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(54) **PROCESS FOR SOLUBILIZING, REDUCING
AND FIXING HEXAVALENT CHROMIUM
CONTAINED IN CHROMITE ORE
PROCESSING RESIDUE INTO TRIVALENT
CHROMIUM**

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(57) **ABSTRACT**

A process for reducing hexavalent chromium, Cr(VI), contained within a chromite ore processing residue matrix comprising the sequential steps of providing a chromite ore processing residue matrix containing Cr(VI), solubilizing the matrix to release Cr(VI), reducing the Cr(VI) to Cr(III) using Fe(II), and, fixing the residual Fe(II) using a effective amount of a Fe(II) precipitating agent to make a Fe(II) precipitate.

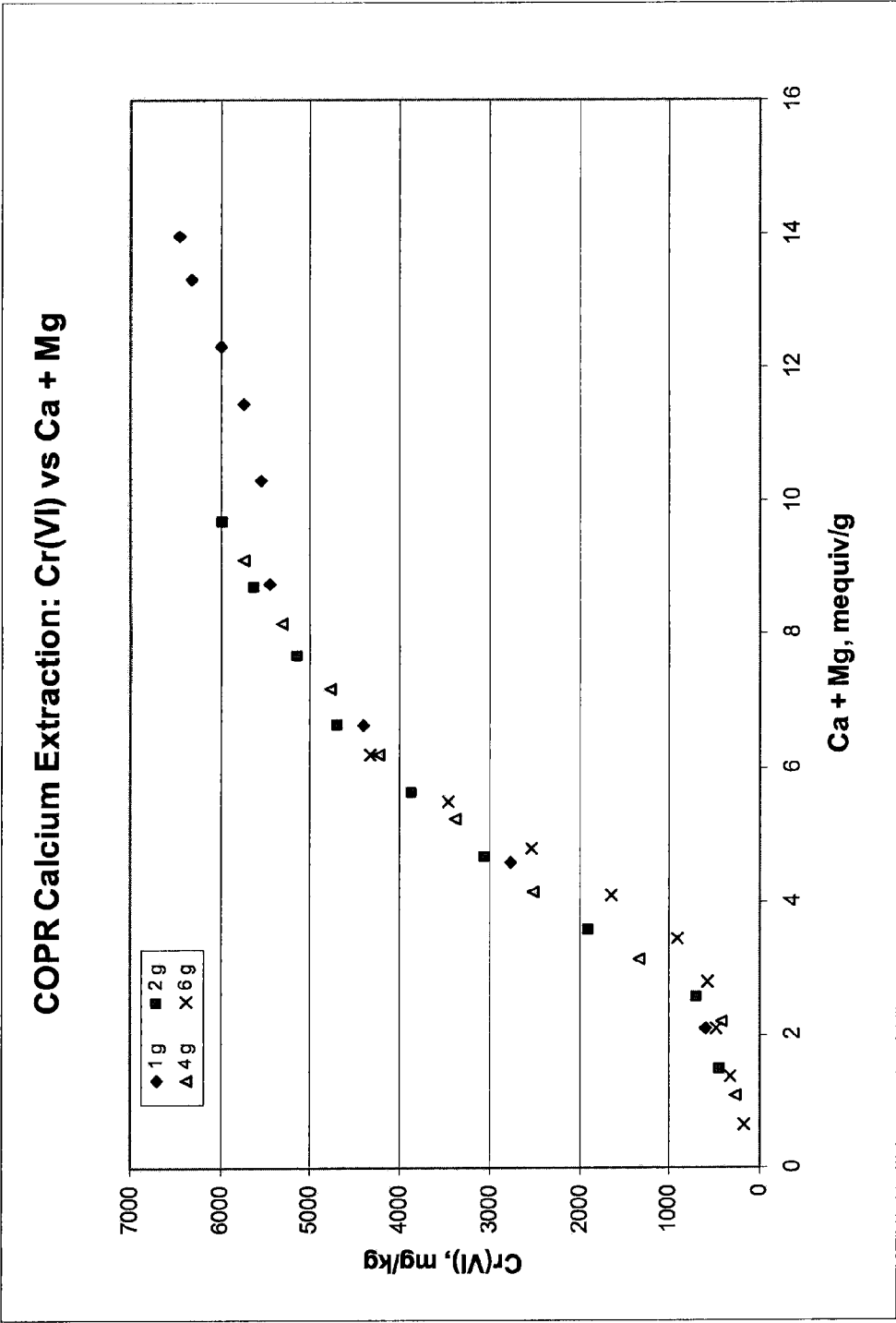


FIG. 1

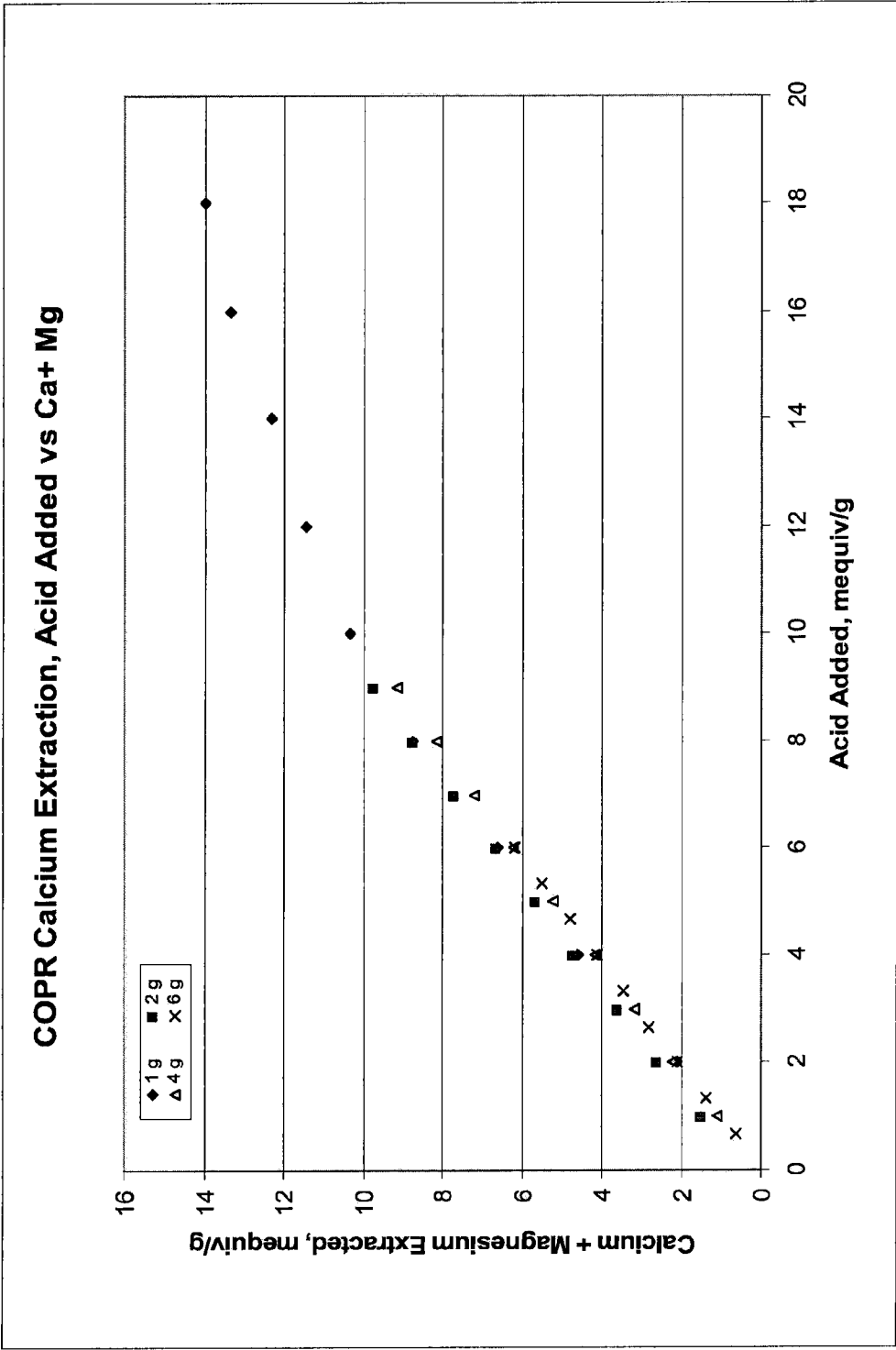


FIG. 2

**PROCESS FOR SOLUBILIZING, REDUCING
AND FIXING HEXAVALENT CHROMIUM
CONTAINED IN CHROMITE ORE
PROCESSING RESIDUE INTO TRIVALENT
CHROMIUM**

**CROSS REFERENCE TO RELATED
APPLICATIONS**

[0001] This application claims the benefit of U.S. Provisional Application No. 61/118,692 filed Dec. 1, 2008, incorporated herein by reference as if set forth in its entirety.

**STATEMENT REGARDING GOVERNMENT
INTEREST**

[0002] Not Applicable

BACKGROUND OF THE INVENTION

[0003] Chromite Ore Processing Residue (COPR) is a waste product from historic chromium manufacturing. From the late 1800's to around 1970, hexavalent chromium (Cr(VI)) was produced from chromite ore by a high temperature, alkaline oxidation of the ore and subsequent extraction of sodium chromate with water. Lime (CaO) was used as the base, sodium carbonate was used as a source of both base and sodium ion, and, atmospheric oxygen was the oxidant. (Tinjum J, 2006, Mineralogical properties of chromium ore processing residue and chemical remediation strategies, *Ph.D. Thesis (Civil Env. Eng)* U. Wisc-Madison). The waste contained unreacted chromite ore, various alkaline calcium compounds, and other waste material. Some hexavalent chrome was still present, predominantly trapped in calcium compounds in the waste.

