Evaluation of the treatment of chromite ore processing residue by ferrous sulfate and asphalt

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ABSTRACT

The effectiveness of the treatment of chromite ore processing residue (COPR) with ferrous sulfate and encapsulation into asphalt were explored separately and in combination. The asphalt treatment was conducted by mixing COPR or ferrous sulfate pretreated COPR with varying amounts of asphalt. To assess the efficacy of the treatment, the leachability of toxicity characteristic leaching procedure (TCLP) total chromium (Cr) from all treated samples was determined for curing periods up to 16 months. X-ray absorption near edge structure (XANES) analyses were also performed to evaluate the Cr^{6+} concentration in the selected samples. The combination treatment of ferrous sulfate and the encapsulation of the treated COPR into asphalt reduced the TCLP total Cr concentration to lower than the regulatory limit of 5 mg/L for Cr contaminated soils, after 16 months. However, the Cr concentrations were still higher than the universal treatment standards (UTS) of 0.6 mg/L for hazardous waste. On the other hand, treatment with ferrous sulfate alone or the encapsulation of the COPR in asphalt failed to meet the TCLP total Cr concentration of 5 mg/L, after 16 months. XANES analyses results showed that more than 75% Cr^{6+} reduction was achieved upon pretreatment with ferrous sulfate.

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1. Introduction

Chromite ore processing residue (COPR) is a by-product generated during the extraction of chromium (Cr) from chromite ore using the high lime process. The detailed description of the high lime extraction process has been previously reported in the literature [1–5]. The major phases identified in COPR are brownmillerite (Ca_2FeAlO_5), periclase (MgO), brucite ($Mg(OH)_2$), hydrotalcite ($Mg_6Al_2(CO_3)(OH)_{16}•4H_2O$), hydrogarnet ($Ca_3Al_2(OH)_{12}$), ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}(26H_2O)$) and calcium aluminum chromium oxide hydrates (CACs) [6]. COPR materials have been used as structural fill materials in England, Japan, West Germany and the USA [7]. The major COPR deposition sites in the USA are in Maryland, New Jersey, Ohio and New York [8]. For example, about 1.5 million tons of COPR have been deposited over a 34-acre area in Hudson Country, New Jersey and significantly larger amounts of COPR have been deposited over an 85-acre site at the Dundalk

Marine Terminal, in Baltimore, Maryland [9,10]. Chromium leaching from these sites is of high environmental relevance associated with the contamination of natural resources with toxic hexavalent chromium (Cr^{6+}).

In the USA, chromium is the second most common inorganic groundwater contaminant after Pb [11]. In the environment, Cr occurs in two oxidation states; Cr^{6+} such as chromate and bichromate (CrO_4^{2-}, $HCrO_4^-$) and trivalent chromium (Cr^{3+}) [12]. Cr^{6+} is mobile, carcinogenic and toxic to humans, while Cr^{3+} is essentially immobile under normal groundwater conditions and is much less toxic [13–15]. The solubility of Cr^{3+} in an aqueous solution is less than 10^{-5} M over a wide pH range (4–12) [12].

Several remediation technologies have been applied in the past for the treatment of Cr^{6+} found in groundwater and COPR. Reductants, such as ferrous sulfate and calcium polysulfide, have been used with various degrees of success [16,17]. For example, the in-situ treatment of Cr^{6+} contaminated groundwater at a site adjacent to the Delaware River with ferrous sulfate was successful in reducing the Cr^{6+} concentration from 85 mg/L to 50 µg/L, with the reduced levels maintained over a 4-year period [18,19]. Another method involves the installation of reactive zones downstream from the source to allow passive treatment, i.e., no need to pump and treat [20]. Dissolved Cr (VI) can be precipitated using ferrous

sulfate in the reactive zones [21], however, barrier integrity verification can be difficult [19]. On the other hand, reduction treatment of Cr^{6+} in COPR has proved unsuccessful in recently published work [4–6]. Initial toxicity characteristic leaching procedure (TCLP) results showing satisfactory total Cr concentrations, using up to 51% (w/w) $FeSO_4(7H_2O)$, were reversed at a later date after a curing period of 420 days. The reversal of the reduction treatment results was attributed to the incomplete reduction of Cr^{6+}, due to mass transfer limitations caused by the sequestration of Cr^{6+} in COPR nodules. The imbedded Cr^{6+} is assumed to be released at a later date, due to the slow reaction of some of the COPR minerals. Vitrification of the Cr contaminated soils using cold top ex-situ vitrification has been shown to be effective however, at a cost that is prohibitively expensive [22]. Electrokinetic remediation suffers from mass transfer issues associated with the formation of insoluble phases [23]. The increased solubility of Cr in high pHs may deem cement encapsulation technologies ineffective for COPR remediation.

