

Reclamation of Chromite Ore Processing Residue (COPR) involving Recovery of Chromate Salt, Detoxification and Fabrication of Clay Brick

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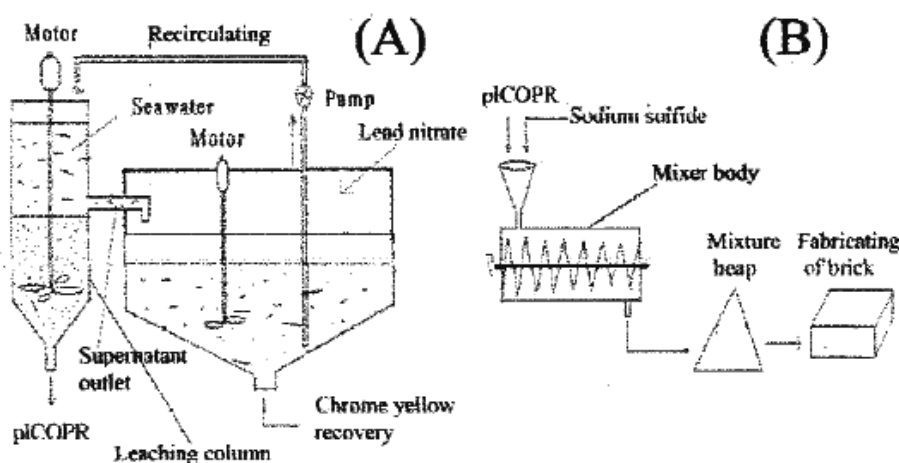
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Abstract

We studied on the methods involving the recovery of chromate salt from COPR, the sequential detoxification of COPR and the reclamation of the detoxified COPR. The results of leaching experiments showed that it is possible to recover Cr (VI) existed in COPR using an inexpensive method, in which ca. 84% of Cr (VI) extraction rate could be under the following condition; seawater as leaching solution, 25% of solid content, leaching period of 30min, intermittent agitation, gravitational sedimentation as solid/liquid separating mode, repetition number of up 5. Cr (VI) contained in leaching liquor was recovered as chrome yellow, followed by recirculating the Cr (VI)-depleted supernatant to the leaching process. For the detoxification of post-leach COPR (pICOPR), pICOPR was mixed with sodium sulfide as a single reductant in a mixer and was discharged from the mixer without retention time for reduction. Cr (VI) content in the mixture became lower than cleanup criteria by US EPA with the Na₂S/Cr (VI) mass ratio of 6 at the reaction time of 36h. Also, the results of the experiment with the detoxified pICOPR as a substitution for sand in fabricating clay brick shows that acceptable compression strength (52N/mm²) is obtained when the detoxified COPR accounts for 30% in raw material mixture, with the Cr (VI) content of 0.5mg/kg-bricks below cleanup criteria by US EPA .

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Keywords: COPR, Reclamation, Recovery of chromate salt, Detoxification, Clay brick, Construction material

1. Introduction

COPR is a kind of alkaline solid waste derived in the production of chromate by roasting lime, having high Cr (VI) content and alkalinity (J, 9) and not only millions of tons of COPR were deposited in parts of the world, but also COPR has been still generated (9). Hexavalent chromium (Cr (VI)) was released to the

environment, causing serious environmental pollution (2, 3) and tremendous diseases including cancer (4), ulceration and dermatitis (5), etc.

COPR was composed of a number of mineral phases, in which Cr(VI) is mainly bound in inner and outer surface of mineral in a manner of electrostatic attraction and ion exchange (6, *JO*, 11). Cr(VI) existed in COPR is able to be exchanged with other anions including SO_4^{2-} (6, 7, 12, 16). Therefore, we have designed the cost-effective leaching strategy of Cr(VI) from COPR by using the seawater containing considerable amount of anions.