[0004] Millions of tons of the waste have been used as landfill material in many areas in the Eastern U.S. (predominantly in New Jersey and Maryland) as well as in Europe. Such waste is highly alkaline, and it contains hexavalent chromium as well as trivalent chromium. Hexavalent chromium leaches out of the waste causing environmental problems. Leaching hexavalent chromium may also render the waste "hazardous" under U.S. EPA regulations. In addition, the waste generates an alkaline leachate and can expand over time, causing heaving problems. (Moon D H et al., 2007, Long-term treatment issues with chromite ore processing residue (COPR): Cr⁶⁺ reduction and heave *J Hazardous Mat* 143:629-635). These environmental problems have driven the need to clean-up such landfill wastes.

[0005] Treatment of COPR has been problematic. Discussion of the problems associated with COPR disposal and treatment studies to remediate them have been conducted and reported for over a decade. (James B R, 1994, Hexavalent chromium solubility and reduction in alkaline soils enriched with chromite ore processing residue, *J Environ Quality* 23:227-233; James B R, 1996, The challenge of remediating chromium-contaminated soil, *Environ Sci Tech* 30:248A-251A; and, Tinjum, 2006). Treatment involves the reduction of hexavalent chromium to the more stable and less toxic trivalent form. While several common approaches exist to reducing hexavalent to trivalent chromium, none have been sufficiently successful with COPR. (Tinjum, 2006).

[0006] Treatment of materials contaminated with Cr(VI) involves the reduction of hexavalent chromium to the more stable and less toxic trivalent form (Cr(III)). Cr(III) is insoluble in neutral and moderately basic solutions due to the

precipitation of Cr(OH)₃ (or, if iron is present, as a mixed iron-trivalent Cr oxide). Several reducing agents are commonly used, including ferrous or elemental iron (Rai D et al., 1989, Environmental chemistry of chromium, *Sci. Total Environ.* 86:15-23; Palmer C D et al., 1991, Processes affecting the remediation of chromium-contaminated sites, *Environ. Health Perspectives* 92:25-40; Stanforth R R et al., 1993, In situ method for decreasing metal leaching from soil or waste, U.S. Pat. No. 5,202,033; James, 1994; 1996; Patterson R R et al., 1997, Reduction of hexavalent chromium by amorphous iron sulfide, *Environ. Sci Tech* 31:2039-2044; Fendorf S et al., 2000, Chromium transformations in natural environments: the role of biological and abiological processes in chromium (VI) reduction, *International Geology Review* 42:691-701; US EPA, *In situ Treatment of Soil and Groundwater Contaminated with Chromium*, EPA 625/R-00/004, Office of Research and Development, US EPA, Cincinnati Ohio. (2000)); and reduced sulfur species (Palmer and Wittbrodt, 1991; Patterson et al., 1997; Fendorf, et al. 2000; US EPA, 2000).

[0007] It is reported in Rai et al. (1989) (a review article on the environmental chemistry of chromium) that Cr(VI) can be reduced to Cr(III) by many reductants, including ferrous iron and sulfide. Palmer and Wittbrodt (1991) report that ferrous iron or sulfide can be used for reducing Cr(VI). Patterson et al., (1997) reports the use of amorphous ferrous sulfide for reducing Cr(VI) in soils and water. The US EPA has stated that ferrous iron must be present for sulfide to reduce Cr(VI), and that iron sulfide needs to be present to reduce Cr(VI) in groundwater (US EPA 2000). Thus, treatment of Cr(VI)-contaminated material with ferrous iron, reduced sulfur species, or the combination of the two is a well-established concept.

[0008] Several reducing agents have been tried on COPR, such as ferrous iron (Geelhoed J S et al., Identification and geochemical modeling of processes controlling leaching of Cr(VI) and other major elements from chromite ore processing residue, *Geochimica Cosmochimica Acta* 66:3927-3942, (2002); Dermatas D M et al., 2006, Ettringite-induced heave in chromite ore processing residue (COPR) upon ferrous iron treatment, *Environ Sci Tech* 40:5786-5792; and, Moon 2007), reduced sulfur species (e.g. sulfide or polysulfide) (Wazne M et al., 2007, Assessment of calcium polysulfide for the remediation of hexavalent chromium in chromite ore processing residue (COPR), *J Hazardous Mat* 143:620-628; Tinjum, 2006; and Brown R L et al., In-situ chemical reduction of hexavalent chrome at chromite ore processing residue sites, May 2008, *Presented at Sixth International Battelle Conference Remediation of Chlorinated and Recalcitrant Compounds, Monterey, Calif.*), ferrous sulfate and sodium dithionate (Su C M et al., 2005, Treatment of hexavalent chromium in chromite ore processing solid waste using a mixed reductant solution of ferrous sulfate and sodium dithionate, *Environ Sci Tech* 39:6208-6216), manganese (II) (James 1994), metallic iron (Lai K C K et al., 2008, Removal of chromium (VI) by acid-washed, zero-valent iron under various groundwater geochemistry conditions, *Environ Sci Tech* 42:1238-1244), pyrite leachate (Chowdhury A, 2003, Method for stabilizing chromium-contaminated compounds, U.S. Pat. No. 6,607,474 B2 and Tinjum 2006), and, organic reductants, such as acetic or ascorbic acid (James 1996).

