Article

Cost-effective strategy of treating chromite ore processing residue (COPR); production of chromate, subsequent detoxification and in-situ stabilization

Hui-Won Kim[1,*], Yong-Nam Kim[2], Myong-Chol Ryu[2], Yong-Gun Han[2]

[1] Department of Daily Food, Institute of Microbiology, State Academy of Sciences, Unjong District, Pyongyang City 355, DPR Korea

[2] Department of Environmental Microbiology, Institute of Microbiology, State Academy of Sciences, Unjong District, Pyongyang City 355, DPR Korea

* Corresponding author: Hui-Won Kim, khw1980@star-co.net.kpl

Abstract: It is a great importance of finding the cost-effective strategy of treating chromite ore processing residue (COPR). Cr(VI), presented in aqueous media, could easily be reduced, adsorption and removed from water body through a proper treatment, but Cr(VI), incorporated in COPR, could not, due to its characteristic inherent to COPR. In general, the reduction and adsorption of Cr(VI) could take place at a low pH, the COPR, however, has a high acid neutralizing capacity, so that a great deal of the inorganic acid would be required to maintain its pH at low value. In this work, a series of treatment trials, comprised of the production of chromate from COPR by leaching process, the subsequent detoxification and in-situ stabilisation of post-leached COPR (plCOPR) were conducted. After column extracting process using the seawater, Cr(VI)-containing leachate of 600~800 mg/L is led to the ion exchange columns, charged with the anion exchange resin, to adsorb the Cr(VI) until the effluent contains Cr(VI) of 5 mg/L. The Cr(VI) loaded ion exchange column was eluted by NaOH solution and the maximum concentration of Cr(VI) in the elution was 43.1 g/L. Afterward, plCOPR was mixed with sodium sulfide and iron sulfide+lime as a reductant and a stabiliser, respectively, and the mixture was discharged directly from the mixer and piled on a certain area. After 360 d of curing, Cr(VI) concentration in the leachate from the toxicity characteristic leaching procedure (TCLP) was arrived at 1.2 mg/L, below the regulatory limit disposal standard (HJ/T 301-2007, 3 mg/L).

Keywords: chromite ore processing residue; detoxification; stabilisation; recovery; chromate; ferrous sulfate

1. Introduction

COPR is a rather refractory hazardous solid waste, having high Cr(VI) content and alkalinity, and derived from production of chromate by lime-based roasting process which have been a main process for producing chrome from chromite ore in the past [1,2]. Hazardous hexavalent chromium Cr(VI), remaining in COPR, was slowly released to the environment, resulting in the serious environmental pollution and tremendous diseases including cancer, ulceration and dermatitis, etc. [3–8]. Cr(VI), presented in aqueous media, could completely be reduced, adsorption and removed from water body through a proper treatment, but Cr(VI), incorporated in COPR, could not, due to its characteristic inherent to COPR. In general, the reduction and adsorption of Cr(VI) could take place at a low pH [9,10], the COPR, however, has a high acid neutralizing capacity, so that a great deal of the inorganic acid would be required to maintain its pH at low value and almost Cr(VI), incorporated in COPR, is released to aqueous solution at 32 [H]$^+$ eq/kg·COPR [11]. In many countries, therefore,

every effort would have made to treat the COPR.

COPR has a complex mineral composition, in which Cr(VI) is mainly bound in a surface of mineral particles in a manner of electrostatic attraction and ion exchange [12–14]. Because the anions with a higher charge density will preferentially exchange with those of lower charge density, the previous studies reported that controlling the transformation of Cr(VI) host phases using hydrothermal methods with suitable mineralisers can effectively improve the extraction of Cr(VI) from solid wastes [12,15–17]. Considering above-mentioned facts, we have examined the effective recovery process of Cr(VI) from COPR by using the low cost leaching agent, containing considerable amount of anions.

After extracting of Cr(VI) from COPR, the Cr(VI) in extraction fluid should be recovered and it needs to be detoxification of solid waste due to the minor remaining Cr(VI) in plCOPR. For the purpose of stripping of Cr(VI) from solution, various types of anion exchange material could be applied [18,19]. So far, S-species and Fe-species have mainly been recommended for the detoxification of COPR, due to its low price and easy purchase [17,20–24]. Among them, sodium sulfide has more widely used as a reductant in detoxification of COPR, due to its relatively higher capacity of reduction in alkaline pH than others [2,16,22]. If the detoxification of COPR by sodium sulfide (Na_2S) has not been affected by chloride-ion, it would be possible to use Na_2S for the detoxification of plCOPR containing seawater. However, there have been problems and limitations for this method, such as toxicity and unpleasant odor of the unreacted reductant toward the living things.

