

# Valuable utilization of ferrochrome slag for wastewater treatment

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**During ferrochrome production, slag is discarded as a waste material in huge quantities. A relatively small percentage finds application whereas majority of the slag is held in dumps. The purpose of the study is valuable utilization of ferrochrome slag. The experimental results showed that 99% removal of chromium (Cr(VI)) was achieved in 1 h by ferrochrome slag from Sukinda chromite mines water. There is an *in situ* generation of ferrous sulphate by the effect of oxidizing agent and iron content of ferrochrome slag which is capable of reducing Cr(VI) to trivalent chromium. Water samples surrounding the slag dumped area were checked to find out the extent of problem caused by them. There is no adverse effect of Cr on the surrounding water samples. Toxicity characteristic leaching procedure test revealed that the slag is environmentally stable. This research concludes that used ferrochrome slag could be utilized as a waste water treatment.**

**Keywords:** Ferrochrome slag, hexavalent chromium, Sukinda chromite mine, sulphuric acid, wastewater.

HUGE quantity of unmanaged industrial solid waste in the form of slag, ash, char, dust, etc. has resulted in an increased environmental concern. Slags are the main sources of waste, produced in a large quantities in pyro metallurgical processes, have to be recycled and utilized accordingly. Ferrochrome (FeCr) slag is basically a waste in the production of FeCr, which is used in the production of different grades of stainless steel, as the most common alloying material. The raw material used in the FeCr production are chromite ore, reducing metallurgical coke and fluxing quartzite. The constituents of chrome ore are essentially  $\text{Cr}_2\text{O}_3$ , FeO,  $\text{Al}_2\text{O}_3$ , MgO, CaO and  $\text{SiO}_2$ . Ferrochromium is produced pyro metallurgically by carbothermic reduction of chromite ore ( $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ). The valuable minerals in the chromium ore are  $\text{Cr}_2\text{O}_3$  and FeO, which are reduced to chromium and iron in the furnace, and make up the sought high-carbon ferrochromium alloy. During FeCr production, slag is discarded as a waste material in huge quantities. A relatively small percentage of this material finds application, but the majority of the slag each year is dumped and as land dis-

posing costs increase, new disposal options are needed. Rapid urbanization and industrialization have resulted in lesser land availability for landfill and the disposal cost is increasing fast. With the enforcement of stringent environmental regulations, alternative utilization and new disposal techniques of slags to minimize the associated environmental pollution are considered to be the way forward.

Ferrochrome slag is useful as a construction material due to its excellent technical material properties. However, an environmental concern has been raised about the content and leachability of toxic metals, especially chromium. Ferrochromium slag is classified as harmless in terms of International Agency for Research on Cancer (IARC) classification, as the chromium exists in ferrochromium slags as Cr(III)<sup>1</sup>. Chromium contamination of water is a significant problem since hexavalent form of chromium is highly toxic and potentially carcinogenic to living organisms. Chromium being insoluble and immobile in its trivalent state (Cr(III)) is nontoxic and used as microelement<sup>2-5</sup>, whereas the hexavalent state (Cr(VI)) is toxic and a priority pollutant<sup>2,5-7</sup> because of its higher water solubility and the resulting higher mobility. Mobility of Cr(VI) is highly regulated by pH<sup>8,9</sup>. In acidic condition, (below pH 5) Cr leaching is contributed by dissolution of Cr(III) and in basic condition (above pH 5), leaching is by Cr(VI)<sup>9</sup>. The leached amount of Cr(VI) increases as pH is increased and the amount is insignificant in acidic environment<sup>10</sup>. Oxidation–reduction potential (Eh) and pH are the two main important parameters, regulating the chromium content in groundwater<sup>11,12</sup>. Cr(VI) species predominately exists as chromic acid ( $\text{H}_2\text{CrO}_4$ ) salts, hydrogen chromate anion ( $\text{HCrO}_4^-$ ), chromate anion ( $\text{CrO}_4^{2-}$ ) and dichromate dianion ( $\text{Cr}_2\text{O}_7^{2-}$ ). At pH < 3,  $\text{Cr}^{3+}$  is predominant while for pH > 7 the  $\text{CrO}_4^{2-}$  is prevalent<sup>13</sup>. Several chemical and physical factors like precipitation–dissolution, alkalinity, redox potential, complexation, organic carbon content, contact time, liquid to solid ratio, particle size, agitation/mixing, common ion effect, partitioning, type of flow, porosity and temperature, influence the release of Cr species from the FeCr slag<sup>14</sup>.

The Sukinda chromite mine (SCM) area in Odisha, India has around 97% of country's total reserve<sup>15</sup>. In Sukinda, groundwater level is 8–11 m depth, and gets contaminated with Cr(VI) from chrome ore mining and atmospheric air<sup>16</sup>. Water discharges from the metal

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mining processes and also leachate and runoff water contaminate nearby water sources. The mining activities in Sukinda has caused Cr(VI) contamination of groundwater and surface water of up to 0.6 and 3.4 mg/l respectively<sup>17</sup>. The existing chemical method in use is chemical precipitation by ferrous sulphate and lime. A large amount of chemical sludge generated in this method requires further attention.

