



Pilot scale treatment of chromite ore processing residue using sodium sulfide in single reduction and coupled reduction/stabilization processes

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ABSTRACT

Single Cr(VI) reduction and coupled reduction/stabilization (R/S) processes were evaluated at pilot scale to determine their effectiveness to treat chromite ore processing residue (COPR). Sodium sulfide was used as the reducing agent and cement, gypsum and lime were tested as the stabilizing agents. The pilot experiments were performed in a helical ribbon blender mixer with batches of 250 kg of COPR and mixing time up to 30 min. Na₂S/Cr(VI) mass ratios of 4.6, 5.7 and 6.8 were evaluated in the single reduction process to treat COPR with Cr(VI) concentration of ≈4.2 g/kg. The R/S process was tested with a Na₂S/Cr(VI) mass ratio of 5.7 and including stabilizing agents not exceeding 5% (w/w_{COPR}), to treat COPR with a Cr(VI) content of ≈5.1 g/kg. The single reduction process with a ratio of 6.8, reached Cr(VI) reduction efficiencies up to 97.6% in the first days, however these values decreased to around 93% after 380 days of storage. At this point the total Cr level was around 12.5 mg/L. Cr(VI) removal efficiencies exceeding 96.5% were reached and maintained during 380 days when the coupled R/S process was evaluated. Total Cr levels lower than 5 mg/l were attained at the initials days in all R/S batch tested, however after 380 days, concentrations below the regulatory limit were only found with gypsum (2%) as single agent and with a blend of cement (4%) and lime (1%). These results indicated that the coupled R/S process is an excellent alternative to stabilize COPR.

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1. Introduction

Chromium (Cr) is one of the world's most strategic and critical materials having a wide range of uses in the metal and chemical industries including pigments, catalysts, ceramics, electronics, corrosion inhibitors, emulsion hardeners, etc. [1]. Although it can exist in nine different oxidation states, the most common species are trivalent and hexavalent chromium compounds. Cr(III), as chromite (FeCr₂O₄), is the most commercially useful of the ores and is used to produce diverse basic salts of chromium such as chromate and dichromate [1,2]. Hexavalent chromium is a critical pollutant commonly released to the environment as a result of industrial activities, including electroplating, tanning, industrial water cooling, paper pulp production, petroleum refining and chromite ore processing industries. Among these, the latter have been reported to generate high environmental impact when there is an uncontrolled disposal of chromite ore processing residue (COPR) [2,3]. In

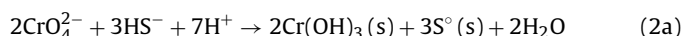
general, the COPR is highly alkaline waste (11–12 pH) and contain residual hexavalent chromium (1–30% of total chromium), which is very water soluble and can migrate to the groundwater [4,5]. COPR can cause serious environmental problems when improperly disposed because it continue to leach chromate salts for decades even if the mineral was previously subject to efficient leaching methods [6]. Diverse countries, including England, Japan, United States, India and Mexico, have reported similar contamination problems caused by chromite ore processing industries [5–8].

Due to the severe environmental impact caused by COPR, numerous reducing agents have been proposed to convert Cr(VI) to the less mobile and toxic Cr(III) as the primary remediation strategy. The reducing agents tested can be grouped in: (i) organic agents (ascorbic acid, citric acid, humic substances, preconditioned organic wastes, etc.); (ii) iron based inorganic agents (zero-valent iron, ferrous sulfate, Fe(II)-bearing minerals, etc.) and (iii) sulfur based inorganic agents (sulfur dioxide gas, sodium metabisulfite, calcium polysulfide, sodium dithionite, hydrogen sulfide, sodium sulfide, etc.) [5,9,10]. Ferrous sulfate has been used as reducing agent for a number of years, and its capacity to reduce Cr(VI) is well demonstrated at laboratory and pilot scale to treat soil and