In the detoxification, only Cr(VI) leached could be reacted with reductant and residual unreacted Cr(VI) incorporated in detoxified chromite ore processing residue (dCOPR) can be slowly released during deposition. Cr(III) and Cr(VI) species could be bound to various materials, such as lime, fly ash and blast furnace slag, and so on, which allows the immobilization of chromium and thus minimising its leachability [16,25,26]. In contrast to Cr(III), Cr(VI) is not readily incorporated into cement hydrate phases. Therefore, it is of great significance to discover the effective method for stabilisation of the dCOPR. Amorphous iron sulfide could be chosen as a proper reductant for the remediation of COPR over both short- and long-term treatment trials [12], demonstrating it would be likely a very promising stabiliser of dCOPR.

Here, in this paper, the cost-effective method for extracting of Cr(VI) incorporated in COPR and stripping of Cr(VI) in lixivium was suggested. In addition, the viable method for detoxification and stabilisation of the plCOPR was discussed.

2. Materials and methods

2.1. Site and sampling technique

COPR dump is located in the middle-eastern coast area of DPRK. COPR sampling was conducted with drill rig at seven locations, in which each drilling depth was 3 m. The cores were undergone enough mixing, before sample of 10 kg was collected and homogenised and stored in sealed plastic bags at 4 °C.

2.2. COPR characterisation

Cr(VI) extraction and determination were performed 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 are shown in **Table 1**. Experiments were conducted in triplicate and the average values were recorded.

Table 1. Initial characterisation for COPR.

pH	CaO (%)	MgO (%)	Al_2O_3 (%)	SiO_2 (%)	Fe_2O_3 (%)	Water leachable Cr(VI) (%) (as Cr_2O_3)	Alkali leachable Cr(VI) (%) (as Cr_2O_3)	Non-leachable Cr(VI) (%) (as Cr_2O_3)
9.7 ± 0.2	19.6 ± 0.6	21.9 ± 0.5	0.98 ± 0.04	28.3 ± 0.9	2.59 ± 0.07	0.62 ± 0.02	0.84 ± 0.04	5.93 ± 0.2

Values are represented as mean $\pm$ SD of three replicate determinations ($p < 0.05$).

2.3. Extraction and recovery of Cr(VI)

2.3.1. Extraction of Cr(VI)

Extraction experiments were performed to confirm the availability of the seawater as leaching agent for extracting the leachable Cr(VI) existed in COPR. Experimental setup was consisted as follows; a cylindrical extracting column, with a height of 10 dm and radius of 1dm, in which 5 outlets (2 cm of radius, 10 cm in length) were arrayed vertically alongside the height of column at the same interval, and a centered mixing blade was installed at 0.2 m of height from the bottom of column.

A dried COPR gently ground and passed through 0.5 mm sieve was mixed with extracting solution, so as to make the solid content of the resultant COPR slurry a fixed value, and then the impact of various parameters affecting the extracting rate of Cr(VI) was investigated. After finishing of extracting 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 proper outlet for temporary storage and clarification before the ion exchange process.

2.3.2. Recovery of Cr(VI)

Abovementioned Cr(VI)-containing lixivium was fed to the anion exchange resin (AXR) column system by the upflow procedure at a certain flow rate. The effluent were sampled at certain time intervals, and the Cr(VI) concentrations were analysed. The adsorption operation was performed until the Cr(VI) concentration of effluent reached at 0.5 mg/L.

The Cr(VI) loaded AXR was eluted with sodium hydroxide solution and the AXR was treated with 0.1 mol/L HCl solution, in order to converted to Cl^- form. Afterward, the regenerated AXR was reused for following operation cycles.

2.4. Detoxification of plCOPR and stabilisation of the dCOPR

In detoxification experiment, the plCOPR, separated from lixivium in extracting process, was mixed with Na_2S as a reductant at certain mass ratios by using a mixer apparatus, before holding it in dump state during a certain period. The effects of some parameters, such as Na_2S/Cr(VI) mass ratio and the elapsed time, on the content of

remaining Cr(VI) in the mixture were discussed. For the stabilisation of the dCOPR, the certain amount of ferrous sulfate and lime was mixed with dCOPR, and after 360 d curing, the efficiency of stabilisation for the dCOPR by toxicity characteristic leaching procedure (TCLP) [27] was evaluated.