[0009] U.S. Pat. No. 5,202,033 to Stanforth et al. report that hazardous wastes or soils containing Cr(VI) can be treated in-situ through the application of ferrous sulfate to reduce

chrome. This method has been shown to be ineffective for COPR. (Geelhoed J S et al., 2003, Chromium reduction or release? Effect of Fe(II) sulfate addition on chromium (VI) leaching from columns of chromite ore processing residue, *Environ Sci Tech* 37:3206-3213).

[0010] Higgins T E (*Process for the in-situ bioremediation of Cr(VI)-bearing solids*) reports that in-situ bioreduction can be used for treating Cr(VI) containing solids, involving the steps of contacting the solids with bacteria, nutrients and water with the pH maintained between 6.5 and 9.5. (U.S. Pat. No. 5,562,588). However, this method would be inappropriate for COPR due to the highly alkaline nature of the COPR and the inherent toxicity of the metals in COPR towards bacteria.

[0011] U.S. Pat. No. 6,578,633 to Yen C Y entitled In-situ process for detoxifying hexavalent chromium in soil and groundwater and U.S. Pat. No. 6,955,501 to Yen C Y entitled In-situ process for detoxifying hexavalent chromium in soil and groundwater report a method for the in-situ treatment of Cr(VI) in soil and water by spreading a reducing agent on top of the contaminated area and adding water to infiltrate the reducing agent into the contaminated zone. Among the reducing agents mentioned are ferrous salts, sulfide salts, sodium thiosulfate and organic reducing agents. However, in-situ injection of ferrous sulfate has been reported to be ineffective for COPR due to the rebound effect. (Geelhoed et al, 2003). It is reasonable to conclude that other agents would also be ineffective for COPR.

[0012] US Publ. Application No. 2007/0088188 to Wazne et al. entitled Method of treatment, stabilization and heave control for chromite ore processing residues (COPR) and chromium contaminated soils reports adding acid to COPR to consume excess alkalinity so as to reduce the pH to below pH 10, and then adding a reducing agent to the COPR to reduce Cr(VI). While not being specific to these additives, Wazne et al. suggests using carbonated water as a source of acid, and ferrous iron, sulfide, or polysulfide as a reducing agent. The amount of alkalinity in some COPR would require large amounts of acid, such that the treated material would be turned into a slurry where a liquid acid is used. That also makes working with the material much more difficult since, under the US EPA'S regulations, landfilled solids must be free of liquids in order to pass the paint filter test.

[0013] US Publ. Application No. 2007/0098502 to Higgins T E et al., entitled In-situ treatment of in-ground contamination reports introducing ferrous iron and sulfide in a liquid state into the pores of COPR or a Cr(VI) contaminated aquifer. Insoluble ferrous sulfide forms which acts as an ongoing reducing agent for any Cr(VI) that may leach out of the COPR or pass through in the groundwater. However, there is no indication that the Cr(VI) bound within the COPR matrix is reduced.

[0014] US Publ. Application No. 2007/0224097 to Chisick et al. entitled Methods of treatment of chromite ore processing residue report the use of sulfide ion and ferrous ion to reduce Cr(VI). There is no indication that the Cr(VI) bound within the COPR matrix is released prior to the formation of ferrous sulfide.

[0015] Current treatment processes fail to reduce sufficient hexavalent chromium in the waste to eliminate Cr(VI) so that it does not leach from COPR. Over time, concerning the treatment methods that have been tested in the field, chrome and alkalinity slowly leach out of the untreated areas resulting in increased pH and increased hexavalent chromium concen-

tration, which is referred to as the "rebound effect." It has been reported that ferrous iron is not a successful reductant for Cr(VI) in COPR because the high pH present in the COPR causes ferrous iron to precipitate as a hydroxide, which is unavailable for reducing Cr(VI). (Brown et al. 2008, and Geelhoed et al., 2003).

SUMMARY OF THE INVENTION

[0016] One aspect of the invention is a process for reducing hexavalent chromium, Cr(VI), contained within a chromite ore processing residue matrix comprising the sequential steps or acts of providing a chromite ore processing residue matrix having a particle size containing Cr(VI), solubilizing the matrix using a dissolution effective amount of FeSO₄, reducing the Cr(VI) to Cr(III) using Fe(II), and, fixing the Fe(II) using a fixation effective amount of a Fe(II) precipitating agent to make a Fe(II) precipitate.

[0017] In an exemplary embodiment of the process, the process further comprises the step or act of reducing the particle size of the matrix to less than 25 mm.

[0018] In another exemplary embodiment of the process, the dissolution effective amount of FeSO₄ can be at least about two times the stoichiometric requirement for Fe(II) based on the Cr(VI) concentration of anhydrous FeSO₄ or an equivalent amount of hydrated FeSO₄ solids.

[0019] In another exemplary embodiment of the process, the dissolution effective amount of FeSO₄ is at least 5% w/w of anhydrous FeSO₄ or an equivalent amount of hydrated FeSO₄ solids.

[0020] In another exemplary embodiment of the process, the Fe(II) precipitating agent is a sulfide containing compound.

