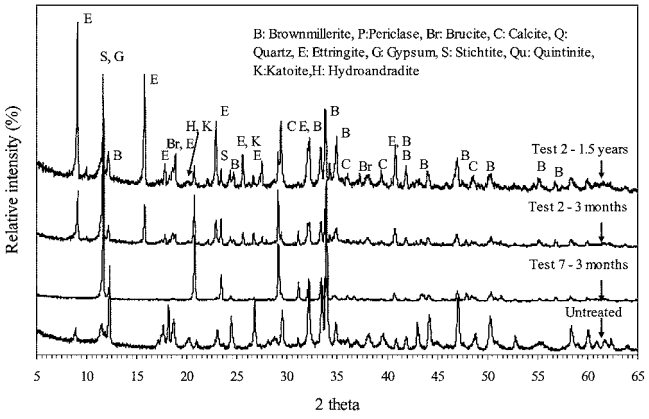

Fig. 3. XRPD patterns for the untreated and ferrous treated samples.

and Rai,1988). Fe(II) has the lowest solubility at pH of 12 (Snoeyink and Jenkins, 1980) and it increases at pH values less or greater than 12. The increase in the solubility of Fe(II) is approximately 2.5 orders of magnitude as the pH decreased from 12 to 9. Conversely, the solubility of Cr(VI) is controlled by Cr(VI)-ettringite and Cr(VI)-hydrocalumite at 10.4 < pH < 11.5 and pH > 11.5 respectively (David and Allison, 1999). At pH < 10.4, the solubility of Cr(VI) is controlled only by adsorption onto metal hydroxides (Zachara et al. 1987; Van Geen et al., 1994). However, Cr(VI) adsorption becomes substantial at pH values less than 7. It appears that decreasing the pH will cause the release of Cr(VI) into solution and increase the availability of Fe(II) which helps the

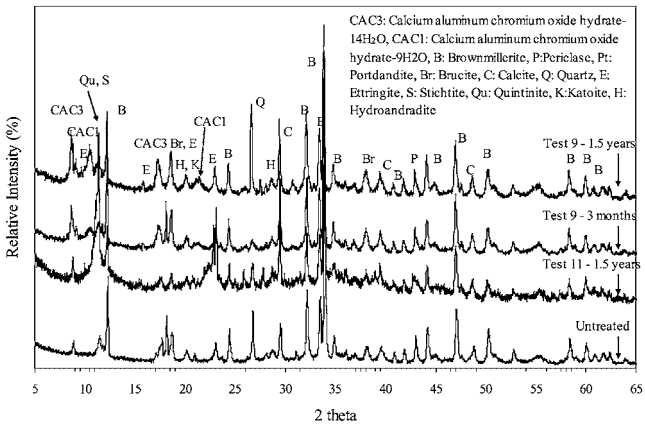

Fig. 4. XRPD patterns for the untreated and calcium polysulfide treated samples.

treatment process. Scavenging of the ferrous iron during the curing period or chemical analysis may have lead to the non-stoichiometric reduction of Cr(VI) especially for the higher pH values. The satisfactory TCLP Cr(VI) results for the Fe(II) dosages of 2X and target pH of 9 were probably due to CrO_4^{2-} adsorption onto the freshly precipitated $Fe(OH)_3$ as evidenced by the pH of the TCLP leachate.

For the calcium polysulfide treatment, more Cr(VI) leached during TCLP than can be accounted for by the alkaline digestion method for some samples. For example, total Cr(VI) and TCLP Cr(VI) concentrations for test 15 were 14.48 mg/kg and 20.10 mg/L respectively (Table 5). The TCLP test has liquid-to-solid ratio of 20 indicating that 402 mg/kg leached during the TCLP test whereas the alkaline digestion indicated that the residual untreated Cr(VI) was 14.48 mg/kg. This discrepancy indicated that the residual Cr(VI) was either reduced during the alkaline digestion process or the sulfide species helped encapsulate Cr(VI) into the COPR matrix during the same process.