3. Results and discussion

3.1. Effect of some factors on extracting rate of Cr(VI) from COPR

3.1.1. Effect of the concentration of sodium chloride on the extracting rate of Cr(VI)

Figure 1 shows the extraction rate of the leachable Cr(VI) from COPR with the increment of NaCl concentration, ranged from 0% to 9%, at certain solid contents. As are shown in **Figure 1**, the extraction rate shows rather steep increment until the concentration of NaCl reached at 3% and insignificant increment above 3% of the concentration of NaCl. Since COPR deposit is located at a coast area and the saltiness of the seawater is ca. 3%, the seawater is considered to be a cost-low leaching agent.

The effect of solid content in COPR pulp, ranged in 10%–30%, on the Cr(VI) extraction rate was investigated. The lower solid content results in the higher extraction rate of Cr(VI), but the difference was not much great (**Figure 1**). Therefore, with regard to the disadvantage in relation to handling too large volume of liquid in extracting process at a lower solid content, the solid content of 25% was chosen.
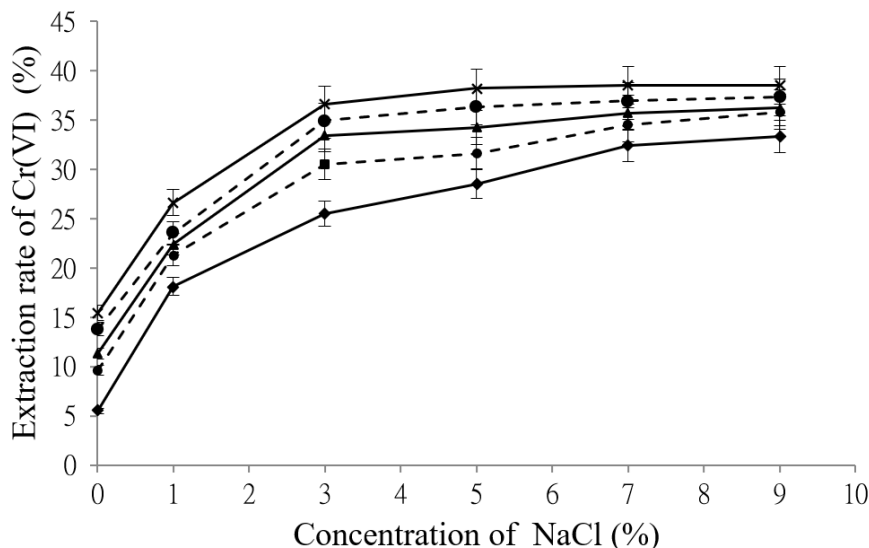

Figure 1. Extraction rate of Cr(VI) vs concentration of NaCl. (—◆— solid content of 10%, --■-- solid content of 15%, —▲— solid content of 20%, --●-- solid content of 25%, —×— solid content of 30%).

3.1.2. Effect of extracting period on the extracting rate of Cr(VI)

The effect of the extracting time on Cr(VI) extraction rate were investigated in an agitating mode of continuous and intermittent. As are shown in **Figure 2**, in the intermittent agitating mode, when the retention time increased from 10 min to 60 min at the interval of 10 min, the remarkable increment in extraction rate is observed within 30 min, but thereafter no considerable difference is appeared. Accordingly, it is

likely perfect that the extracting time is 30 min in intermittent agitating mode.