Adsorption is considered as the more suitable alternative out of the other available physicochemical methods like precipitation, reduction, ion exchange, co-precipitation for Cr(VI) remediation<sup>18,19</sup>. Adsorbents like clay minerals, sawdust, charcoal, activated carbon, metal oxides, carbon nanotubes, organic polymers, nanoparticles have been used in Cr(VI) removal<sup>20-23</sup>, but, many of them have low adsorption capacity, high cost and slow kinetics<sup>5,19,24</sup>. Several studies have shown the use of industrial slag as an adsorbent for removal of heavy metals<sup>25-28</sup>. Erdem *et al.*<sup>25</sup> showed the use of FeCr slag in removing Cr(VI) from aqueous solution with sulphuric acid treatment. Therefore, FeCr slag could be useful as a reductant for removal of toxic elements.

Therefore, this study aims at valuable utilization of FeCr slag for analysing physical, chemical and geotechnical characterization and evaluates its utilization for mitigation of chromium content in mines waste water.

## Materials and methods

### Materials

*Sukinda chromite mine processed water:* Tailing pond recirculating water samples were collected from quarry water storage area of beneficiation plant in SCM. Wastewater analysis was done to quantify physico-chemical parameters like pH, total dissolved solid (TDS), dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD), Ca, Mg, Cr(VI),  $\text{SO}_4^{2-}$ , Fe before and after the treatment. The value at zero day was denoted as initial value while the value noted after the treatment was indicated by final value. Here, zero day means initial day.

*Ferrochrome slag and its characterization:* Slag samples were collected from Bramnival Ferro Alloy plant of Tata Steel Limited, India. The size fraction analysis was carried out in the slag samples and also physical and geotechnical analysis. Chemical elemental characterization was done before and after the treatment for observing the effect of elements on sorption of FeCr slag. Particle size distribution (PSD) analysis is an important requirement in leaching study and in utilization aspects. PSD of granulated FeCr slag and lumped slag were determined by standard sieve analysis methods as stipulated in Indian Standard (IS: 2386 (Part I) – 1997). For particle size

analysis of FeCr slag, sieve analysis was carried out. Sieve analysis is a procedure to assess PSD of a granular material by allowing the sample to pass through a series of sieves of progressively smaller mesh size and weighing the amount of material that is stopped by each sieve as a fraction of the whole mass.

To find a suitable utilization of FeCr slag, physical and geotechnical characteristics were identified and tested according to IS codes. Standard procedures followed are listed in Table 1.

*Collection of water samples surrounding the slag dumping area:* Water samples from seven different locations of tube wells around FeCr slag dumped area were collected and analysed to find out the extent of toxic element contamination to the water wells.

### Methods

pH of the mines waste water was analysed using a pH-meter (Systronics, India, digital pH meter, model no. 335). The variation of pH during experiment with the passage of time was measured.

TDS is a measure of combined content of all inorganic and organic substances contained in a liquid in molecular, ionized or micro-granular (colloidal sol) suspended form. TDS was measured at a regular basis during experiment using TDS meter (Systronics, India, model no. 308).

Hexavalent chromium concentration in ppm was measured in spectrophotometer (Thermo scientific – Genesys 10S UV-Vis spectrophotometer), at 540 nm wavelength after developing a purple colour by using diphenylcarbazide (DPC) solution according to standard procedure<sup>29</sup>.

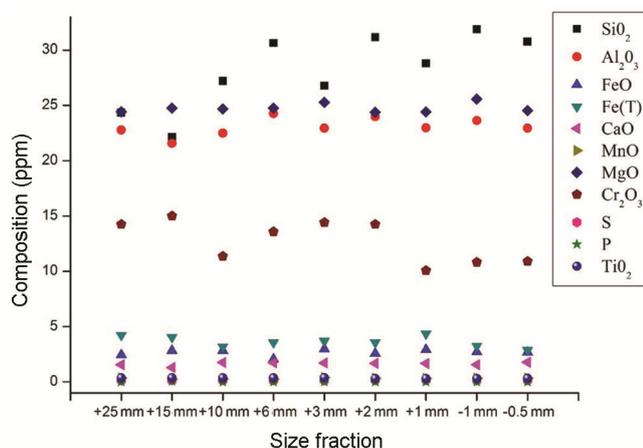
Apart from chromium, SCM water contains other elements like Ca, Mg, Fe, Si,  $\text{SO}_4^{2-}$ , etc. These elemental concentrations in the SCM water were determined before and after experiment by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) (Spectro Arcos). The instrument's working wavelengths were set according to APHA<sup>29</sup>.

Leaching analysis of FeCr slag was done to find out any adverse effect of chromium leaching or other elements on the surrounding area. Different sizes of slag were taken in a beaker and different quantities of water were mixed with slag and stirred at different time intervals – 1, 2, 3, 4, 6 and 24 h. The water to slag ratio was optimized at 1 : 20 (20 g slag in 1 litre of distilled water)<sup>14</sup>. Cr(VI) concentrations were analysed at UV-Vis spectrophotometer at 540 nm wavelength<sup>30</sup> and other elemental analysis was done by ICP-AES method<sup>31</sup>.