After leaching of Cr(VI) from COPR, it needs to be detoxified for minor remaining Cr(VI) in pCOPR. In detoxification of COPR, diverse reduction agents could be used, in which S-species (14-16) and Fe-species (17-19) have been commonly used because it is low in price and easy to purchase. Among them, Na_2S is in more frequent use as a reductant because of the relatively higher capacity of reduction in alkaline pH than others (9, 12, 17). If there should be no influence of Cr upon reduction reaction of Cr(VI) by Na_2S , it would be possible to detoxify the pCOPR containing seawater based on this reaction. In addition, there would be room for saving the utilization time of the equipment, if the detoxification of COPR would be carried out sufficiently at the heap state.

Some investigations showed that Cr(III) and Cr(VI) species could be bound to cement and cementitious materials (lime, fly ash and blast furnace slag, etc.), which allows the immobilization of chromium and thus minimizing its leachability (12, 20, 21). Cr(III) is very effectively immobilized in cement or cementitious materials, while Cr(VI) is not readily incorporated into cement hydrate phases. Thus, the reduction of Cr(VI) contained in COPR to Cr(III) and the immobilization by cement or cementitious materials seem to be a possible method for COPR treatment. Nevertheless, this approach is unfavorable in reclamation of the S-species-based detoxified COPR, because of swelling of ettringite ($\text{C}_3\text{A} \cdot 3\text{SO}_4 \cdot 2\text{H}_2\text{O}$) (J3, 18) in COPR and the potentiality of reoxidation of Cr(III) to Cr(VI) with the lapse of time while being exposed to the atmosphere (18, 22). Therefore, it is of great importance to find out the effective method for stabilization of Cr(III) in the detoxified COPR in reclamation of COPR.

The major aims of this study were; (i) to find the cost-effective method for leaching of Cr(VI) in COPR by using the seawater and stripping of Cr(VI) in lixivium, (ii) to assess the possibility of Na_2S -based detoxification of pCOPR containing seawater at a heap state, (iii) to find the reliable method for reclamation of the detoxified COPR.

2. Materials & Methods

2.1 Site and Sampling Technique

COPR heap is found in coastal areas in middle-eastern part of DPRK, underlain by a dense layer of the silty clay. COPR sampling was conducted with a Geoprobe™ drill rig at five locations, in which each core reached depth of 3 meters. The cores were mixed up evenly, before sample of 10kg was collected and homogenized and stored in sealed plastic bags at 4°C.

2.2 COPR Characterization

Hexavalent chromium extraction and measurement were carried out by alkaline digestion and colorimetric determination with diphenylcarbazide, according to EPA method 3060A and EPA method 7196A, respectively. pH and moisture were measured according to ASTM methods D 4980-89 and D 2216-98, respectively. The constituent of chromium and main elements in COPR were shown in table 1. Sample analysis was conducted in duplicate and average values were recorded.

TABLE 1. Initial Characterization for COPR

pH	CaO, %	MgO, %	Al ₂ O ₃ %	SiO ₂ %	Fe ₂ O ₃ %	Water	Alkali	Non-leachable Cr(VI). % (as Cr ₂ O ₃)
						leachable Cr(VI), % (as Cr ₂ O ₃)	leachable Cr(VI), % (as Cr ₂ O ₃)	
9.7	19.6	21.9	0.98	28.3	2.59	0.62	0.84	5.93

2.3 Leaching and Recovery of Cr(VI)

Lab scale experiments were made to confirm the availability of leaching and the recovery of the leachable Cr(VI) in COPR by using the seawater. Experimental make-up consisted of; (i) a cylindrical leaching column with the height of 100cm and radius of 10cm, with 5 outlets (2cm in radius, 10cm in length) alongside the height of the column at the same interval, in which a centered mixing blade was installed 0.2m away from the bottom of the column, the axis of the blade was fixed in motor-controlled rotating velocity; (ii) a conical barrel for recovering of Cr(VI) from the lixivium containing Cr(VI), with its available volume of 30dm³, having a mixing blade and a system recirculating barren liquid to the leaching column. A dried COPR gently ground and passed through 0.5mm sieve was mixed with leaching solution, so as to give the solid content of the resultant COPR slurry a fixed value, and then the impact of various parameters affecting the leaching rate of Cr(VI) was investigated.