Meanwhile, in a continuous agitating mode, the Cr(VI) extracting rate increased steeply between 0 min and 20 min, and reached at equilibrium from 20 min of elapsed time (**Figure 2**). Compared aforementioned modes in the standpoint of energy consumption, it is prefer to select the intermittent mode for extracting Cr(VI) from COPR.
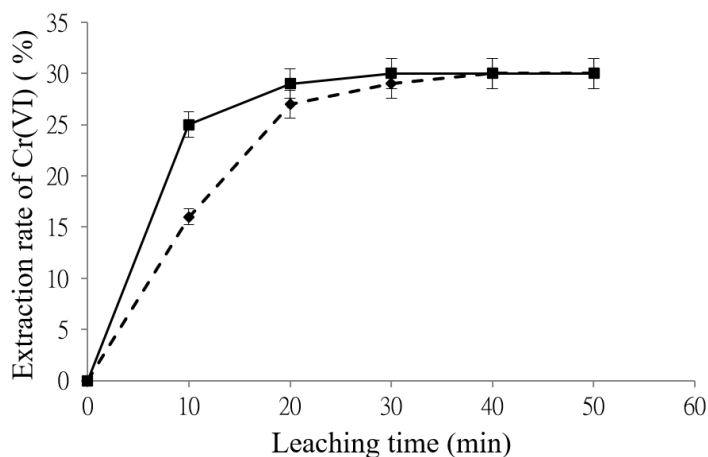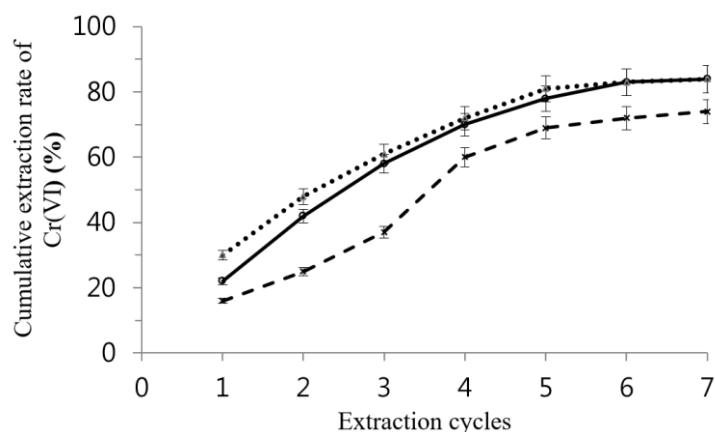

Figure 2. Cr(VI) extraction rate vs the extracting time in a different agitating mode (…◆… intermittent agitating mode, —■— continuous agitating mode).

3.1.3. The effect of the repetition extraction cycles on the cumulative Cr(VI) extraction rate at different seasons

In the large-scale extraction process, it is undesirable to control the temperature of lixivium, because Cr(VI) concentration in lixivium is rather poor, on the contrary, much of energy should be needed for providing the required temperature. Multi-step operation (once-through outflow of 50% of total liquid volume) is thought be a crucial part in recovering of chromate from COPR by using simple apparatus without any special equipment. Here, the determination of suitable cycles of repetition is of great importance. **Figure 3** shows the change of the cumulative extraction rate of Cr(VI) with the cycles of repetition extraction at a different season.

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

These results suggested a possibility to extracting Cr(VI) from COPR by using seawater, which could be applied in pretreatment of COPR before detoxification, irrespective of seasonal variation.

Figure 3. Cr(VI) extraction rate with the repetition extracting cycles. (—◆— summer (20–25 °C), —■— autumn (10–15 °C), —▲— winter (−6–0 °C)).

3.1.4. Change in relative sedimentation height with the retention time

After Cr(VI)-extraction from COPR was completed, the utilization of simple and amenable process for separating the solid residue from COPR pulp is of great significance. The conventional filter apparatuses, utilized in solid-liquid separation, have some of difficulties in handling the COPR pulp, because COPR has poor filterability, so the filter apparatus needs a great deal of energy consumption. The separation of supernatant using the gravitational sedimentation is promising and feasible for solid and liquid separation, in which Cr(VI) involved in supernatant was stripped and recovered as chromate, thereafter barren supernatant was reused as extracting solution.

In order to determine the proper position of supernatant draining outlet, the relative sedimentation heights (the height ratio between the sedimentation boundary and the surface of a supernatant) were investigated with the retention time (**Table 2**).

As shown in **Table 2**, the uniform sedimentation section laid in the range of the relative sedimentation heights between 0.59 to 1.0, followed by the compressive sedimentation and the final relative sedimentation height was 0.38. As a result, the suitable supernatant-draining outlet is thought be located at the position where it is 60% of column height.

Table 2. Relative sedimentation height at a different retention time.

Time (min)	2	4	6	8	12	16	20	30	∞
Relative sedimentation height ($h_{boundary}/h_{total}$)	0.96 ± 0.03	0.92 ± 0.03	0.89 ± 0.02	0.86 ± 0.04	0.80 ± 0.04	0.74 ± 0.03	0.59 ± 0.03	0.55 ± 0.01	0.38 ± 0.01

Values are represented as mean $\pm$ SD of three replicate determinations ($p < 0.05$).