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wastewater [11,12]. However, Geelhoed et al. [4] reported that ferrous sulfate was not effective to treat COPR, because the high pH and buffering capacity causes Fe(II) precipitation. Furthermore, sulfate ion can exchange for chromate in Cr(VI)-bearing minerals causing Cr(VI) leaching. For these reasons, in the last two decades Cr(VI) reduction methods using sulfur-based reducing agents such as sodium dithionite, hydrogen sulfide (H₂S) and calcium polysulfide have been implemented for Cr(VI) in soil and sediments remediation and COPR treatment [13,14]. Gaseous H₂S, is an effective reducing agent and can attain elevated hexavalent chromium reduction (>90%) in sediments, contaminated soil and COPR at pH values between 8 and 10 [13,15]. Unfortunately, H₂S is very toxic and corrosive, which limits its applicability in chromium contaminated sites with high hexavalent chromium concentration [15]. Sodium sulfide, (Na₂S) has been proposed to avoid the use of gaseous H₂S. Na₂S, being a solid material, is more easily handled than gaseous H₂S and can quickly dissolve attaining an ionic equilibrium between H₂S_(liq), HS⁻ and S²⁻, depending on the pH. The exothermic reactions with Na₂S are the following (Eqs. (1), (2a) and (2b)):



Trivalent chromium hydroxide, Cr(OH)₃ is the end product of Cr(VI) conversion and is insoluble at pH between 6.5 and 12 but its solubility increases at pH < 6.5 or pH > 12 due to its amphoteric behavior [16]. Although elemental sulfur is the main by-product, sulfate can also be produced under some conditions by the reaction of HS⁻ with chromate ion (Eq. (2b)) [10,17].



Some studies reported that Cr(III) and Cr(VI) species can bind to cement and cementitious materials (lime, fly ash and blast furnace slag, among others) by chemical substitution of the aluminum or sulfate ions in some crystalline calcium sulfoaluminate hydrates as ettringite and monosulfate (hydrocalumite) phases, which allows the immobilization of chromium and thus minimizing its leachability [2,18,19]. Although, calcium sulfoaluminate hydrate phases favor anion and cation crystallochemical substitution reactions, the effective stabilization of chromium compounds in the solid phase depends on the suitable concentration and oxidation state of the metal, in the latter, Cr(III) immobilization is very effective in cement or cementitious materials, while Cr(VI) is not readily incorporated into cement hydrate phases [19].

The aim of this at pilot scale study was to evaluate the effectiveness of two strategies for chromate conversion and chromium immobilization in COPR. Initially, the single Cr(VI) reduction process with Na₂S was tested and then it was further developed by coupling a chemical stabilization process using diverse agents such as cement, lime and gypsum.

2. Materials and methods

2.1. Contaminated material

Two COPR samples of about 2 tons each one were collected from the contaminated area of the abandoned chromite ore processing plant “Cromatos de México”, where around 70,000 ton of COPR and others raw materials were confined since 1983. The samples COPR I and COPR II were collected from the zone marked as C-SON 01 and C-SON 05 in the characterization study of Schmidt et al. [8]. After collection, the samples were transported to a storing area and each sample was mechanically pre-mixed with a mini excavator to homogenize its composition and then subsamples were collected for analyses. COPR I was used to evaluate the sin-



Fig. 1. Picture of the pilot plant implemented to treat COPR.

gle reduction process and COPR II was used to assess the coupled reduction/stabilization (R/S) process. COPR I contained total Cr and Cr(VI) concentrations of 190 ± 11 mg/L and 4.27 ± 0.45 g/kg while COPR II had 287 ± 14 mg/L and 5.10 ± 0.53 g/kg, respectively.

2.2. Pilot plant

The experiments were performed from January to March of 2009, to determine the treatability of COPR using sodium sulfide as reducing agent, then cement, lime and gypsum as stabilizing agents at the pilot scale. The pilot plant was laid inside a 200 m² closed tent installed inside the premises of the processing plant. The pilot plant (Fig. 1) consisted in a 200 kg feed hopper, two screw conveyors having a length of 1.8 and 8 m with an internal diameter of 6 in., a hammer mill with 300 kg/h working capacity, a 500 kg material storage tank and a helical ribbon blender mixer (U-shaped horizontal of 1.4 m × 0.7 m × 1.1 m) with a working capacity of 500 kg and a mixing velocity of 45 RPM. All the equipment was built and installed by Veyco Company (Mexico City, Mexico).

The COPR material was transported from the feed hopper through the screw conveyors to the hammer mill where the milled material passed through a screen having a sieve size ≤ 10 mm. Then the sieved material was transported to the upper storage bin where it was discharged to the ribbon blender mixer where the Cr(VI) reduction process and the coupled reduction/stabilization process were performed. The weight of COPR in the ribbon blender mixer was recorded with a load cell with an analog output. Batch experiments were carried out with 250 ± 2 kg of COPR having a ≤ 10 mm particle size. Temperature was recorded with thermocouples.