After finishing the leaching process, solid/liquid separation was performed by gravitational settling and then Cr(VI)-containing lixivium, the supernatant, was drained out into a conical barrel through the selected outlet, where Cr(VI) settling occurs as chromate by adding 15% of the lead nitrate solution at a certain volume, followed by recirculating the barren liquid to the leaching process and recovering the chromium in chromate form.

2.4 Detoxification of plCOPR and Reclamation of the Detoxified COPR

Detoxification were performed by mixing the plCOPR separated from lixivium with Na₂S as a reductant at a certain mass ratio by using a mixer apparatus and holding it irt dump state during a certain period. The influences of the Na₂S/Cr(VI) mass ratio and the elapsed time on the content of remaining Cr(VI) in the mixture were investigated. Reclamation of the detoxified COPR was achieved by manufacturing clay brick, in that the detoxified COPR was used instead of the sand as viscosity reducer. The resultant clay bricks with the addition of the different portion of the detoxified COPR were investigated for the compression strength.

3. Results and Discussion

3.1 Effect of some Factors on Leaching of Cr(VI) in COPR

3.1.1 Change in Cr(VI) Extraction Rate with. he Concentration pf Sodium Chloride

Fig. 1 depicts the extraction rate of alkaline leachable Cr(VI) in COPR with the increment of NaCl concentration from 0% to 9%, at different solid content, agitating speed 60r/min and leaching period of 30min. As shown in Fig. 1, the extraction rate was remarkably increased until the concentration of NaCl reached at 3%, and then approximately leveled with further increasing of the concentration of NaCl at every content of solid. Considering the saltiness of the seawater is ca. 3%, the utilization of seawater as a leaching solution is advantage over other leaching agents from the Economic viewpoint. The change in extraction rate was investigated with the decrease of solid content from 30% to 10%(Fig. 1). Decrement of solid content results in gradual increment in extraction rate of Cr(VI), but difference was not much great. We selected solid content of 25% with regard to the disadvantage in relation to handling too large volume of liquid in leaching process at a lower solid content.

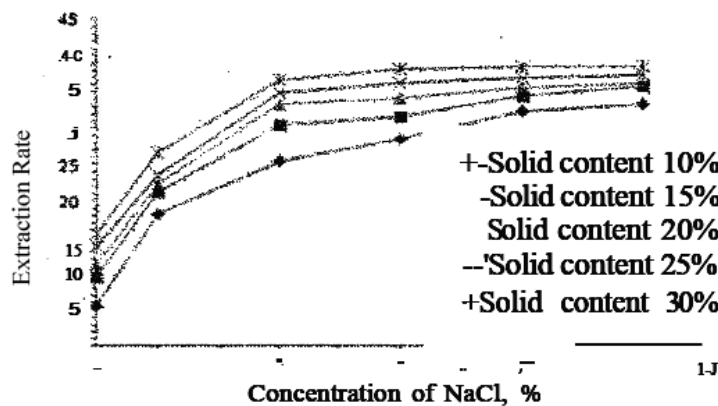


FIGURE 1. Extraction rate of Cr(VI) at different concentration of NaCl.

3.1.2 Change in Cr(VI) Extraction Rate with Leaching Period

Cr(VI) extraction rate with leaching time were recorded in an agitating mode of continuous and intermittent. The results are shown in Fig. 2. In the intermittent agitating mode, with the increase of the retention time from 10min to 60min at the interval of 10min, the remarkable increment in extraction rate is observed till 30min, but thereafter no considerable difference is appeared. Accordingly, it is reasonable to be 30min of leaching time in intermittent agitating mode.