[0021] In another exemplary embodiment of the process, the Fe(H) precipitating agent is an alkali metal sulfide.

[0022] In another exemplary embodiment of the process, the Fe(II) precipitating agent is an alkaline earth metal sulfide.

[0023] In another exemplary embodiment of the process, the Fe(II) precipitating agent is sodium sulfide, bisulfide or calcium polysulfide.

[0024] In another exemplary embodiment of the process, the fixation effective amount can be at least about one half the stoichiometric requirement of the Fe(II).

[0025] In another exemplary embodiment of the process, the Fe(II) precipitating agent is phosphoric acid.

[0026] In another exemplary embodiment of the process, the Fe(II) precipitating agent is an orthophosphate containing compound.

[0027] A second aspect of the invention is a process for reducing hexavalent chromium, Cr(VI), contained within a chromite ore processing residue matrix comprising providing a chromite ore processing residue matrix having a particle size containing Cr(VI), solubilizing the Cr(VI) to trivalent chromium, Cr(III), using at least about two times the stoichiometric requirement for Fe(II) based on the Cr(VI) concentration of anhydrous FeSO₄ or an equivalent amount of hydrated FeSO₄ solids, and reducing the Cr(VI) to Cr(III) using Fe(II).

[0028] In an exemplary embodiment of the process, the process further comprises fixing the Fe(II) using a fixation effective amount of a Fe(II) precipitating agent to make a Fe(II) precipitate.

[0029] In another exemplary embodiment of the process, the process further comprises the step of reducing the particle size of the matrix to less than 25 mm in diameter.

[0030] In another exemplary embodiment of the process, the Fe(II) precipitating agent is a sulfide containing compound.

[0031] In another exemplary embodiment of the process, the Fe(II) precipitating agent is an alkali metal sulfide.

[0032] In another exemplary embodiment of the process, the Fe(II) precipitating agent is an alkaline earth metal sulfide.

[0033] In another exemplary embodiment of the process, the Fe(II) precipitating agent is sodium sulfide, sodium bisulfide, or calcium polysulfide.

[0034] In another exemplary embodiment of the process, the fixation effective amount can be at least about one half the stoichiometric requirement of the Fe(II).

attributes the rise in Cr(VI) to dissolution of the compounds holding the Cr(VI) in the COPR followed by sorption of Cr(VI) on iron oxides at the slightly acidic pH values.

[0041] Set forth herein are the results of a study on Cr(VI) release from COPR conducted using solutions of different acidity. The results of the study demonstrate a linear increase in Cr(VI) and calcium release for samples at pH 7 and above (FIG. 1). Without being bound to any specific theory, if Cr(VI) is held in a calcium compound, e.g. brownmillerite ($\text{Ca}_2\text{AlFeO}_5$), then the correlation may be explained as follows (note that the Cr(VI) is shown as being a trace constituent trapped in the brownmillerite). Possible reactions occurring in the instant invention are shown in Table 1.

TABLE 1

REACTIONS	
Dissolution	$\text{Ca}_2\text{AlFeO}_5 \cdot \text{Cr(VI)} + 5\text{H}^+ \rightarrow 2\text{Ca}^{2+} + \text{Al}^{3+} + \text{Fe}^{3+} + 5\text{OH}^- + \text{Cr(VI)}$
Al precipitation	$\text{Al}^{3+} + 3\text{OH}^- \leftrightarrow \text{Al(OH)}_3$
Fe precipitation	$\text{Fe}^{3+} + 3\text{OH}^- \leftrightarrow \text{Fe(OH)}_3$
Net Reaction	$\text{Ca}_2\text{AlFeO}_5 \cdot \text{Cr(VI)} + 4\text{H}^+ + \text{H}_2\text{O} \rightarrow 2\text{Ca}^{2+} + \text{Al(OH)}_3 + \text{Fe(OH)}_3 + \text{Cr(VI)}$

[0035] In another exemplary embodiment, the Fe(II) precipitation agent is an orthophosphate containing compound.

BRIEF DESCRIPTION OF DRAWINGS OF EXEMPLARY EMBODIMENTS

[0036] FIG. 1 is a graph showing a linear increase in Cr(VI) and calcium/magnesium release from COPR for samples at pH 7 and above using solutions of different acidity.

[0037] FIG. 2 is a graph showing the extracted amount of calcium and magnesium correlated with the amount of acid added to the COPR sample.

DETAILED DESCRIPTION OF THE EXEMPLARY EMBODIMENTS

[0038] The instant invention is directed to a method of advantageously reducing substantially all of the Cr(VI) in the COPR, which requires releasing and treating substantially all of the Cr(VI) in the COPR matrix. Cr(VI) is bound within the COPR matrix.

[0039] Evaluation of COPR treatments can be difficult. Analysis of the degree of effectiveness can be obscured by uncertainties. Various criteria for measuring effectiveness may be used, such as alkaline extractable Cr(VI) (SW 846 Method 3060A), Toxicity Characteristic Leaching Procedure (TCLP) Cr (SW 846 Method 1311), Synthetic Precipitation Leaching Procedure (SPLP) Cr(VI) (SW 846 Method 1312), or complete reduction of compositional Cr(VI), which can be very difficult to measure.