2.3. Single reduction experiments

Three sodium sulfide/hexavalent chromium mass ratios [Na₂S/Cr(VI) mass ratio]: 4.6, 5.7 and 6.8 were tested (Table 1), these ratios were selected based on previous laboratory results [20] and from preliminary experiments in the pilot plant (data not shows). Industrial grade anhydrous sodium sulfide (Solvay & CPC BS Monterrey, México) was used in both processes. Each Na₂S/Cr(VI) ratio was evaluated by triplicate with COPR I. The total mixing time of sodium sulfide with COPR I in the helical ribbon blender was 20 min, then the treated material was placed into containers and subsamples were placed in a tightly closed 5 L plastic vessel for long-term monitoring. Water (18 L) with a flow rate of 3 L/min was added after 5 min of the initial mixing time to favor the dissolution of the sodium sulfide flakes.

Table 1

Sodium sulfide used in the 250 kg batch experiment at different sodium sulfide/hexavalent chromium mass ratios.

Samples	Hexavalent chromium (g/kg)	Ratio	Na ₂ S ^a (g/kg COPR)	Na ₂ S (kg/250 kg COPR)	%Na ₂ S (W/WCOPR)
COPR I	4.27	4.6	33.0	8.2	3.3
		5.7	40.8	10.2	4.1
		6.8	48.7	12.2	4.9
COPR II	5.10	5.7	48.4	12.1	4.9

^a Considering Na₂S at 60% purity.

2.4. Coupled reduction/stabilization experiments

COPR II samples were used with a Na₂S/Cr(VI) mass ratio of 5.7. The reduction process with sodium sulfide was carried out for the initial 20 min, and then the stabilizing agents were added and mixing continued for 10 min. Water (25 L) with a flow rate of 3 L/min was added 5 min after start up. After a total time of 30 min of coupled process, the treated material was placed into containers and samples were placed in tightly closed 5 L plastic vessel for long-term monitoring. Ordinary Portland cement (5%, w/w_{COPR}), lime (1%, w/w_{COPR}), gypsum (2%, w/w_{COPR}), blend of cement (4%, w/w_{COPR}) and lime (1%, w/w_{COPR}) and the blend of cement and gypsum (2.5%, w/w_{COPR} each) were evaluated as stabilizing agents. One experimental batch was performed for each stabilizing agent.

2.5. Analyses

Hexavalent chromium extraction and measurement were realized by alkaline digestion and colorimetric determination with diphenylcarbazide, according to EPA method 3060A [21] and EPA method 7196A [22], respectively. Total Cr extracted by the Toxicity Characteristic Leaching Procedure, TCLP, was made according to EPA method 1311 [23] and its concentrations in TLCP leachate was measured by Inductive Coupled Plasma/Atomic Emission Spectrometry (ICP/AES) (Optima 3300 DV, PerkinElmer). pH and moisture were measured according to ASTM methods D4980-89 and D 2216-98 [24], respectively. H₂S concentration in air was measured with a hydrogen sulfide analyzer with a detection range of 0.003–50 ppm (Jerome 631-X, Arizona Instrument). All sample analyses were conducted in duplicates and average values are reported.

3. Results

3.1. Single reduction process

The results of the treatment of COPR with sodium sulfide after 7 days of processing show that the reduction efficiency attained values ranging from 93.6% to 97.6% when the Na₂S/Cr(VI) mass ratio increased from 4.6 to 6.8. However, these values decreased after 380 days of storage (Fig. 2). The difference of Cr(VI) conversion efficiency between 7 and 380 days were 8.3%, 5.7% and 4.5%, for the 4.6, 5.7 and 6.8 ratios, respectively. Cr(VI) conversions higher than 90% were only maintained with a Na₂S/Cr(VI) mass ratio of 6.8 at 380 days. All ratios showed a steep loss in conversion efficiency in the first 50 days of storage but leveled thereafter and were stable in the next 330 days (Fig. 2). Total Cr concentration at 7 days were 17.2, 10.4 and 7.7 mg/L for Na₂S/Cr(VI) mass ratios of 4.6, 5.7 and 6.8, but almost doubled to values of 33.8, 18.3 and 12.5, respectively, after 380 days of storage.