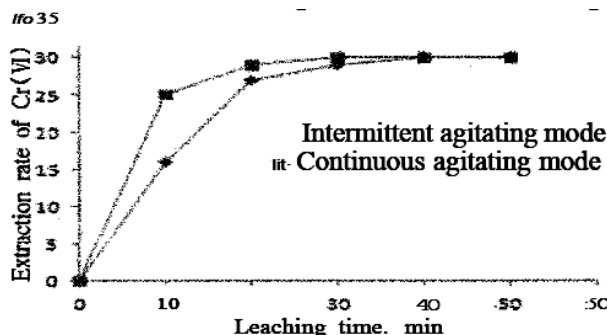


FIGURE 2. Change in Cr(VI) extraction rate with leaching time in a different agitating mode.

Meanwhile, in a continuous agitating mode, more steep increment in Cr(VI) extraction rate was appeared in a time range between 0min and 20min, following by a flat section after 20min of elapsed time (Fig. 2). Compared two sorts of modes in the standpoint of energy consumption, it is preferred to select the intermittent mode for the leaching.

3.1.3 Change in Cr(VI) Extraction Rate with the Number of Repetition of Leaching at a different season.

In the industrial scale for Cr(VI) extraction from COPR, it is undesirable to control the temperature of lixivium, because Cr(VI) content in lixivium is rather poor, on the contrary much of energy should be provided for maintaining the required temperature. Multi-leaching operation (once-through outflow of 50% of total liquid volume) is thought to be a crucial component involving in recovery of chromate from COPR by using simple apparatus(without using special equipment), for which the setting of suitable number of repetition is of great importance. Fig. 3 shows the change of the extraction rate of Cr(VI) with the number of leaching repetition at a different season.

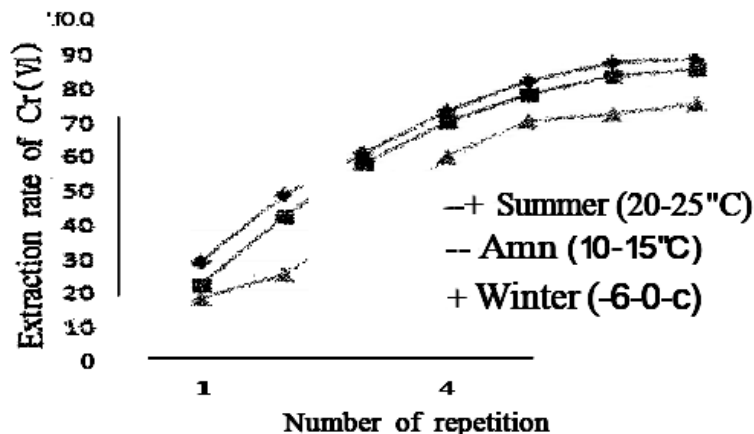


FIGURE 3. Cr(VI) extraction rate with the number of repetition of leaching.

The results of the multiple leaching experiment indicate that in summer and autumn, the total extraction rate of Cr(VI) reached nearly 82% and 83% when the number of repetition reached 5 and 6, respectively, while in winter, the extraction rate of 75% was achieved at the 7 times of repetition. Thus it is possible to recover the sufficient amount of Cr(VI) by increasing the number of repetition of leaching process even in winter.

These findings show the possibility to recover Cr(VI) from COPR by using seawater, which could be applied, in pretreatment of COPR before detoxification, irrespective of season.

3.1.4 Change in Relative Sedimentation Height with Elapsed Time

After finishing of Cr(VI) leaching from COPR, the preferential task to be solved is to separate the solid and liquid by means of possible separation methods. In separating of solid and liquid, the use of some filter apparatus causes a few difficulties in handling the separation process., because COPR has poor filterability and the filter apparatus requires a great deal of energy consumption. The recovery of supernatant using the gravitational sedimentation is promising and reasonable for solid and liquid separation, in which Cr(VI) involved in supernatant was stripped and recovered as chromate, thereafter barren supernatant was reused as leaching solution.