To understand the toxicity characteristics of chromium of FeCr slag, toxicity characteristic leaching procedure (TCLP) method was applied. 100 g of pulverized and sieved (9.5 mm screen) slag with 2 litre of extraction fluid (liquid/solid ratio of 1 : 20) in a plastic bottle was kept for

**Table 1.** Percentage obtained of different size fractions from the dumped ferrochrome (FeCr) slag

| Size fraction | +25 mm | +15 mm | +10 mm | +6 mm | +3 mm | +2 mm | +1 mm | -1 mm | -0.5 mm |
|---------------|--------|--------|--------|-------|-------|-------|-------|-------|---------|
| Percentage    | 0.87   | 2.8    | 3.8    | 9.4   | 11    | 7.3   | 40    | 9.8   | 12      |

**Figure 1.** Chemical analysis result of different size fractions of ferrochrome slag.

24 h at 18 rpm and filtered using a 0.45  $\mu\text{m}$  glass fibre filter. The extraction fluid used was acetic acid–sodium acetate buffer solution (pH = 4.93). Cr(VI) concentration in the filtrate was found out by spectrophotometric method at 540 nm wavelength<sup>32</sup>.

pH is an inevitable parameter dictating chromium sorption. The method of analysis used for pH optimization was point of zero charge and variations of solution pH, to find out maximum adsorption of chromium. A solution of 10 g/l of FeCr slag was mixed with electrolyte solution (0.01 and 0.1 M  $\text{KNO}_3$ ). pH of the solution was adjusted in the range 2.0–12.0 by 0.5 M HCl or 0.5 M NaOH. The solutions were shaken for 24 h at 250 rpm to reach an equilibrium pH value. The difference of initial pH and final pH against solution pH were plotted for two electrolyte solutions and the intersection point of the two curves gave the point of zero charge. Cr(VI) removal percentages with variation in pH were found out by batch experiments done at room temperature ( $24^\circ \pm 2^\circ\text{C}$ ). Fixed masses of slag (10 g/l) were shaken at 250 rpm for 24 h with 5 mg/l standard potassium dichromate solutions with pH values varying from 2 to 9. The solutions after agitation were filtered and analysed for Cr(VI).

Slag samples were sieved using mesh nos 20, 30 and 36 and used as adsorbent for chromium adsorption. Potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) was used to prepare standard solutions of Cr(VI) with concentrations in the range 1 to 4 mg/l. Batch experiments were done to find out adsorption characteristics. pH was set at 2.

Adsorption isotherms were calculated by treating different concentrations of hexavalent chromium from 1 to 4 mg/l with an adsorbent dose of 10 g/l and 60 min of equilibration time.

To find the kinetic model, standard solutions in the range 1–4 mg/l were added to 10 g/l slag in water in a series of Erlenmeyer flasks and stirred on a mechanical shaker at 150 rpm. While agitating, samples were removed at set time intervals and filtered for analysis.

SCM water contains high amount of chromium content. The reduction of Cr(VI) was performed by using waste slag and a strong oxidizing agent, sulphuric acid ( $\text{H}_2\text{SO}_4$ ). To get the optimized result, three parameters were varied; water/slag ratio, amount of  $\text{H}_2\text{SO}_4$  and the experimental duration. The water/slag ratios used were 1 : 5, 1 : 10 and 1 : 20; an amount of 5 M  $\text{H}_2\text{SO}_4$  was varied as 2, 2.5, 3, 4, 5, 6, 8, 10 and 12 ml. Stirring duration was varied at 30 min, 1 h, 2 h and 5 h. Used FeCr slag was repeatedly reused in SCM processed water to find out its reusability. The filtered samples were then analysed for Cr(VI) concentration in spectrophotometric method and pH and TDS of the samples were also noted.

The mean number of pH, TDS, reduction study of Cr(VI) of SCM processed water were calculated before and after the experiment and subjected to Student's *t* test and significant differences were calculated between treatments<sup>33</sup>.

## Results and discussion

### Chemical analysis of FeCr slag

Chemical analysis of FeCr slag showed that the major constituents present were  $\text{SiO}_2$  (~31%),  $\text{MgO}$  (~24%),  $\text{Al}_2\text{O}_3$  (~24%) and  $\text{Cr}_2\text{O}_3$  (~14%) (Figure 1). In all the size fractions, major constituents were  $\text{SiO}_2$  (~25%–30%),  $\text{MgO}$  (~24%),  $\text{Al}_2\text{O}_3$  (~22%) and  $\text{Cr}_2\text{O}_3$  (~10%–14%) (Figure 1). Size fraction analysis showed that the size +1 mm is present in highest amount (40%) (Table 1). Our chemical composition results are in close agreement of results obtained by Erdem *et al.*<sup>25</sup>.