The pH increased from initial values of around 9.6 in the untreated material to around 12 with all the Na₂S/Cr(VI) mass ratios at 7 days after processing (Fig. 3), caused by the formation of sodium

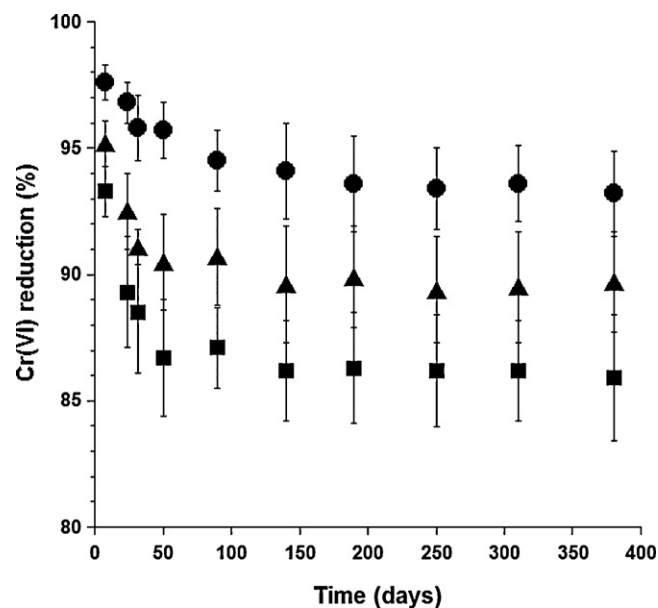


Fig. 2. Cr(VI) content of treated COPR I. Single reduction process. Na₂S/Cr(VI) mass ratio of 4.6 (■), 5.7 (▲) and 6.8 (●).

hydroxide during the water dissolution of sodium sulfide (Eq. (1)). However, pH values decreased around one unit after 380 days. The pH values dropped within the first 80 days, and then kept stable during 300 days (Fig. 3).

Measurements of gaseous hydrogen sulfide during the reaction of COPR with sodium sulfide were between 0.5 and 2.5 ppm in the overhead of the helical ribbon blender and below 0.2 ppm around the pilot plant area.

3.2. Coupled reduction/stabilization process

The results of the coupled reduction and stabilization process are shown in Fig. 4. The results indicated that Cr(VI) removal efficiencies in the R/S process with the different stabilizing agents were almost 99% after 7 days, however it decreased to values between 96.7% and 98.2% after 380 days. The minimum efficiency

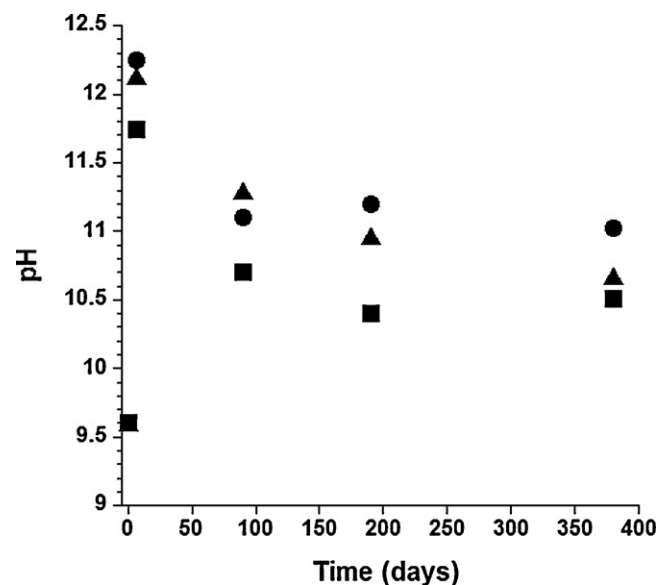


Fig. 3. pH of treated COPR I. Single reduction process. Na₂S/Cr(VI) mass ratio of 4.6 (■), 5.7 (▲) and 6.8 (●).