In order to set the suitable position of supernatant outlet, the relative sedimentation height (the height ratio between the sedimentation boundary and the surface of a supernatant) was recorded with elapsed time (Table 2).

Table 2 indicates that the uniform sedimentation section laid in the range of the relative sedimentation height between 0.59 and 1.0, followed by the compressive sedimentation and the final relative sedimentation height was 0.38. Consequently, it is favorable to set out the supernatant outlet at the point where it is 60% of column height.

TABLE 2. Relative Sedimentation Height at a Different Time.

Time, min	2	4	6	8	12	16	20	30	8
Relative sedimentation height (b _{boundary} /h _{total})	0.96	0.92	0.89	0.86	0.80	0.74	0.59	0.55	0.38

3.2 Effect of the Parameters on the Recovery of Chromate Salt from the Lixivium

Cr(VI) in lixivium was recovered in form of the insoluble chromate by using lead nitrate, according to the below chemical reaction. $\text{CrO}_4^{2-} + \text{Pb}^{2+} = \text{PbCrO}_4 \downarrow$

In practice of recovering of Cr(VI), not only above-mentioned reaction takes place without any byproduct, but other reactions could be accompanied with, depending upon reaction conditions such as pH, salty and so on, resulting in a complex material related with the lead chromate and lead hydroxide, etc.

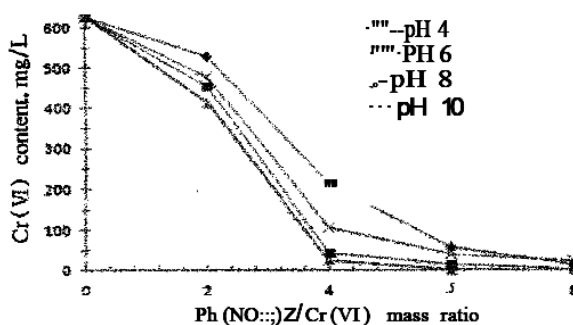


FIGURE 4. Change -in Cr(VI) content with different mass ratios between lead nitrate(Pb(NO₃)₂) and Cr(VI) (temperature of lixivium 20-23°C).

Fig. 4 illustrates the relationship between the Pb(NO₃)₂ to be added/Cr(VI) mass ratio and Cr(VI) concentration in liquid, in which Cr(VI) concentration was recorded at 5 min after various amounts of lead nitrate were added into the Cr(VI) leach liquor with predetermined concentration. As shown in Fig. 4, the preferable results were obtained when a dose of lead nitrate would be six times as much as Cr(VI) in the liquid in relation to its weight. The study on the consumption of lead nitrate while changing the pH from 4 to 10 elucidates that the consumption of lead nitrate is minimized at pH of 8, in this case, the Cr(VI) content in lixivium became decreased to 1.7mg/L, corresponding to the recovery rate of 97.3%.

3.3 Reductive Detoxification of pICOPR

By studying the Na₂S-based detoxification process of pICOPR containing the leaching agent (mainly chloride anion), applicability of the reductive detoxification, proposed by Velasco A et al., to pICOPR containing the leaching agent has been confirmed. We used sodium sulfide as a single reductant without retention time for reaction completion, in that the mixture of pICOPR and reductant with the different mass ratios, prepared through mechanically blending for 5min in mixer apparatus, was piled on a certain place. The content of Cr(VI) in the mixture of pICOPR and reductant was determined with the time elapsed since the various amounts of Na₂S were added (Fig. 5).

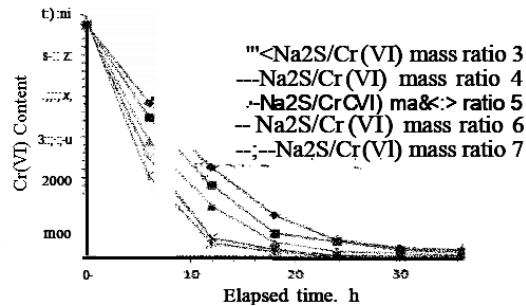


FIGURE 5. Cr(VI) content vs. the elapsed time at the different mass ratios between Na Sand Cr(VI).