[0040] One way of obtaining complete treatment is to release all of the Cr(VI) from the COPR matrix so that it is available for reduction, and, then adding sufficient reducing agent to convert the Cr(VI) to Cr(III). Agents for releasing all the Cr(VI) from the matrix are employed. It is important to understand the controls for releasing Cr(VI) from the COPR matrix. Geelhoed et al. (2002) and Tinjum (2006) both report a release pattern for Cr(VI) vs pH, whereby Cr(VI) concentrations increase with decreasing pH to around pH 8, and, then decrease as the pH is lowered further. Tinjum (2006)

[0042] Brownmillerite has the following characteristics: chemical formula $\text{Ca}_2(\text{Al,Fe}^{3+})_2\text{O}_5$, molecular weight 240.09 gm, Calcium 33.39%, CaO 46.71%, Aluminum 12.36%, Al_2O_3 23.36%, Iron 20.93%, FeO 26.93%, Oxygen 33.32%, 97.00% total oxide, Empirical Formula $\text{Ca}_2\text{Al}_{1.1}\text{Fe}^{2+}_{0.9}\text{O}_5$, present in thermally metamorphosed limestone blocks included in volcanic rocks, IMA Status.

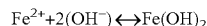
[0043] Al(OH)_3 and Fe(OH)_3 are essentially insoluble at the pH values used in the study. Therefore, the soluble products of the brownmillerite dissolution are calcium and Cr(VI). Brownmillerite is used in the example because it is a significant chromium-containing compound in Maryland COPR. (Tinjum, 2006)

[0044] As shown in FIG. 2, the amount of calcium and magnesium extracted from the $\text{Ca}_2\text{AlFeO}_5 \cdot \text{Cr(VI)}$ is correlated with the amount of acid added. Up to 10 mequiv/g of acid added, the amount of calcium+magnesium extracted equals the amount of acid added, which indicates that the acid is dissolving alkaline calcium and magnesium compounds, but nothing else. If so, then the calcium concentrations in solution (and hence the amount of Cr(VI) extracted) are controlled by the amount of acid added, and not by any solubility controls.

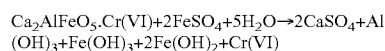
[0045] Thus, the instant invention involves reducing Cr(VI) in the COPR to solubilize the chromium-containing calcium compounds binding the Cr(VI) within the COPR matrix.

[0046] Solubilizing Cr(VI). Solubilizing Cr(VI) in COPR may be accomplished by a combination of particle size reduction and solution treatment. Particle size reduction enhances chemical contact with the Cr(VI) within the interior of the particles. The particle size of the chromite ore processing residue matrix should be reduced to less than 25 mm in diameter, preferably less than 15 mm in diameter, more preferably less than 10 mm in diameter, and most preferably less than 2 mm in diameter. Solution treatment and reagent addition dissolves the calcium compounds that bind the Cr(VI). Ferrous sulfate enhances the dissolution of the calcium compounds.

[0047] Under alkaline conditions, ferrous iron neutralizes the solution through the formation of ferrous hydroxide as shown below.



[0048] Sulfate also enhances dissolution of the calcium compounds by the formation of calcium sulfate. The overall reaction is shown below.



[0049] Precipitation of calcium as calcium sulfate and alkalinity neutralization within the brownmillerite (or other suitable calcium-containing compounds) both drive the above reaction to the right solubilizing the Cr(VI) for subsequent reduction.

[0050] Base neutralization of the COPR by adding ferrous sulfate is seen from the final pH values in TCLP tests on COPR treated with various ferrous sulfate doses. (See Table 2, TCLP test results for COPR treated with various doses of ferrous sulfate).

TABLE 2

Ferrous Sulfate Heptahydrate Dose (% w/w)	TCLP Final pH	TCLP Chromium Concentration, mg/L
0	11.7	21
5	10.90	7.2
10	8.34	5.3
15	7.07	<0.02
20	6.72	<0.02

[0051] Solubilization of Cr(VI) from COPR. A final pH of around 7 corresponds to essentially complete release of the Cr(VI) in the COPR matrix. A 15% dose of ferrous sulfate heptahydrate generated sufficient neutralizing capacity to release Cr(VI) from the COPR as shown by the TCLP test.

[0052] Reduction. Once the Cr(VI) has been released from the COPR matrix, it is advantageously and efficiently reduced to Cr(III). Such reduction may be accomplished using a variety of the Cr(VI) reductants. The Fe(II) used to solubilize the calcium compounds may also be used in the COPR reduction step.

[0053] The solubilization reaction occurs prior to the reduction reaction since the Cr(VI) is released before it is reduced. Thus, oxidation of ferrous iron occurs after it reacts to release the Cr(VI). The solubilization reaction is not reversible. Brownmillerite and other Cr(VI)-containing calcium compounds in the COPR were formed under high temperature. High pH conditions are present in the chromite ore processing. Brownmillerite does not form under ambient environmental conditions.