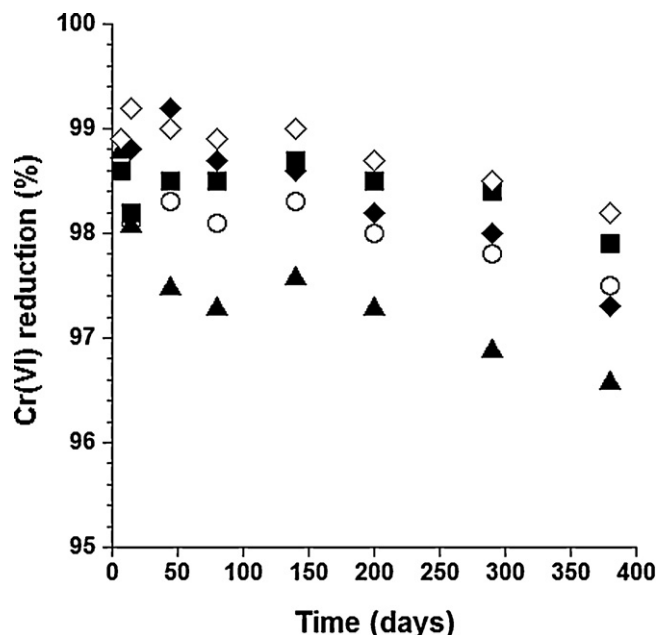


Fig. 4. Cr(VI) content of treated COPR II. Coupled reduction/stabilization process. 5% cement (◆); 2% gypsum (■); 1% lime (▲); blend of 4% cement and 1% lime (◇) and blend of cement and gypsum 2.5% each one (○).

was reached with lime (1%, w/w) while the maximum value was obtained with the cement (4%, w/w) and lime (1%, w/w) blend after 380 days (Fig. 4).

Total Cr concentrations below the Mexican regulatory limit of 5 mg/L [25] were registered at 7 days after reaction with all stabilizing agent tested. However, total Cr concentrations increased to values ranging from 3.8 to 6.7 mg/L after storing the material for 380 days. Only gypsum (2%, w/w) and the blend of cement (4%, w/w) and lime (1%, w/w) kept the concentrations below 5 mg/L. Total Cr concentration average for the different stabilizing agents at 7 and 380 days was around 1.56 and 5.3 mg/L, respectively.

The pH increased from an initial value of 9.8 in the untreated COPR II to 11.8 with gypsum and to around 12.6 with cement, lime and their blends after 7 days. Similarly to the previous tests, the pH of treated COPR decreased in all the assays after 380 days. The decrease was less steep with the COPR treated with cement (5%, w/w) and the blend of cement (4%, w/w) and lime (1%, w/w) (Fig. 5).

4. Discussion

4.1. Experimental sodium sulfide dosage

Sodium sulfide proved to be an efficient reducing agent to transform Cr(VI) to Cr(III) in COPR at pilot plant. Experimental sodium sulfide dosages of 7.6, 9.5 and 11.2 times the stoichiometric value (Eq. (2a)) were required to attain high Cr(VI) initial conversion efficiencies of 93.6%, 95.2% and 97.6%, respectively. A high sodium sulfide dosage was needed to compensate for the possible sodium sulfide losses due to its high reactivity with oxygen and most metals or its leakage as H_2S gas. Other COPR treatability studies with reducing agents such as calcium polysulfide (CaS_5) and ferrous sulfate ($FeSO_4$) used experimental dosages of two and eight times, respectively, the stoichiometric value to attain Cr(VI) conversions exceeding 90% [11,14]. In iron based processes, the high requirements of $FeSO_4$ can be related with the loss of $Fe(II)$ as $Fe(OH)_2$ caused by the high pH of COPR [4].

The H_2S gas levels detected during the reaction step in the overhead of the helical ribbon blender and around the pilot plant area