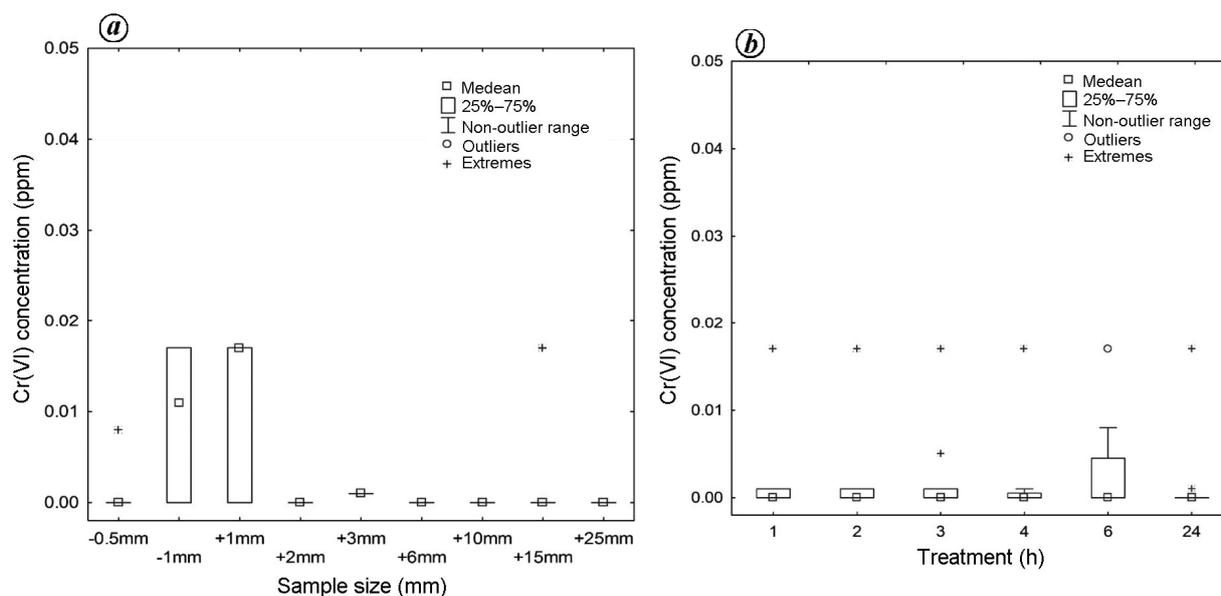
### Analysis of water collected from tube wells around FeCr slag dumped area

Water samples from tube wells around the FeCr slag dumping area were analysed to find out leaching of any toxic element, specially Cr(VI) from the slag dumps. Chemical analysis showed that water of one of the dumping slag area sites (07A) had Cr(VI) concentration above the permissible limit at about 1.2 ppm (Table 2). The IS permissible limit for Cr(VI) for drinking water is 0.05 ppm (IS 10500: 2012) with no relaxation. This

**Table 2.** Chemical analysis of water samples collected from tube wells around FeCr slag dumped areas

| Source | pH   | Cl    | Cu   | Cr    | Ca  | Mg | Fe    | Na    | K  | PO <sub>4</sub> <sup>3-</sup> |
|--------|------|-------|------|-------|-----|----|-------|-------|----|-------------------------------|
| NALA   | 8.06 | 120.7 | 0.12 | 0.000 | 36  | 90 | 0.001 | 12    | 50 | 0.36                          |
| 07A    | 8.5  | 42.6  | 0.11 | 1.2   | 27  | 65 | 0.001 | 2     | 17 | 0.001                         |
| 010A   | 7.26 | 49.7  | 0.11 | 0.001 | 70  | 37 | 0.02  | 0.001 | 40 | 0.001                         |
| T6     | 7.45 | 92.3  | 0.11 | 0.000 | 65  | 43 | 0.11  | 0.001 | 21 | 0.001                         |
| T9     | 6.8  | 35.5  | 0.11 | 0.000 | 47  | 23 | 0.75  | 0.001 | 15 | 0.001                         |
| T10    | 7.2  | 28.4  | 0.11 | 0.001 | 39  | 19 | 0.001 | 0.001 | 18 | 0.001                         |
| T15    | 7.34 | 35.5  | 0.11 | 0.000 | 28  | 10 | 0.001 | 0.001 | 12 | 0.001                         |
| 013A   | 7.15 | 56.8  | 0.11 | 0.001 | 107 | 13 | 0.001 | 11    | 43 | 0.001                         |

All values in ppm except pH.



**Figure 2.** *a*, Leaching analysis of Cr(VI) from the different size fractions of the FeCr slag. *b*, Leaching analysis of Cr(VI) in water from the slag in neutral pH condition at different exposure duration of size fraction of +1 mm.

particular tube well of concern was shut down with immediate effect.

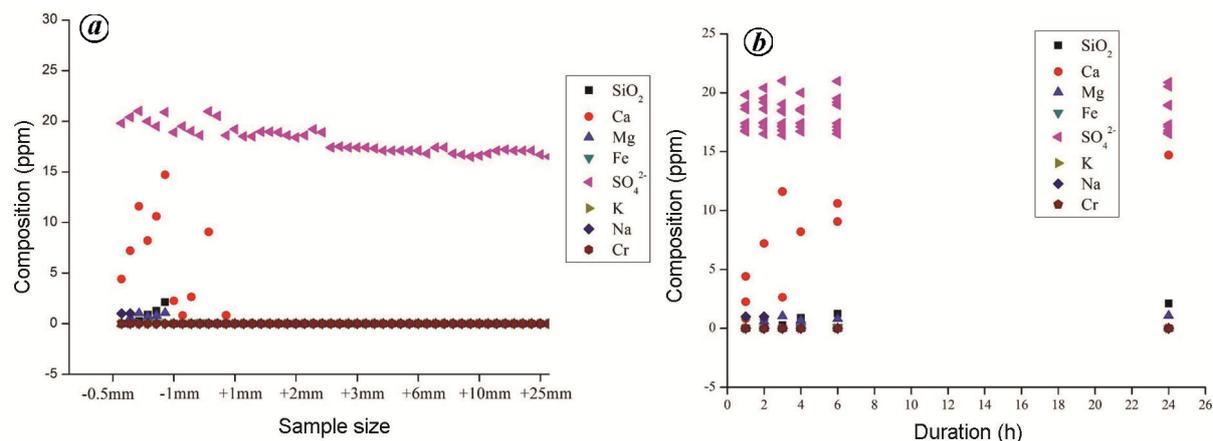
#### Leaching analysis of Cr(VI) from FeCr slag