In this study, the efficacies of three methods were explored for the treatment of COPR materials, namely, chromium reduction with ferrous sulfate, asphalt encapsulation, and the combination of chromium reduction with ferrous sulfate followed by encapsulation in asphalt. Although most attempts in the literature using ferrous sulfate reduction have been unsuccessful for COPR materials [24–26], this method was used for benchmarking and comparison to the other two methods that were applied. Asphalt has received considerable attention and has been widely used for waste encapsulation due to its low cost [27]. Moreover, asphalt is highly hydrophobic, chemically and biologically very stable and it is widely produced [28]. Asphalt encapsulation can be applied to solid wastes with a variety of structural and compositional characteristics. Even wet wastes or sludge after solidification can be treated by asphalt emulsion [29]. For example, Phillips et al. [27] studied bitumen encapsulation of radioactive wastes. Bednarik et al. [30] applied asphalt emulsion to galvanic sludges. Huang et al. [31] investigated both physical and environmental properties of asphalt mixtures containing incinerator bottom ash (IBA). However, there is very limited information available for asphalt treatment of COPR materials and there are no current reports on the effectiveness of the combination of chemical treatments with encapsulation for the treatment of COPR.

The main objective of this study is to evaluate the effectiveness of two asphalt encapsulation methods: (1) ferrous pretreated COPR and (2) COPR without ferrous pretreatment. Toxicity characteristic leaching procedure (TCLP) tests were used to evaluate the effectiveness of treatment and the total Cr concentration in the TCLP leachate was compared with both the 0.6 mg/L limit based on the universal treatment standards (UTS) (Title 40 of the US Code of Federal Regulations (CFR) Sec. 268.48) and the 5 mg/L TCLP limit for Cr contaminated soils. The TCLP limit was utilized in this study as supplementary criteria in case COPR is classified as hazardous contaminated soils [9]. Long-term effectiveness of the treatment was also investigated based on long curing periods of up to 16 months.

2. Experimental methodology

2.1. Characterization of COPR samples

COPR materials were obtained from zones B1 and B2 from a site located in Hudson County, NJ. The details of the physical characterization for the COPR materials were reported in Wazne et al. [5]. The composite B1B2 sample used in this study was prepared by mixing equal amounts of composite B1 and composite B2. The average Cr^{6+} concentration in composite B1B2, based on alkaline digestion tests,

was 4 g/kg in accordance with EPA Method 3060A [32]. The composite B1B2 samples were always thoroughly homogenized before COPR material was removed.

2.2. Asphalt characterization

A number of asphalt samples were procured and characterized for their suitability for the encapsulation of COPR. The linear viscoelastic material functions of the asphalt samples were characterized using an ARES rheometer (from TA Instruments) in conjunction with parallel plate and cone-and-plate fixtures, at various temperatures. It was determined that in general the linear viscoelastic range over which the dynamic properties, i.e., the storage, G', and loss moduli, G'', and the magnitude of the complex viscosity, $|\eta^*| = ((G'/\omega)^2 + (G''/\omega)^2)^{0.5}$, values remained independent of the strain amplitude, was relatively broad (up to a strain amplitude of 30%). For the encapsulation task, the asphalt needs to have a relatively low shear viscosity at the targeted processing temperature. A certain degree of elasticity is desired to allow the development of adequate mechanical properties for the encapsulated COPR. On the basis of the respective rheological material functions of various candidate asphalt samples, including their shear viscosity and the magnitude of complex viscosity, storage modulus and loss modulus material functions, an asphalt (Bitumar Ref. AOC030304), available from Bitumar, Inc. (Baltimore, MD) was selected for the encapsulation. This asphalt sample had the following properties: softening point, 106.1 °C; penetration, 15 (1.5 mm) at 25 °C (100 g, 5 sec); flash point (COC), 321.1 °C; and a reported viscosity of 1200 Pa s at 110 °C.