3.2. Effect of the parameters on the recovery of chromate salt from the lixivium

The breakthrough exchange capacities and elution and regeneration of adsorption column system for the recovery of Cr(VI),were evaluated. Here, anion exchange resin (trade name Ceralite IRA 400) is a Cl⁻ form strongly basic AXR. The breakthrough adsorption capacity (q_b) with varying flow rate was depicted in **Figure 4**.
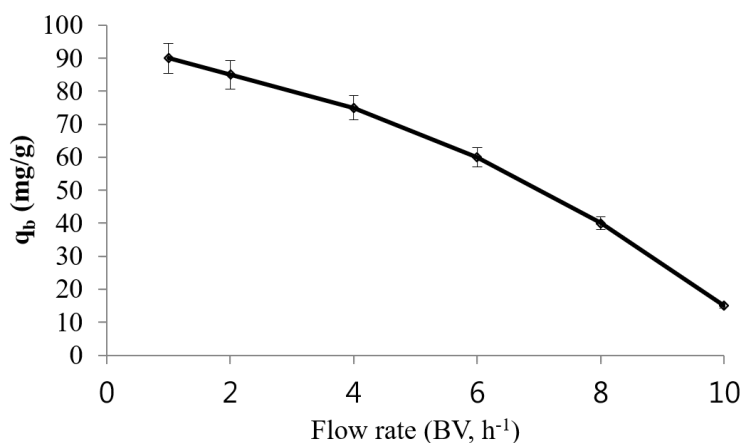
Figure 4. Effect of flow rate (BV; bed volume/h) on the breakthrough adsorption capacity. Data show the mean ± SD (*n* = 3).

When the flow rate increased by 4.0 BV, the q_b was above 80 mg/g, further increase in flow rate resulted in rapid decrease in q_b. In the consideration of economic aspect, the flow rate of 4.0 BV is recommended.

The Cr(VI)-loaded column was eluted with 2.5 M NaOH according to the reference literature [14]. The final concentration of Cr(VI) in the elution liquid was up to 43.1 g/L. As a result, the adsorption columns were regenerated for following operation cycles.

3.3. Reductive detoxification of plCOPR

Here, the applicability of the reductive detoxification, proposed by Velasco et al. [16], to plCOPR containing the leaching agent, was discussed. In detoxification trials of plCOPR, Na_2S was used as a single reductant, in which a proper amount of plCOPR were mixed with the reductant with varying mass ratios, before being piled on a certain place without retention time for reaction completion. The content of Cr(VI) in the mixture of plCOPR was determined at a certain time elapsed since the various amounts of Na_2S were added (**Figure 5**).

The results showed that the content of Cr(VI) in plCOPR became lower than the cleanup criteria by US EPA [28], when the Na_2S/Cr(VI) mass ratio were kept up to 6. Therefore, it is proper to keep the mass ratio about 6, based on the analysis of remaining Cr(VI) in plCOPR, in accordance with the reference [2]. Also, the contents of Cr(VI) in the mixture of plCOPR and reductant were determined with a certain time interval to have the correct time data for completion of detoxification. The result showed it was not until 36 h that the content of Cr(VI) in plCOPR became lowered below cleanup criteria at Na_2S/Cr(VI) mass ratio of 6, accordingly the proper retention time was thought be 36 h (**Figure 5**). These results give a possibility of sodium sulfide to detoxify the seawater-leached plCOPR at a heap manner and of saving the operation time of the equipment.
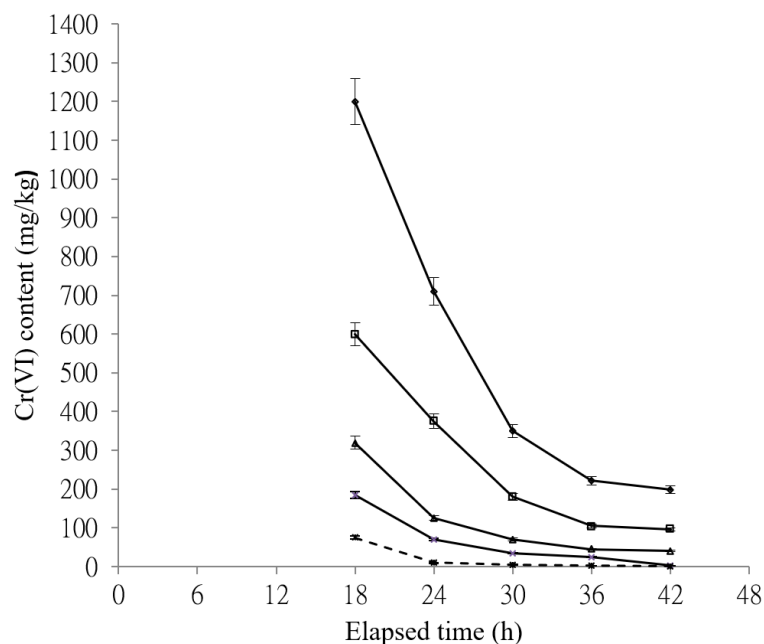
Figure 5. Cr(VI) content vs the elapsed time at the different mass ratios between Na$_2$S and Cr(VI) (—◇— mass ratio of 3, —□— mass ratio of 4, —△— mass ratio of 5, —×— mass ratio of 6, ---×--- mass ratio of 7).