Leaching analysis data revealed almost negligible leaching of Cr(VI) from all size fractions of FeCr slag (Figure 2 *a*) and even at different time durations (Figure 2 *b*). Slag samples are granular and are not soluble in water. The maximum amount of Cr(VI) leached was 0.017 ppm at a leaching time of 6 h. These results are similar to that obtained by Shadreck and Tawanda<sup>34</sup>, and Tanskanen and Makkonen<sup>35</sup>. One of the two controlling factors of Cr leaching is the ratio of calcium oxide (CaO) and silicon dioxide (SiO<sub>2</sub>) with the amount of magnesium. When CaO/SiO<sub>2</sub> ratio is less than 2, Cr is present as magnesiochromite spinel phase (MgCr<sub>2</sub>O<sub>4</sub>), whereas Cr exists predominantly as calcium chromite when the ratio is greater than 2 (ref. 36). Magnesiochromite phase is resistant to

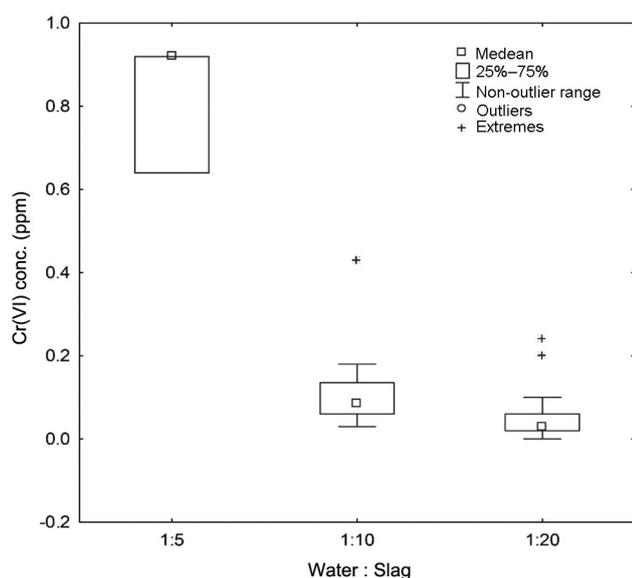
oxidation and dissolution, however, calcium chromite can be oxidized to calcium chromate and leaching by acid treatment is possible<sup>37</sup>. Chemical constituent analysis showed that CaO/SiO<sub>2</sub> ratio was less than 2 in all the cases. Thus it can be said that the Cr is in magnesiochromite spinel phase.

#### Leaching analysis of other elements from FeCr slag

Other elemental data showed low leachability of most elements from the slag. Leachate of different size fractions showed negligible leaching of most elements including Ca, Mg, Fe, K, Na, SiO<sub>2</sub>, Cr. Different sample sizes (Figure 3 *a*) with different time interval (Figure 3 *b*) showed all the values within permissible limits according to IS: 10500: 2012. Data analysis result revealed that maximum leaching was observed in sulphate element (around 16–20 ppm) but this was also within the



**Figure 3.** *a*, Leaching analysis of other elements from different size fractions of the slag in water in neutral pH condition. *b*, Leaching analysis of other elements in water from the slag at different exposure duration.



**Figure 4.** Concentration of Cr(VI) after adsorption experiment using FeCr slag in Sukinda water with variation in water/slag ratio as 1:5, 1:10, 1:20 (time: 60 min, H<sub>2</sub>SO<sub>4</sub> used: 3 ml).

**Table 3.** Chemical analysis result of SCM processed water before and after the experiment

| Parameters                    | Concentration (ppm) mean $\pm$ SE |                   |
|-------------------------------|-----------------------------------|-------------------|
|                               | Before treatment                  | After treatment   |
| Ca                            | 16 $\pm$ 0.45                     | 16 $\pm$ 0.45     |
| Mg                            | 46.23 $\pm$ 0.07                  | 45 $\pm$ 0.06     |
| SO <sub>4</sub> <sup>2-</sup> | 1.7 $\pm$ 0.45                    | 1.7 $\pm$ 0.45    |
| SiO <sub>2</sub>              | 30 $\pm$ 0.45                     | 30 $\pm$ 0.45     |
| Total Cr                      | 2.52 $\pm$ 0.071                  | 2.46 $\pm$ 0.04   |
| Fe                            | <0.001                            | <0.001            |
| Cr(VI)                        | 2.52 $\pm$ 0.071                  | 0.01 $\pm$ 0.03   |
| TDS                           | 290 $\pm$ 0.0089                  | 290 $\pm$ 0.080   |
| pH                            | 8.48 $\pm$ 0.0089                 | 4.89 $\pm$ 0.0085 |

SE, Standard error. Data represents mean  $\pm$  SE (standard error) of  $n = 5$ ; \* $P < 0.05$ , \*\*\* $P < 0.001$  (Student's  $t$ -test).