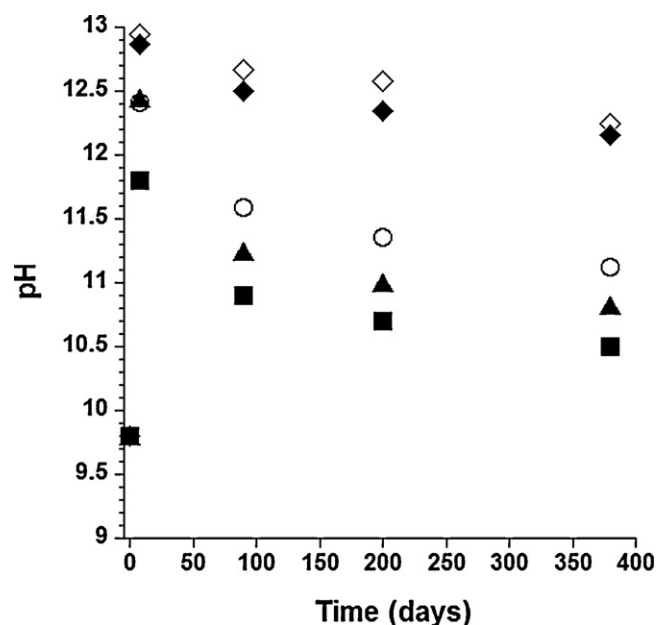


Fig. 5. pH of treated COPR II. Coupled reduction/stabilization process. 5% cement (◆); 2% gypsum (■); 1% lime (▲); blend of 4% cement and 1% lime (◇) and the blend of cement and gypsum 2.5% each one (○).

were maintained within the limit of 10 ppm established by the National Institute for Occupational Safety and Health as occupational exposure limit in EE.UU [26]. The low values registered were due to the high pH which displaces equilibrium toward the non volatile HS^- and S^{2-} forms and to the fast reaction rates of sulfides with the soluble Cr(VI) and other metals contained in the COPR. The exothermic nature of the reactions involved increased the temperature within the mixer to values between 54 and 67 °C.

4.2. Cr(VI) release and pH evolution

The reversion in the Cr(VI) reduction efficiency (Fig. 2) and the pH decrease (Fig. 3) observed in the single reduction process in the first 50 days after the sulfide reaction possibly can be related to mineralogical transformations or anion exchange of sulfate for chromate in the solid phase of the treated COPR. Dermatas et al. [11] observed that the progressive increase in Cr(VI) concentrations, measured by alkaline digestion, were caused by ongoing mineralogical transformations in the treated COPR upon ferrous sulfate treatment, while the pH increased due to gypsum formation as secondary mineral phase. Geelhoed et al. [4] observed an additional Cr(VI) release from the solid matrix possible due to anion exchange of sulfate for chromate in the interlayer of Cr(VI)-bearing minerals, however they observed a pH decrease due to $Fe(II)$ precipitation as $Fe(OH)_2$ in their study with ferrous sulfate.

In the present study, probably the release of Cr(VI) observed during the first 50 days was caused by mineral dissolution instead of anion exchange mechanisms, because the latter requires a sulfate influx as ferrous sulfate. Geelhoed et al. [27] mentioned that the key process responsible for the release of Cr(VI) is the mineral dissolution of solid phases in COPR, however the dissolution of Cr(VI)-bearing minerals as Cr(VI)-hydrocalumite, Cr(VI)-ettringite, Cr(VI)-hydrogarnet and Cr(VI)-hydrocalcites depend on their stability at certain pH range [11,18,28,29]. Perkins and Palmer [29] reported that chromate ettringite is stable in a narrow pH range between 10.5 and 12.5, while chromate hydrocaluminitite is stable at $pH > 12$. Considering this information, we suggest that Cr(VI) released from COPR after the Cr(VI) reduction process could be related to the dissolution from the Cr(VI)-bearing minerals induced

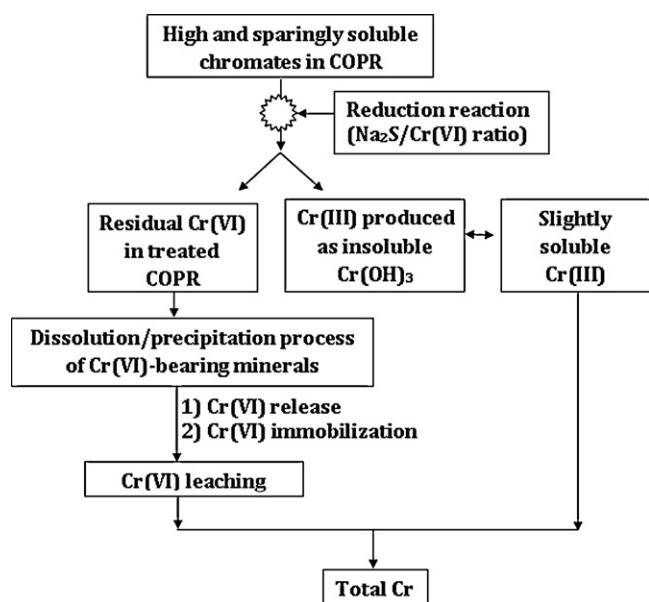


Fig. 6. Proposed scheme for the evolution of the different chromium species in: (1) single and (2) coupled reduction/stabilization process.