The result showed that the content of Cr(VI) in pICOPR became lower than the cleanup criteria (8) by US EPA, when the Na₂S/ Cr(VI) mass ratio were kept up to 6. Therefore, it is proper to keep the mass ratio of about 6, based on the analysis of remaining Cr(VI) in pICOPR, in accordance with the reference to (9). Also, the contents of Cr(VI) in the mixture of pICOPR and reductant were determined with the time elapsed to have the correct time data for completion of detoxification.

3.4 Alternative Utilization of the Detoxified COPR to the Sand being used as Viscosity Reducer in Fabrication of Clay Brick

In fabrication of clay brick, the use of COPR as viscosity reducer makes it possible to stabilize and reclaim the detoxified COPR. The fabrication of clay brick was proceeded through some steps including the mixing of COPR, clay and fly ash, kneading of the mixture, molding, aging, roasting, and cooling. The compression strengths of clay bricks added various amount of COPR were measured. The results of compression test (23) indicated that the appreciable compression strength was achieved at dose of 30wt %, such that it could be used in construction (Table 3).

TABLE 3. Compression Strength of Clay Brick added Various Amount of COPR.

Dose of COPR. %	10	20	30	40	50
Compression strength, N/mm ²	95	76	52	38	25

Analysis result of Cr(VI) in clay brick made of COPR illustrates that the content of Cr(VI) was 0.5mg/kg, that is, less than cleanup criteria by US EPA.

Consequently, by using these processes in series, it would be expected that convenient and cost-effective reclamation of COPR could be accomplished, saving the cost of treatment of COPR (Fig. 6).

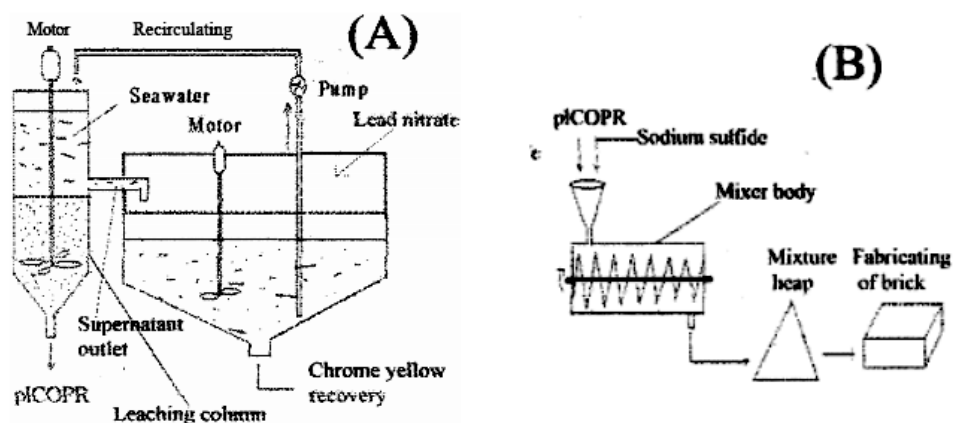


FIGURE 6. Schematic flow diagram for reclamation of COPR
(A- chromate recovery; B- detoxification and fabrication of brick)

4. Conclusions

This study attempted to recover Cr(VI) existed in COPR by means of leaching, with seawater as a lixivium, the rationale being to exchange the Cr(VI) with Cl^- in seawater. The results of the above-mentioned leaching experiments showed that it is possible to recover Cr(VI) existed in COPR with an inexpensive method, in which ca. 82% of Cr(VI) extraction rate could be achieved under the following condition; seawater as leaching solution, 25% of solid content, 30-min leaching, intermittent agitation, gravitational sedimentation as solid/liquid separating mode, repetition of up to 5. In the leaching of Cr(VI) from COPR, Cr(VI) in lixivium was easily recovered to chrome yellow form by adding lead nitrate and the resultant Cr(VI) depleted liquid was recirculated to leaching column as leaching solution. The advantage of the proposed leaching method is that the 'inexhaustible natural seawater is used as a leaching agent and a solid/liquid separation is made by using gravitational settling, needless to use any special equipment such as filter press.