IS limits. A similar observation was reported by Lind *et al.*<sup>38</sup>.

#### TCLP test

In USEPA's TCLP, Cr(VI) limit was 0.1 mg/l and total chromium was 5.0 mg/l (ref. 32). This test is used to determine whether the waste is hazardous or non-hazardous. TCLP results showed that Cr concentration in TCLP extract was 0.045 mg/l which fitted with the USEPA limit and consistent with those reported by other researchers<sup>1,14,25</sup>. According to the regulatory TCLP test, FeCr slag is a non-hazardous element.

#### Reduction of Cr(VI) by FeCr slag

The elemental analysis of Sukinda water sample results on the initial day and after the experiment is shown in Table 3. The pH and TDS were found to be 8.48 and 290 ppm respectively, which were consistent with the report by Saha *et al.*<sup>31</sup>. Cr(VI) concentration was 2.52 ppm which exceeded the permissible limit of hexachrome, i.e. 0.05 ppm. After the experiment, it was observed that 99% of Cr(VI) was reduced along with reduction of other elements also. It is well-established that Cr(VI) species predominate at basic pH range<sup>8–10</sup>. Chromium formation in wastewater depends on pH, type of waste and process involved. Cr(III) species predominate at acidic pH whereas in basic pH, as in SCM water, Cr(VI) species like CrO<sub>4</sub><sup>2-</sup>, HCrO<sub>4</sub><sup>-</sup> or Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> are present. The chromium speciation depends on pH and concentration of Cr(VI)<sup>39</sup>.

Series of batch experiments were done to find out the effect of water to slag ratio, amount of H<sub>2</sub>SO<sub>4</sub> and duration for the reduction of Cr(VI) concentration by FeCr slag. These three parameters were found to be important to measure the Cr(VI) reduction capacity of FeCr. To

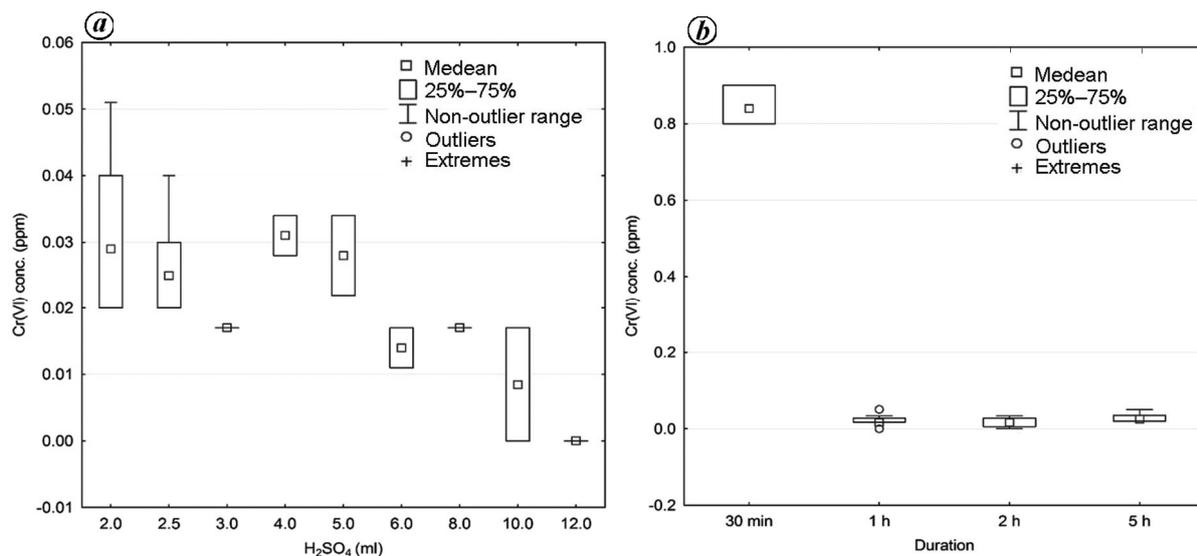


Figure 5. a, Effect of oxidizing agent on the reduction of Cr(VI). b, Effect of time interval on the reduction of Cr(VI).

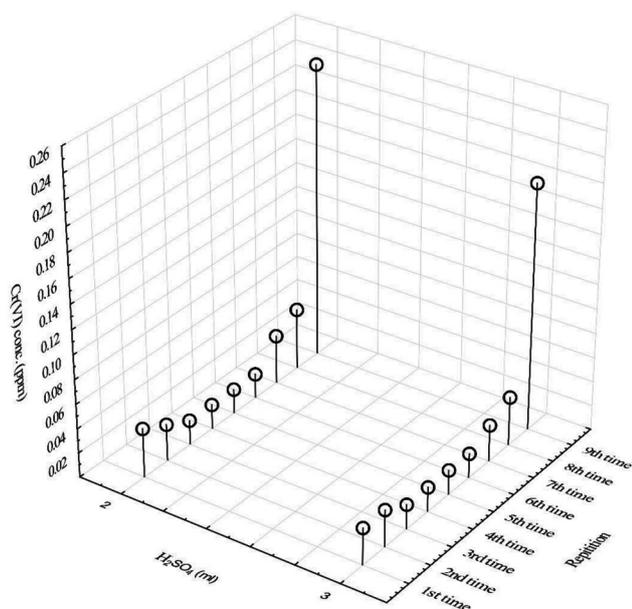


Figure 6. Recovery of FeCr slag.