2.3. Chemical reagents

All chemical reagents used in this study were of analytical grade and were obtained from Fisher Scientific (Suwanee, GA). Deionized water was used in preparation of all standards and stock solutions.

2.4. Ferrous sulfate treatment

The ferrous sulfate treatment was conducted using 100 g COPR samples with ferrous sulfate dosages of $2\times$ (16.62% w/w of $FeSO_4(7H_2O)$), whereas the ferrous sulfate pretreatment, prior to asphalt encapsulation, was conducted using a ferrous sulfate dosage of $1.5\times$ (12.47% w/w of $FeSO_4(7H_2O)$). The stoichiometric requirements were calculated based on the number of electrons transferred during the oxidation reduction reactions, and based on an average Cr^{6+} concentration of 4 g/kg. Ferrous iron was assumed to oxidize to ferric iron by Cr^{6+} whereas Cr^{6+} was assumed to reduce to Cr^{3+} by ferrous iron. The ferrous sulfate treatment and pretreatment were conducted by initially passing the COPR samples through a 4.75 mm (mesh 4) sieve. The water content was adjusted to one for all samples concomitant with the addition of the required ferrous sulfate dosage. The samples were then thoroughly mixed using a spatula. All samples were prepared in duplicate and allowed to cure in 250 mL plastic bottles. After curing, the samples were analyzed for TCLP total Cr, TCLP Cr^{6+} and pH. The reported results are the mean values of two replicate measurements. The ferrous sulfate pretreated samples were cured for 1 day before they were subjected to asphalt encapsulation.

2.5. Encapsulation of the treated COPR with asphalt

The high intensity mixer that was used for the encapsulation of chemically treated and untreated COPR at the lab scale (with Banbury type mixer elements), is shown disassembled in Fig. 1. This device uses two intermeshing and counter-rotating blades that
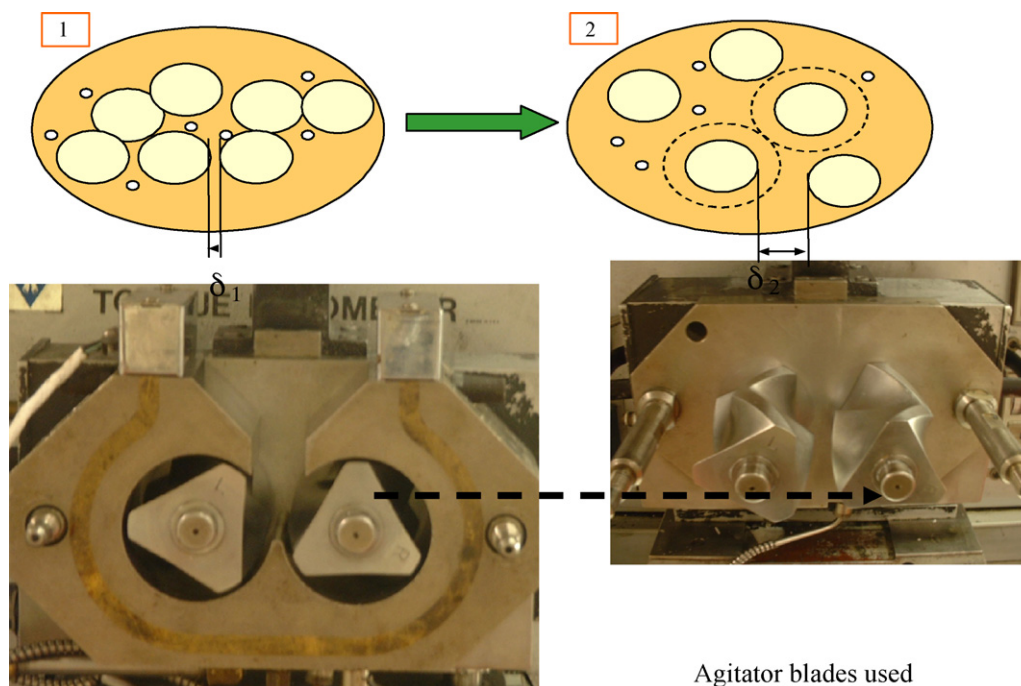
Fig. 1. The high intensity mixer with Banbury type mixer elements used for the encapsulation of COPR with the asphalt: side view with the barrel wall removed and the schematics of the break-up of the floccules and the encapsulation of particles of COPR during shearing.