And then, the results of detoxification examination of pICOPR containing Cl^- shows that sodium sulfide can be also used as a single reductant, as prior researchers did, in which reaction mixture was discharged from reactor without retention time for reduction, thereafter reduction of Cr(VI) occurs in a certain place outside of mixer apparatus. According to this method, processing time can be shortened greatly than prior methods.

In addition, in this study, the soil waste, detoxified COPR was used to fabricate the clay brick in placing sand as a viscosity reducer, having the stabilization and reclamation of COPR.

Consequently, by using these processes in series, it would be expected that both objects of recovery of leachable Cr(VI) and reutilization of COPR as building materials could be accomplished, saving the cost of treatment of COPR.

For further improvement of the reclamation process of COPR, we are going to recover the chromite ore remained in COPR, accounting for 0.5-5%, during the chromate salts-leaching process, and to reduce the cost of reductant in detoxification process.

5. List of abbreviations

The following are the list of abbreviations used in this paper:

1. COPR - Chromite Ore Processing Residue
2. pICOPR - post-leach Chromite Ore Processing Residue

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Literature Cited

- (1) Burke T.; Fagliano J.; Coldoft M.; Hazen R. E.; Eglewicz R. and McKee T. Chromite ore processing residue in Hudson County, New Jersey. *Environ. Health Perspect.* 1991, 92, 131-137.
- (2) Palmer C.D.; Wittbrodt P.R. Processes affecting the remediation of chromium contaminated sites, *Environ. Health Perspect.* 1991, 92, 25-40.
- (3) U.S. Environmental Protection Agency, 2000. In situ treatment of soil and groundwater contaminated with chromium, in: *Technical Resource Guide*. EPA 625/R-00/005, Office of Research and Development. Washington DC, 84 p.
- (4) Stout M.D.; Herbert R.A.; Kissling G.E.; Collins B.J.; Travlos G.S.; Witt K.L. Melnick R.L.; Abdo K.M.; Malarkey D.E.; Hooth M.J. Hexavalent Chromium Is Carcinogenic to F344/N Rats and B6C3F1 Mice after Chronic Oral Exposure. *Environ. Health Perspect.* 2009, 117, 716-722.
- (5) CL: ATRE technical bulletin. Treatment of Chromium Contamination and Chromium Ore Processing Residue. TB 14, 2007, 1-4.
- (6) Chunming su; Ralph Ludwig. Treatment of Hexavalent Chromium in Chromite Ore Processing Solid Waste Using a Mixed Reductant Solution of Ferrous Sulfate and Sodium Dithionite. *Environ. Sci. Technol.* 2005, 39, 6208-6216.
- (7) Geelhoed J.S.; Meeussen J.C.L.; Roe M.J.; Hillier S.; Thomas R.P.; Farmer J.G.; Paterson E. Chromium remediation or release? Effect of iron(II) sulfate addition on chromium(VI) leaching from columns of chromite ore processing residue. *Environ. Sci. Technol.* 2003, 37, 3206-3213.
- (8) Katz S.A.; Salem H.; *The Biological and Environmental Chemistry of Chromium*. VCH, New York, 1994.
- (9) Tao Sun; Jieyu Chen; Xinrong Lei; Chunyu Zhou. Detoxification and immobilization of chromite ore processing residue with metakaolin-based geopolymer. *J. Environ. Chem. Eng.* 2014, 2, 304309.