increase the reduction efficiency, addition of H<sub>2</sub>SO<sub>4</sub> is a common modification step<sup>40</sup>. Water to slag ratio varied as 1 : 5, 1 : 10 and 1 : 20. Experimental data showed that Cr(VI) reduction was maximum when water to slag ratio was 1 : 20 (Figure 4). Most of the cases of 1, 2 and 5 h stirring of slag in Sukinda water showed excellent reduction of Cr(VI) up to 99%. However, for 30 min, Cr(VI) reduction was limited to 40%, 45%, 47% for 2, 3 and 4 ml of 5 M H<sub>2</sub>SO<sub>4</sub> applied respectively. One hour was found to be the sufficient duration for Cr(VI) removal with 96% efficiency for 2 ml H<sub>2</sub>SO<sub>4</sub> used and 99% for 3 ml H<sub>2</sub>SO<sub>4</sub> used. Other parameters were also optimized

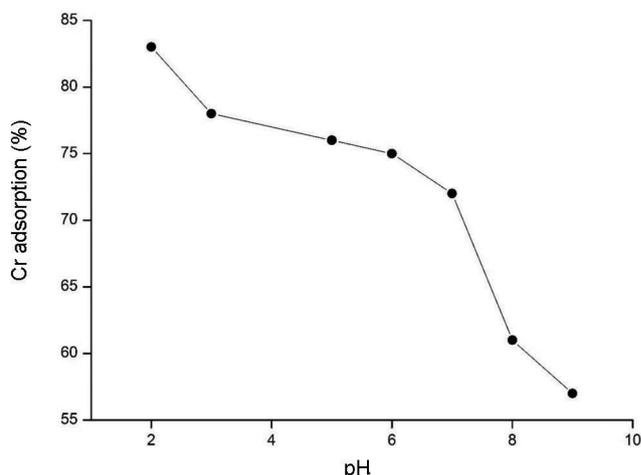


Figure 7. Cr(VI) adsorption efficiency of the FeCr slag with variations of solution pH (10 g/l slag, 5 ppm standard Cr(VI) solution, pH range 2–9).

to observe the effect of oxidizing agent and time interval on the reduction of Cr(VI) (Figure 5 a and b). The used FeCr slag did not lose reduction capacity up to eight cycles of application with the residual Cr(VI) concentration remaining within the IS: 10500: 2012 limit of 0.05 mg/l (Figure 6). After the 9th cycle, the residual Cr(VI) concentration exceeded the permissible limit. pH of SCM water before experiment was 8.48 and it was reduced to ~4.5 after the addition of H<sub>2</sub>SO<sub>4</sub>. The pH did not change during the experiment. The used FeCr slag was again analysed for chemical composition which further proved that there was negligible leaching of Cr(VI) from the slag.

Some of the previous studies<sup>25</sup> and experiments with standard Cr(VI) solution showed that FeCr slag was able

to reduce almost 100% Cr(VI) in as low as 15 min with the help of H<sub>2</sub>SO<sub>4</sub>. In a standard solution, there are no interferences present whereas in mining wastewater, several other elements were present which caused slower reduction in our experiments. Our aim was to reduce the chemical cost for valuable utilization of slag. Slag being a waste material is dumped and is available in plenty for convenient use in wastewater treatment. Increase in the TDS value can be explained by the action of H<sub>2</sub>SO<sub>4</sub> on the iron content in the slag which can result in the formation of ferrous sulphate. Ferrous sulphate is a chemical precipitating agent commonly used in industries to chemically reduce Cr(VI) to Cr(III)<sup>41</sup>. Ferrochrome slag works as a matrix in Cr(VI) reduction to Cr(III) and precipitates Cr(III) which is non-toxic.

The real mechanism behind this reduction process is *in situ* generation of ferrous sulphate by the reaction of sulphuric acid and iron present in the FeCr slag. Therefore, *in situ* generated ferrous sulphate has the capability to reduce Cr(VI) to Cr(III). After treatment, there is no generation of sludge as generally formed in the normal ferrous sulphate treatment.

#### *pH optimization of FeCr slag for Cr(VI) removal*

pH is a dictating parameter for chromium sorption. The point of zero charge (pH<sub>PZC</sub>) of FeCr slag is at pH 6, where the value of ΔpH is zero. Natale *et al.*<sup>13</sup> also found that Cr adsorption capacity was maximum between pH 6 and 7. The value of pH<sub>PZC</sub> is important in understanding the adsorption mechanism. At pH < pH<sub>PZC</sub>, adsorption of anions is dominant while for cations it is at pH > pH<sub>PZC</sub>. From Figure 7 it is evident that Cr(VI) removal efficiency of FeCr slag is enhanced in the acidic pH range (2–6). Chromium ions coexist mainly as anions at acidic pH range. At low pH, there is excess release of H<sup>+</sup> ions, which causes a strong electrostatic attraction between chromium anions and positively charged adsorbent surface and the increased adsorption in acidic pH range facilitates this process. However, in high pH, lower rate of adsorption mainly occurs due to the competition between anions (chromate ions and OH<sup>-</sup>) in getting adsorbed on the adsorbent surface which is positively charged, when OH<sup>-</sup> predominates. Thus, it can be concluded from both the experiments, that the Cr(VI) adsorption is facilitated in low pH.