Ferrous sulfate and calcium polysulfide provided sulfate sources for the COPR matrix; however, sulfate is readily available upon ferrous sulfate treatment whereas sulfides have to be oxidized to form sulfate and hence it is released at a slower pace. Gypsum is the sulfate sink in COPR at pH less than 9.58 whereas ettringite is the major sink for sulfate at pH greater than 10.4 pending availability of alumina. The release of alumina may be kinetically controlled, therefore there may be a transition period going form gypsum to ettringite as pH rebounds and alumina is released. This transition is displayed by test 2 for curing periods of 3 months and 1.5 years (Table 6) where gypsum seem to have transformed to ettringite as pH increased from 10.67 to 11.20 for curing periods of 3 months and 1.5 years.

The calcium polysulfide treatment resulted in the formation of ettringite at pH greater than 9.27. Calcium polysulfide provides more sulfur species than ferrous sulfate for the same stoichiometric ratio which indicates that the slow oxidation of sulfides to sulfate is the cause of the lower ettringite content in the calcium polysulfide treated samples. It also indicates that ettringite content will increase as sulfides are transformed to sulfates. The content of CACs increased upon the calcium polysulfide treatment at pH greater than 11.55; however, CACs and monsulfates have similar XRPD patterns and it is difficult to distinguish between CACs and monosulfates peaks. Therefore it is not feasible to resolve the discrepancy between the total Cr(VI) and TCLP Cr(VI) measurements and hence the encapsulation versus reduction

Table 6. The resultant mineralogy of the COPR matrix upon ferrous sulfate or calcium polysulfide treatments

Test No.	--	2	2	7	9	9	11
Curing Period	Untreated	3 months	1.5 years	3 months	3 months	1.5 years	1.5 years
pH	12.5	10.67	11.20	9.58	11.55	12.08	9.27
CAC1	-	-	-	-	2.8	4.6	-
CAC3	3.1	-	-	-	4.9	7.7	4.6
Brownmillerite	39.0	20.6	19.2	26.9	40.3	38.7	35.1
Katoite	16.6	-	1.9	-	4.5	2.1	-
Periclase	3.6	-	1.4	-	2.8	3.4	4.2
Brucite	9.3	5.7	3.8	2.8	10.2	9.1	4.4
Portlandite	7.8	-	-	-	1.3	-	-
Calcite	8.1	11.4	11.5	5.4	14.1	12.7	19.0
Ettringite	-	24.9	44.8	-	5.1	4.9	-
Gypsum	-	20.6	4.5	64.1	-	-	-
Quartz	4.6	2.5	-	0.8	1.8	7.7	2.9
Sjogernite	4.7	-	9.6	-	3.2	3.5	21.9
Quintinite	3.1	14.2	-	-	4.5	-	-
Hydroandradite	-	-	3.2	-	4.5	5.6	4.4
Sulfur	-	-	-	-	-	-	0.7

of Cr(VI) by calcium polysulfide in COPR especially since the amorphous content was not quantified in this study.

It seems that the ferrous sulfate treatment resulted in the dissolution of brownmillerite; however, the apparent decrease in brownmillerite percentage could be due to a dilution effect. The added sulfate may have reacted with a non-crystalline calcium source or the released calcium, and the released alumina to form gypsum and ettringite. The total increase in the content of the crystalline phases may have resulted in the reduced percentage of brownmillerite. It is worth mentioning that brownmillerite is not stable thermodynamically in the presence of water. However, it is still present at up to 50 percent of the crystalline phases in the COPR matrix some 80 years after deposition on site. Its slow hydration explains its presence and the delayed alkalinity release of COPR.

4. CONCLUSIONS

Ferrous sulfate and calcium polysulfide were found effective for the remediation of COPR contaminated sites. The treatment results indicated that four times the stoichiometric amount of ferrous iron or two times the stoichiometric amount of polysulfide were needed to meet both the NJDEP regulatory limit of 240 mg/kg for Cr(VI) and EPA TCLP regulatory limit of 5 mg/L for Cr, for a curing period of one month. It is important to note that the slow release of a minute fraction of Cr(VI) during curing, which could be imbedded in slow dissolving minerals, may cause the treatment to fail if the reductants are not protected from scavengers such as oxygen. pH adjustment was found necessary for effective treatment and to prevent the formation of ettringite, a swell causing mineral. The slow hydration of some COPR minerals caused the treated COPR pH to creep upward during curing. However, if enough acid is added, the pH value could be controlled below the stability region of ettringite.

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