[0054] The effectiveness of ferrous iron as a reductant for Cr(VI) is well known. Such effectiveness is demonstrated by observing the Cr(VI) concentrations in the TCLP tests on COPR treated with various FeSO_4 doses shown in Table 1 above. Treatment at the 15% and 20% levels resulted in substantially complete reduction of Cr(VI). The final pH using the listed doses was in a range of values such that essentially/substantially all Cr(VI) was solubilized from the COPR, which indicates that the treatment successfully solubilized and reduced essentially/substantially all the Cr(VI) in the COPR.

[0055] Such treatment is not stable against oxidation. If the treated samples are allowed to air dry and oxidize (as evidenced by a change in color from dark grey to the reddish brown of ferric hydroxide), the TCLP numbers for Cr(VI) revert back to hazardous levels, as shown below in Table 3, TCLP and alkaline extraction results for treated COPR before and after drying in air.

TABLE 3

Sample	TCLP Cr, mg/L		Alkaline Extraction Cr(VI), mg/kg	
	Wet	Dry	Wet	Dry
20% w/w FeSO_4	<0.02	22	<1	1100

[0056] A process of drying the sample greatly increased the Cr(VI) concentrations in both the TCLP and alkaline extraction tests. Without being bound to any theory, the increase may be due to reoxidation of Cr(III) to Cr(VI) by atmospheric oxygen under the conditions of the COPR. It may also be due to elimination of the reductant as the Fe(II) oxidizes. In any event, the treatment is ineffective where the samples are exposed to a significant amount of air. Thus, the treatment reagents need to be advantageously fixed against oxidation.

[0057] Fixation. Ferrous iron may be fixed against oxidation by adding sulfide to form an insoluble precipitate with the iron. Sulfide also advantageously acts as a reducing agent for Cr(VI). Sulfide addition readily precipitates ferrous iron as evidenced by the change in color of the sample from grey to black. The color stays black even upon air drying indicating that the ferrous sulfide has not oxidized during the drying process.

[0058] Sample test results show that the Cr(VI) in the treated samples has been reduced as shown by alkaline extraction Cr(VI) values of <1 mg/kg. The treated test samples also demonstrated low leaching potential in both the TCLP and SPLP tests as shown in Table 4, Alkaline Extraction, TCLP and SPLP Test results for samples treated with ferrous sulfate (monohydrate and heptahydrate) followed by sulfide addition. Both sodium bisulfide (NaHS) and calcium polysulfide (CaS_x) may be used as the sulfide source. NaHS may be used at a lower dose than the calcium polysulfide.

TABLE 4

Sample		Alka- line Extraction Cr (VI)	Screening TCLP		Screening SPLP	
		mg/kg	pH	Cr	pH	Cr
FeSO_4	S					
	Untreated	4829	11.57	32	12.67	13
		4700	11.97	17	12.64	13
		4230	11.68	21	12.75	4.7
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + \text{NaHS}$ or CaS_x						
10%	0	71	9.77	8.6	12.40	2.4
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	1% NaHS	<1	9.14	<0.020	12.17	<0.020
	2% NaHS	<1	9.06	<0.020	12.43	<0.020
	4% NaHS	<1	8.65	<0.020	12.31	<0.020
	1% CaS_x	<1	8.87	5.1	12.01	1.5
	2% CaS_x	<1	9.99	4.0	12.22	<0.020
	4% CaS_x	<1	8.86	2.6	12.26	<0.020

TABLE 4-continued

Sample		Alka- line Extrac- tion Cr (VI)	Screening TCLP		Screening SPLP	
		mg/kg	pH	Cr	pH	Cr
FeSO ₄	S					
	6% CaS _x	<1	8.86	0.19	12.26	<0.020
	10% CaS _x	<1	8.13	<0.020	12.05	<0.020
15%	0	<1	8.35	<0.020	12.05	3.3
FeSO ₄ •7 H ₂ O	1.5% NaHS	<1	7.05	0.084	6.91	0.081
	3% NaHS	<1	7.33	0.036	12.03	<0.020
	6% NaHS	<1	8.60	<0.020	12.21	<0.020
20%	0	<1	6.76	<0.020	11.77	<0.020
FeSO ₄ •7 H ₂ O	2% NaHS	<1	6.90	<0.020	11.69	<0.020
	4% NaHS	<1	6.72	0.051	11.99	<0.020
	8% NaHS	<1	7.52	0.039	12.20	<0.020
	FeSO ₄ •H ₂ O + NaHS					
10%	0	3	8.21	0.84	12.17	0.28
FeSO ₄ •H ₂ O	1% NaHS	<1	7.68	<0.020	12.26	<0.020
	2% NaHS	<1	7.66	<0.020	12.21	<0.020

Note:

All percentages are % w/w.

[0059] Fixation agents other than sulfide may be employed. Any anion that precipitate ferrous iron so as to leave a low dissolved ferrous iron concentration at the pH of the mixture may be effective. Phosphate forms low solubility compounds with ferrous iron, and may be used as an alternative to sulfide. Samples of COPR were treated with ferrous sulfate, and, then with a 3:1 P:Fe mole ratio dose of phosphoric acid. The samples were tested for compositional Cr(VI) using the alkaline extraction test and leachable chrome using the TCLP and SPLP tests. Results are shown in Table 5.