can impart relatively high shearing stresses by passing the mixture repetitively through the small gaps available between the two blades with one hand and between the blades and the barrel wall with the other hand.

In some experimental runs, prior to exposure to asphalt, COPR samples were pretreated with $FeSO_4(7H_2O)$ as described previously. The asphalt was processed in the mini Banbury mixer using multiple rotational speeds. Upon ferrous sulfate and asphalt treatment, oxidation of ferrous ions can be prevented over time, due to asphalt encapsulation. A $300\,cm^3$ mixing chamber was utilized at 70% of the full capacity and at the temperature selected as the optimum from rheological characterization, i.e., at 110 °C. Chunks of asphalt were gradually fed to the mixing chamber and were allowed to soften before the addition of the wet COPR. The liquid to solid ratio for all asphalt treated samples was adjusted to one. The torque on the blades had increased upon addition of cold and hard asphalt, but leveled off as soon as it softened. It was noticed that the COPR was in chunks as big as couple of millimeters in size. As the COPR was mixed in the chamber, the large particles were crushed and we were able to form a homogeneous and flowable paste. The torque did not increase sharply due to the hardening of the asphalt by the incoming cold material, but rather stayed relatively low owing to the presence of water in COPR contributing to a low viscosity binder. The incoming cold material cooled down the entire mixing chamber and the torques stayed relatively low. As the temperature stabilized around 110 °C, the significant water evaporation resulted in gradual increase in the torque. After most/all of the water was lost, the torque decreased a little due to the increase in temperature. At this point 50 g of sample was collected for analyses. The concentrations of asphalt used in this study were 40%, 50% and 60% (based on dry mass basis). These correspond to the solids volume fraction of 0.36, 0.27 and 0.2, respectively.

The typical specific energy input values during processing were relatively high, i.e., in the 15–35 kJ/kg range. With increasing specific energy input the floccules of COPR could be broken down to give rise to better encapsulation of the COPR with the asphalt, as shown schematically in Fig. 1.

2.6. Analytical testing

TCLP tests were conducted in duplicate, in accordance with the EPA method 1311 [33] with minor modifications. Specifically, 3 g of treated COPR materials ($\leq$4.75 mm) were placed in 60 mL high-density polyethylene (HDPE) bottles and mixed with 60 mL of one of two TCLP extraction fluids. The selection of the extraction fluids was made based on the pH and buffering capacity of the COPR samples. The samples were tumbled at 30 rpm in a TCLP tumbler for 18 h. After tumbling, the pH was measured using a Denver Instrument UB-10 pH meter. The leachates were filtered with a 0.45 μm pore-size membrane filter prior to analysis. TCLP tests were conducted on the COPR samples after 1 day, 5 months and 16 months of curing. Cr^{6+} concentrations in the TCLP leachate were measured by the U.S. EPA method 7196A [34]. TCLP total Cr concentrations in the TCLP leachate were analyzed by Inductive Coupled Plasma/Atomic Emission Spectrometry (ICP/AES) (Thermo Varian Vista-MPX, Varian, Palo Alto, CA). The total Cr content in the untreated sample was measured by acid digestion and ICP/AES in accordance with the EPA 3015A [35] and 6010B methods [36]. All sample analyses were conducted in duplicate and averaged values were reported. Two different quality control standards as well as, the method of standard addition (spiking) were used.

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

XANES analyses were conducted for selected treated COPR samples cured for 16 months, 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 (1 1 1) double crystal monochromator was used and 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_2 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 chromium compounds K_2CrO_4 and $Cr(NO_3)_3(9H_2O$ were used as the standard reference for Cr^{6+} and Cr^{3+}, respectively. Quantitative XANES analyses were performed using the ATHENA program in the IFEFFIT computer package [37].