by the Cr(VI) gradient between the solid phase and the pore water in the treated COPR. The gradient becomes more important after the conversion of soluble chromate salts (K_2CrO_4 , Na_2CrO_4 , $CaCrO_4$ or $PbCrO_4$) to insoluble trivalent chromium hydroxide caused by the reducing agent. This difference in concentration may destabilize the solid matrix, fostering a dissolution/precipitation process until a new equilibrium is eventually attained. The new dissolution/precipitation equilibrium was probably attained in around 2 months (Fig. 2). In this respect, Burke et al. [6] mentioned that COPR continues to leach chromate salts for decades even though it was previously subject to efficient leaching methods. The amount of Cr(VI) released during mineral dissolution in the treated COPR will depend on the total Cr(VI) concentration, type of Cr(VI)-bearing minerals, water content, pH and buffering capacity. Fig. 6 shows the scheme of chromium release at single reduction process.

The pH increases initially with the NaOH formed in the reaction of sodium sulfide and water (Eq. (1)) decreasing thereafter in the treated COPR, (Fig. 3). This can be attributed to the formation of metal hydroxides, produced as a result of the dissolution of some metals (Al, Ca, Mg, Fe, even other) from the solid phase and to the free OH^- generated from the dissolution of sodium sulfide in water (Eq. (1)). Geelhoed et al. [27] mentioned that the dissolution of solid phase in COPR can result in the formation of a large amount of amorphous phases. It is important to mention that the initial COPR samples have a lower pH (around 9.8) compared with the typical COPR that have pH values between 11 and 12 [4,5].

4.3. Chemical mechanism of coupled R/S process

The hexavalent chromium conversion efficiency and total Cr results in the coupled reduction/stabilization process confirmed that the stabilizing agents tested improved the immobilization of Cr(VI) after the reduction process as compared with the single reduction process with a $Na_2S/Cr(VI)$ ratio of 5.7, suggesting that Cr(VI) released from the treated COPR solid phase was partially bound by the stabilizing agent tested. Fig. 4 shows that Cr(VI) conversion efficiencies values in coupled R/S process maintained more stable during 380 days of storage than Cr(VI) values in single reduction process (Fig. 2). Differences in pH evolution after the reduction reaction (Fig. 5) show the lowest pH drop when cement alone or with lime were used. This may be due to their stronger pH buffering

capacity, whereas gypsum has not the ability to uphold alkaline pH and consequently lower pH values were found. In the case of lime, maybe the amount tested (1%, w/w) was low to maintain the pH in the treated COPR. pH decreased in the treated COPR after single reduction (Fig. 3) or coupled R/S treatment (Fig. 5) suggesting that in both cases the metals released from the solid phase precipitated as hydroxides, while Cr(VI) remained soluble because it does not form insoluble hydroxo complexes. The soluble Cr(VI) leached from the matrix can be partially bound by the additives in the coupled R/S process (Fig. 6).

In recent years, it has been reported that calcium sulfoaluminate cement and cementitious materials (fly ash, blast furnace slag, among other) can efficiently stabilize chromium compounds as they form sulfate–ettringite ($Ca_6[Al(OH)_6]_2 \cdot (SO_4)_3 \cdot 26H_2O$), and/or sulfate–hydrocalumite ($Ca_4[Al(OH)_6]_2 \cdot SO_4 \cdot 9H_2O$) as hydrated products, which are responsible of the immobilization of chromium compounds due to crystallochemical substitution reactions [18,30]. Moreover, some studies indicate that when high levels of Na_2SO_4 and NaOH are present in cement or cementitious materials, a sodium-substitute of sulfate–hydrocalumite mineral called “U phase” ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 0.5Na_2SO_4 \cdot 15H_2O$) is formed, which is also associated with the stabilization of chromium compounds [31,32]. Luz et al. [32] reported that “U phase” was detected in calcium sulfoaluminate cement in the presence of high concentrations of chromium salts, their results shows a removal efficiency of about 99% for Cr(III) and 60% for Cr(VI).