- (10) Margaret C.; Graham, John G.; Farmer; Peter Anderson; Edward Paterson; Stephen Hillier; David G.; Lumsdon; Richard J.F. Calcium polysulfide remediation of hexavalent chromium contamination from chromite ore processing residue. *Sci. Tot. Environ.* 2006, 364, 32-44.
- (11) Geelhoed, J. S.; Meeussen, J. C. L.; Hillier, S.; Lumsdon, D. G.; Thomas, R. P.; Farmer, J. G.; Paterson, E. Identification and geochemical modeling of processes controlling leaching of Cr(VI) and other major elements from chromite ore processing residue. *Geochim. Cosmochim. Acta* 2002, 66, 3927-3942.
- (12) Velasco A.; Ramírez M.; Hernandez S.; Schmidt W.; Revah S. Pilot scale treatment of
- (13) chromite ore processing residue using sodium sulfide in single reduction and coupled reduction/stabilization processes. *J. Hazard. Mater.* 2012, 207-208, 97-102.
- (14) Demlatas D.; Chrysochoou M.; Moon D.H.; Grubb D.G.; Wazne M.; Christodoulatos C.
- (15) Etringite-induced heave in chromite ore processing residue (COPR) upon ferrous sulfate treatment. *Environ. Sci. Technol.* 2006, 40, 5786-5792.
- (16) Maria Chrysochoou; Daniel R. Ferreira; Chad P. Johnston. Calcium polysulfide treatment of Cr(VI)-contaminated soil. *J. Hazard. Mater.* 2010, 179, 650-657.
- (17) Kim C.; Zhou Q.; Deng B.; Thornton E.C.; Xu H. Chromium(VI) reduction by hydrogen sulfide
- (18) in aqueous media: stoichiometry and kinetics. *Environ. Sci. Technol.* 2001, 35, 2219-2225.
- (19) Thornton E.C.; Amonette J.E. Hydrogen sulfide gas treatment of Cr(VI) contaminated sediment samples from a plating-waste disposal Site: Implications for in-situ remediation. *Environ. Sci. Technol.* 1999, 33, 4096-4101.
- (20) Mathew P. Watts; Victoria S. Coker; Stephen A. Parry; Richard A.D. Patrick; Russell A.P. Thoms; Robert Kalin; Jonathan R. Lloyd; Biogenic nano-magnetite and nano-zero valent iron treatment of alkaline Cr(VI) leachate and chromite ore processing residue. *Appl. Geochem.* 2015, 54, 27-42.
- (21) Moon D.H.; Wazne M.; Demlatas D.; Christodoulatos C.; Sanchez A.M., Grubb D.G.; Chrysochoou M.; Kim M.G. Long-term treatment issues with chromite ore processing residue(COPR): Cr(6+) reduction and heave. *J. Hazard. Mater.* 2007, 143, 629-635.
- (22) US DOE , 2009. Chromium Treatment Technology Information Exchange for Remediation of Chromium in Groundwater at the Department of Energy Hanford Site, SGW-38255.
- (23) Demlatas D.; Meng X. Utilization of fly-ash for stabilization/solidification of heavy metal contaminated soils. *Engin. Geo.* 2003, 70, 377-394.
- (24) Zhang J. Provis J.L. Feng D.; J.S.J. van Deventer. The role of sulfide in the immobilization of Cr(VI) in fly ash geopolymers. *Cem. Coner. Res.* 2008, 38, 681-688.
- (25) Geelhoed J.S.; Meeussen J.C.L.; Hillier S.; Lumsdon D.G.; Thomas R.P.; Farmer J.G.; Paterson

- (26) E. Identification and geochemical modeling of processes controlling leaching of Cr(VI) and other major elements from chromite ore processing residue. *Geochim. Cosmochim. Acta.* 2002, 66, 3927-3942.
- (27) British Standard Institution, 2013. Specification for clay bricks. BS 3921:1985. Incorporating amendment, No. 1, 30p.