2.8. Scanning electron microscopy (SEM) analyses

Prior to SEM analyses, sub-samples were air dried and cut with a razor blade into cubes. These samples were then prepared using double-sided carbon tape to examine the freshly exposed interior surface. In order to minimize charging problems, the samples were coated with gold using a SPI sputter (West Chester, PA). SEM analyses were performed using a LEO-810 Zeiss microscope equipped with an ISIS-LINK system.

2.9. Sample designation

In order to simplify nomenclature, the samples treated with $FeSO_4(7H_2O$ were designated as "Fe" while the samples treated with $FeSO_4(7H_2O$ and asphalt were designated as "Fe-A". The samples treated with asphalt were designated as "A" and the weight percent of asphalt was included in the designation. For example, the sample treated by $FeSO_4(7H_2O$ and 60% asphalt was designated as "Fe-A-60".

3. Results and discussion

3.1. TCLP tests

The TCLP results for $FeSO_4(7H_2O$, asphalt as well as, asphalt and $FeSO_4(7H_2O$ treated samples upon curing, along with the TCLP regulatory limit of 5 mg/L, are presented in Table 1; since the TCLP total Cr concentrations upon curing for 5 months were not available, the TCLP Cr^{6+} concentrations are presented instead. The total Cr concentrations for untreated samples upon curing were higher than 96 mg/L.

The TCLP results for asphalt treated samples without pretreatment of ferrous sulfate showed that even though a significant reduction in total Cr concentration (>91%) was achieved upon 16 months of curing, asphalt treatment alone failed to meet the UTS of 0.6 mg/L. TCLP total Cr concentrations upon 16 months curing ranged between 5.3 and 8.74 mg/L, which were similar to the TCLP total Cr concentrations upon 1 day of curing. It appears that there was no significant difference in the TCLP Cr concentrations from the samples treated with various asphalt contents used in this study (40–60%). Thus, the generation of a diffusion barrier with only asphalt surrounding the COPR particles is not sufficient to prevent the migration of Cr. However, TCLP total Cr values remained approximately stable over time, suggesting that the encapsulation achieved by asphalt is stable over time. It is worth noting that the reduction of TCLP total Cr concentrations could not have been due

to dilution effects because the TCLP total Cr concentration was reduced from 96 mg/L to less than approximately 8.7 mg/L, using 60% asphalt, after a curing period of 16 months.

The TCLP results of Fe samples indicated that the TCLP total Cr concentrations for Fe samples were less than 5 mg/L (2.25 mg/L) but higher than 0.6 mg/L after 1 day (Table 1). Moreover, these samples failed to meet the limit of 5 mg/L after 16 months even though a stoichiometric ratio of 2:1 for the $FeSO_4(7H_2O$ to Cr^{6+} was utilized during treatment. The reductive remediation of Cr^{6+} involves the reduction of Cr^{6+} to Cr^{3+} and pH adjustment to precipitate Cr^{3+} as $Cr(OH)_3$. Cr^{3+} is sparingly soluble at pHs greater than 5 [5]. The failure of the ferrous sulfate treatment could be thus attributed to the incomplete reduction of Cr^{6+} upon mixing and the oxidation of residual Fe^{2+} by molecular oxygen during curing [4,6]. Recently published results [4,6] attempting to treat the same COPR materials using ferrous sulfate have indicated the partial reduction of Cr^{6+} due to mass transfer limitations. It has been reported that large percentages of Cr^{6+} were found sequestered in Cr^{6+} minerals [38] and these minerals were in turn found imbedded inside COPR nodules composed of slow reacting unstable minerals such as brownmillerite [5,38]. Initially, upon the ferrous sulfate treatment, the imbedded Cr^{6+} is not available to react with ferrous ions. But at a later date, the minerals encapsulating the unreacted Cr^{6+} start to react and they release their Cr^{6+} contents. However, upon their release with elapsed time, most of the ferrous ions would have been consumed by scavengers such as oxygen from the ambient environment.