The sulfate–ettringite and the sulfate–hydrocalumite phases can co-exist, however the domain mineral phase will depend on hydration reaction conditions such as temperature, pH and sulfate content [18,33]. Some studies have reported that both mineral phases have the ability to accept substitutions of a number of cations and anions [30,32]. Trivalent ions such as Fe(III), Cr(III), Mn(III), can replace Al(III) ions in the crystal structure, while SO_4^{2-} can be replaced by CO_3^{2-} , SeO_4^{2-} , CrO_4^{2-} , among other anions. Wiczorek-Ciurawa et al. [34] suggested that the substitution of Cr(III) by Al(III) in cement hydrate products is influenced by alkalinity because at high pH ($pH > 9.5$) the formation of chromium (III) hydroxo complex ($Cr^{3+} + 6OH^- = [Cr(OH)_6]^{3-}$) is induced and can substitute the Al(III) hydroxo complex ($[Al(OH)_6]_2$) in cement hydrates to form Cr(III)-ettringite ($Ca_6[Cr(OH)_6]_2 \cdot (SO_4)_3 \cdot 26H_2O$). While, Cr(VI)-ettringite ($Ca_6[Al(OH)_6]_2 \cdot (CrO_4)_3 \cdot 26H_2O$) and Cr(VI)-hydrocalumite ($Ca_4[Al(OH)_6]_2 \cdot CrO_4 \cdot 9H_2O$) synthesis is induced at pH higher than 10.5 [18,35].

Although ordinary Portland cement, lime and gypsum have not been reported as efficient Cr(VI) stabilizing agents, Fig. 4 shows that these materials are able to reduce the release of Cr(VI) in COPR after treatment with sodium sulfide. The results suggest that the combination of these materials with COPR induce the formation of calcium sulfoaluminate hydrate phases, maybe due to the cementitious nature of COPR. Chrysochoou and Dermatas [18] reported that COPR have the potential to generate ettringite mineral when sufficient calcium, aluminum and sulfate compounds were provided, while Dermatas et al. [11] mentioned that COPR is favorable candidates for ettringite formation upon sulfate influx. Consequently, cement, lime and gypsum were sources of aluminum, calcium and sulfate that possibly influence the formation of sulfate–ettringite and/or sulfate–hydrocalumite, while the blend of these materials may support better the formation of these hydrate compounds. The addition of lime can also favor the dissolution of available aluminum and sulfate in COPR improving the formation of sulfate–ettringite and/or sulfate–hydrocalumite.

However, according to the results (Fig. 4), lime addition to COPR rendered the lowest Cr(VI) immobilization efficiency, indicating that COPR may require a source of sulfate and/or aluminum to induce the formation of hydrate phases to bind released Cr(VI). In contrast, gypsum (2%, w/w) and the blend of cement (4%, w/w) and

lime (1%, w/w) maintained values below 5 mg/L after 380 days of storage.

According to the mentioned above, diverse minerals that allow Cr(VI) immobilization (ettringite, monosulfate, U phase, hydrogarnet, among other) could be formed when cement, lime, gypsum or their blends are used as stabilizing agents. However, this hypothesis is being investigated in more detail under different reaction and storage conditions including Na₂S/Cr(VI) ratio, pH, moisture, and amount of stabilizing agents added.

A preliminary economic analysis for the proposed processes at pilot scale showed costs of around \$70 and \$80 USD/ton of COPR for the single and coupled processes respectively. From the total cost, 60% corresponds to chemical reagents and 40% to other operating costs.

5. Conclusion

The pilot plant studies show that sodium sulfide is an efficient reducing agent to transform hexavalent chromium to less toxic Cr(III) in COPR samples. A Na₂S/Cr(VI) mass ratio of 6.8 was required to attain Cr(VI) conversions efficiencies up to 97.6% in single reduction process within the first days, however this value decreased due to Cr(VI)-bearing minerals dissolution in treated COPR, causing Cr(VI) leaching and an increase in Cr total level. The coupled reduction/stabilization process allowed further Cr(VI) reduction and stabilization during the storage time. Total Cr concentrations below the regulatory limit of 5 mg/L were only found in coupled R/S with gypsum (2%) as single agent and with a blend of cement (4%) and lime (1%) during 380 days. This suggests that coupled R/S process is an excellent alternative to treat COPR when mineral dissolution continues after the conversion of the soluble chromate salts.

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