3.4. Stabilisation of the dCOPR

There remains a considerable amount of the reductive species in dCOPR, such as thiosulfate (intermediate species) and sulfide (unreacted) and so on. It is likely possible to immobilize these reductive species to dCOPR by adding ferrous sulfate. To find the amount of ferrous sulfate for perfect stabilisation, the TCLP test of 360 d curing samples were performed. For the satisfied stabilisation of dCOPR, a series of the experiment with varying the specific FeSO$_4$ dosage (w/w FeSO$_4$:Na$_2$S) were carried out, in which the 5% lime was added. Experimental results are shown in **Figure 6**.
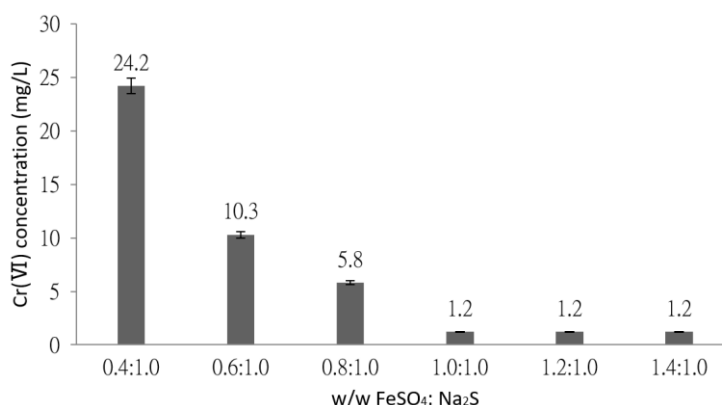
Figure 6. Cr(VI) concentration in TCLP leachate vs. the specific FeSO$_4$ dosage (w/w FeSO$_4$:Na$_2$S). Data show the mean ± SD ($n = 3$).

The concentration of Cr(VI) in TCLP leachate quickly decreased with the increase of the amount of FeSO$_4$, and remained constant above 1.0:1.0 of specific dosage. When the specific FeSO$_4$ dosage was 1.0:1.0, Cr(VI) concentration in the

leachate was arrived at 1.2 mg/L by the toxicity characteristic leaching procedure (TCLP), within the regulatory limit disposal standard (HJ/T 301-2007, 3 mg/L). The results revealed that for the purpose of desirable stabilisation of dCOPR, the specific $FeSO_4$ dosage was thought be equal to the amount of Na_2S to be added in detoxification.

4. Conclusions

In this paper, the cost-effective strategy of treating chromite ore processing residue (COPR) were investigated by multiple processes including a extraction, adsorption and elution of Cr(VI) incorporated in COPR, a detoxification for plCOPR and stabilisation for dCOPR.

The results of extracting experiments showed that it is possible to recover Cr(VI) incorporate in COPR with inexpensive extracting agent-seawater, in which ca. 82% of Cr(VI) extraction rate could be achieved under the following condition;

the seawater as extracting solution, 25% of solid content, extracting period of 30 min, intermittent agitation, gravitational sedimentation as solid/liquid separating mode, repetition number of up 5.

Following the extracting of Cr(VI) from COPR, Cr(VI) in lixivium was easily recovered by using a series of ion exchange column system, resulting in Cr(VI) solution of up to 47.1 g/L.

And then, the results of detoxification trials of plCOPR containing Cl^- shows that sodium sulfide can be also used as a single reductant, in this case the reaction mixture was discharged from reactor without retention time for reduction completion, thereafter reduction of Cr(VI) occurs in a certain place outside of mixer apparatus. By applying this method, processing time could be shortened greatly than prior methods.

The detoxification and stabilisation of the post-leached COPR(plCOPR) was performed by reacting the amount of Na_2S (Na_2S/Cr(VI) mass ratio of 6) with plCOPR, followed by mixing the 5% lime and a specific dosage of $FeSO_4$ with dCOPR. After 360d of curing, in toxicity characteristic leaching procedure (TCLP), Cr(VI) concentration in the leachate was arrived at 1.2 mg/L, below the regulatory limit disposal standard (HJ/T 301-2007, 3 mg/L).

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