Therefore, the rationale for using asphalt encapsulation following the ferrous sulfate pretreatment is to prevent the scavenging of residual ferrous ions during curing. The unreacted ferrous ions will further reduce the residual Cr^{6+} when it is released. In essence, the asphalt will create an enclosure that will encapsulate the unreacted ferrous ions along with the residual Cr^{6+}. Hence, the unreacted imbedded Cr^{6+} that may potentially leach out can be effectively reduced over time by active ferrous ions. Indeed the COPR samples treated with both $FeSO_4(7H_2O$ and asphalt showed that the total Cr concentrations from all treated samples were less than 5 mg/L over time but higher than the UTS, except for the sample Fe-A-40 upon 1 day curing time, where the total Cr concentration was 5.66 mg/L (Table 1). However, the total Cr concentration of this sample was less than 5 mg/L after 5 months of curing. Moreover, it was observed that the Cr concentrations decreased as the asphalt concentration increased indicating that the efficacy of the diffusion barrier increased with increasing asphalt concentration. During potential field applications, the combined asphalt and ferrous sulfate treatment would also prevent exposure of the COPR to water present in deposition sites and thus prevent the leaching of water into the reaction zone. Overall, even though the COPR samples treated with both $FeSO_4(7H_2O$ and asphalt showed a drastic reduction in total Cr concentrations, they remained higher than the UTS of 0.6 mg/L. Further research is needed to satisfy the UTS criteria upon treatment.

Table 1
TCLP results for untreated and treated COPR samples.

Samples	1 day			5 months		16 months		
	TCLP Cr^{6+} (mg/L)	TCLP Total Cr (mg/L)	TCLP pH	TCLP Cr^{6+} (mg/L)	TCLP pH	TCLP Cr^{6+} (mg/L)	TCLP Total Cr (mg/L)	TCLP pH
Untreated	94.9	96.0	9.63	119.4	9.95	99.1	103.9	9.65
Fe	1.91	2.25	6.84	–	–	21.98	22.43	8.77
A-60	5.47	6.01	5.07	6.49	5.30	8.68	8.74	5.71
A-50	7.68	8.25	5.19	6.80	5.29	5.72	5.78	5.62
A-40	5.91	6.78	5.07	7.66	5.35	5.27	5.30	5.58
Fe-A-60	2.34	3.80	5.10	3.49	5.41	2.46	2.51	5.59
Fe-A-50	2.93	4.80	5.27	4.53	5.50	4.42	4.63	5.94
Fe-A-40	3.78	5.66	5.34	2.87	5.35	3.82	4.06	5.96

Table 2
Quantitative XANES analyses of treated samples.