[0060] Immediately after treatment, the treated samples had low leaching potential (generally <0.020 mg/L chromium) and low alkaline extractable Cr levels. After air drying, the alkaline extractable C(VI) increased to around 1500 mg/kg (no phosphate addition) and remained at below detection levels with the 3:1 phosphate addition. The leaching tests demonstrated similar results. The treated sample free of phosphate fixation showed elevated chromium concentrations in the TCLP and SPLP tests. The 3:1 phosphate fixed sample had chromium levels that were near the detection limit and well below relevant regulatory criteria. The results demonstrate that ferrous iron can be fixed by phosphate as well as by sulfide.

[0061] Table 5: Alkaline Extraction, TCLP, and SPLP Test Results for P Fixation of Fe(II) in COPR Treatment.

TABLE 5

Sample		Alkaline Extraction,	TCLP		SPLP	
Drying	Rep	mg/kg	pH	Cr	pH	Cr
+20% FeSO ₄ •H ₂ O						
Before	A	<5	7.15	<0.02	11.97	<0.02
Drying	B	<5	7.15	<0.02	12.06	<0.02
After	A	1550	9.06	27	10.95	8.6
Drying	B	1400	8.84	29	11.26	8.9
+20% FeSO ₄ •H ₂ O & 21% H ₃ PO ₄ (3:1 P:Fe)						
Before	A	<5	4.71	0.05	5.04	<0.02
Drying	B	<5	4.72	0.042	4.85	<0.02

TABLE 5-continued

Sample		Alkaline Extraction,	TCLP		SPLP	
Drying	Rep	mg/kg	pH	Cr	pH	Cr
After	A	<1	4.75	0.043	7.11	<0.02
Drying	B	<1	4.74	0.046	7.02	<0.02

I claim:

1. A process for reducing hexavalent chromium, Cr(VI), contained within a chromite ore processing residue matrix comprising the sequential steps of:

providing a chromite ore processing residue matrix having a particle size containing Cr(VI),
solubilizing the matrix using a dissolution effective amount of FeSO₄,

reducing the Cr(VI) to Cr(III) using Fe(II), and,

fixing the Fe(II) using a fixation effective amount of a Fe(II) precipitating agent to make a Fe(II) precipitate.

2. The process of claim 1, further comprising the step of reducing the particle size of the matrix to less than 25 mm in diameter.

3. The process of claim 1, wherein the dissolution effective amount of FeSO₄ is at least about two times the stoichiometric requirement for Fe(II) based on the Cr(VI) concentration of anhydrous FeSO₄ or an equivalent amount of hydrated FeSO₄ solids.

4. The process of claim 1, wherein the dissolution effective amount of FeSO₄ is at least 5% w/w of anhydrous FeSO₄ or an equivalent amount of hydrated FeSO₄ solids.

5. The process of claim 1, wherein the Fe(II) precipitating agent is a sulfide containing compound.

6. The process of claim 1, wherein the Fe(II) precipitating agent is an alkali metal sulfide.

7. The process of claim 1 wherein the Fe(II) precipitating agent is an alkaline earth metal sulfide.

8. The process of claim 1, wherein the Fe(II) precipitating agent is sodium sulfide, sodium bisulfide, or calcium polysulfide.

9. The process of claim 1, wherein the fixation effective amount is at least about one half the stoichiometric requirement of the Fe(II).

10. The process of claim 1, where the Fe(II) precipitating agent is an orthophosphate containing compound.

11. The process of claim 1, wherein the Fe(II) precipitating agent is phosphoric acid.

12. A process for reducing hexavalent chromium, Cr(VI), contained within a chromite ore processing residue matrix, the process comprising:

providing a chromite ore processing residue matrix having a particle size containing Cr(VI),

solubilizing the Cr(VI) to trivalent chromium, Cr(III), using at least about two times the stoichiometric requirement for Fe(II) based on the Cr(VI) concentration of anhydrous FeSO₄ or an equivalent amount of hydrated FeSO₄ solids, and

reducing the Cr(VI) to Cr(III) using Fe(II).

13. The process of claim 12 further comprising:

fixing the Fe(II) using a fixation effective amount of a Fe(II) precipitating agent to make a Fe(II) precipitate.

14. The process of claim 12 further comprising the step of reducing the particle size of the matrix to less than 25 mm and preferably less than 2 mm.

15. The process of claim 12, wherein the Fe(II) precipitating agent is a sulfide containing compound.

16. The process of claim **12**, wherein the Fe(II) precipitating agent is an alkali metal sulfide.

17. The process of claim **12**, wherein the Fe(II) precipitating agent is an alkaline earth metal sulfide.

18. The process of claim **12**, wherein the Fe(II) precipitating agent is sodium sulfide, sodium bisulfide, or calcium polysulfide.

19. The process of claim **12**, wherein the fixation effective amount is at least about one half the stoichiometric requirement of the Fe(II).

20. The process of claim **12**, wherein the Fe(II) precipitating agent is an orthophosphate containing compound.

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