Samples	Total Cr (mg/kg)	XANNES			
		Cr^{6+} (%)	Cr^{3+} (%)	Cr^{6+} (mg/kg)	Cr^{3+} (mg/kg)
A-40	22,000	14	86	3,080	18,920
Fe-A-40	22,000	3.5	96.5	770	21,230
Fe-A-60	22,000	3.3	96.7	726	21,274
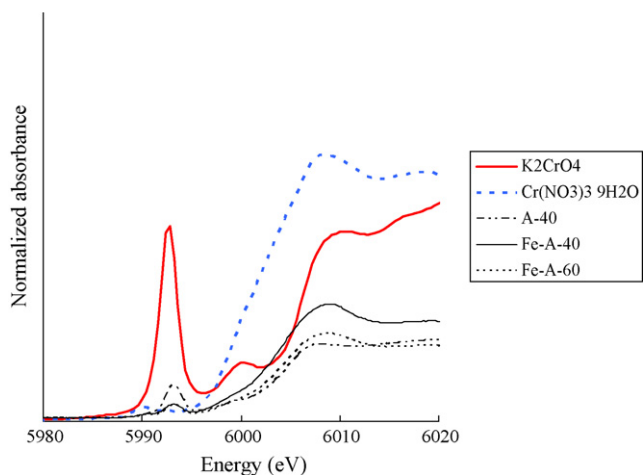
Fig. 2. Chromium K-edge XANES spectra for K_2CrO_4, $Cr(NO_3)_3(9H_2O)$ and treated samples.
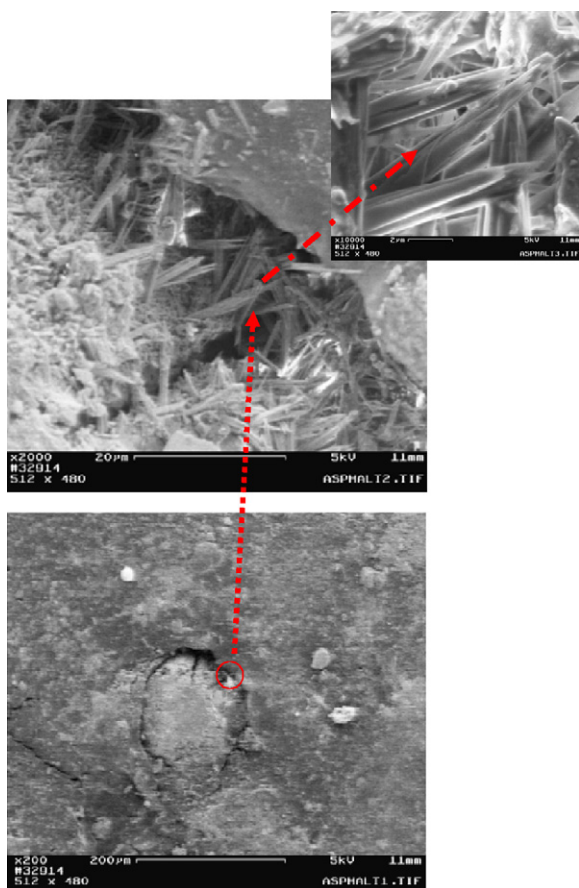

Fig. 3. Scanning electron microscope (SEM) micrograph of encapsulated COPR sample Fe-A-60 which was cured for 16 months.

3.2. XANES analyses

XANES results obtained from treated samples are presented in Table 2 and Fig. 2. The XANES data showed that more than 75% Cr^{6+} reduction was achieved upon ferrous pretreatment. There was no major difference between the results from the Fe-A-40 and Fe-A-60 samples, indicating that the XANES data were consistent, due to no asphalt effects on Cr^{6+} reduction.

3.3. SEM analyses

The typical SEM micrograph obtained from the encapsulation of the COPR with asphalt (sample Fe-A-60 which was cured for 16 months) is shown in Fig. 3. This typical micrograph indicates that the COPR could be effectively encapsulated with asphalt using the high intensity mixing methodology. Furthermore, at a number of locations the presence of Ettringite needles was detected at sufficiently large magnifications (2000–10,000× in Fig. 3). Ettringite formation could be due to the sulfate source added as ferrous sulfate. Ettringite could be formed upon as little as 0.1% (w/w) sulfate addition, in as fast as few hours [39] and can be associated with heaving phenomena in COPR materials [6,10,40].

Overall, SEM images showed that the COPR materials were encapsulated by the asphalt. The ettringite needles shown in the SEM images may have been formed during the ferrous sulfate pretreatment of the COPR materials. Asphalt encapsulation should prevent further exposure of the treated material to water, thus mitigating the formation and growth of ettringite crystals.

4. Conclusions

The effectiveness of the treatment of COPR materials by ferrous sulfate, encapsulation of COPR materials by asphalt and the combined treatment of COPR materials with ferrous sulfate followed by asphalt encapsulation of the pretreated COPR materials were investigated. Overall, even though the UTS of 0.6 mg/L was not achieved, COPR treatment by the combined ferrous sulfate and asphalt encapsulation method was determined to be effective in lowering the total Cr concentrations to less than 5 mg/L upon 16 months of curing. On the other hand, neither ferrous sulfate treatment alone nor the encapsulation of COPR materials by asphalt alone were effective in meeting the 5 mg/L after 16 months of curing for the applied experimental conditions. Moreover, asphalt treatment was found to be stable over time due to encapsulation, while ferrous sulfate treatment showed an increase in TCLP Cr concentration, presumably due to the incomplete reduction of Cr^{6+} and the oxidation of residual ferrous ions. XANES results showed that Cr^{6+} was significantly reduced, upon ferrous pretreatment.

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