#### *Sorption isotherm and adsorption kinetics*

Cr(VI) removal percentage increases with the increase in mesh number due to the increase in surface area of adsorbent, thereby providing more active sites available for adsorption. Based on the equilibrium data of adsorption experiment, the Langmuir isotherm exhibits better fitted

model than Freundlich and Temkin isotherms, as the value of linear regression correlation ( $R^2 = 0.98$ ) was found highest for Langmuir type of isotherm (Figure 8a). Monolayer Cr(VI) adsorption takes place on the homogenous surface of FeCr slag containing the uniform distribution of active sites for adsorption in spite of any surface modifications. Previously Strkalj *et al.*<sup>27</sup> and Saki *et al.*<sup>28</sup> got similar results in case of chromium adsorption by steel slag. Sarkar *et al.*<sup>42</sup> also found the Langmuir isothermal model to be the best to explain hexavalent chromium adsorption by organoclay sorbent. Langmuir equation is

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L \times q_m},$$

where  $q_e$  is the amount adsorbed at equilibrium (mg/g),  $C_e$  the equilibrium concentration of the adsorbate (mg/l),  $q_m$  (mg/g) and  $K_L$  are constants.

The adsorption kinetics was analysed by comparing the experimental data for two common models (pseudo-first-order and pseudo-second-order kinetic model). These kinetic models are applicable to adsorption studies by correlation coefficient,  $R^2$  value. Here,  $R^2$  values for pseudo-second-order model were >0.99 (Figure 8b), which is higher than  $R^2$  values for pseudo-first-order kinetic model. Therefore, the adsorption kinetics of Cr(VI) on FeCr slag is more convincingly explained by pseudo-second-order kinetic model. Strkalj *et al.*<sup>27</sup> and Saki *et al.*<sup>28</sup> got similar results for steel slag. Sarkar *et al.*<sup>42</sup> found that pseudo-second-order kinetic model was ideal to explain hexavalent chromium adsorption by organoclay sorbent. Pseudo-second-order equation is

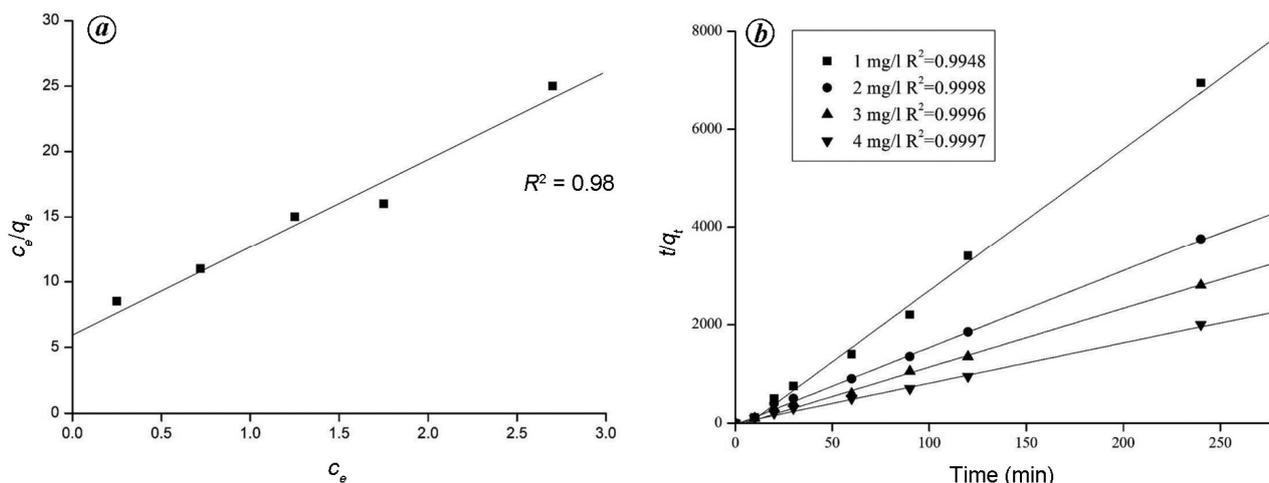
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e},$$

where  $q_e$  and  $q_t$  are the amount adsorbed (mg/g) at equilibrium at any time  $t$  and  $k_2$  is the constant.

The Cr(VI) binding affinity ( $K_L$ ) of FeCr slag was found to be 1.062 mg/l, which denotes the affinity of the active sites of the adsorbent. Therefore, it suggests that after the monolayer adsorption on homogenous active sites of adsorbent based on their binding affinity, the saturation takes place in active sites, resulting in no further adsorption.

#### *Physical and geotechnical characterization of FeCr slag*

Any material to be used in road making has to be strong enough to bear the load. The physical and geotechnical characteristics of FeCr slag obtained are tabulated in Table 4 along with their standard tests to be followed.



**Figure 8.** *a*, Plot of Langmuir isotherm model ( $R^2 = 0.98$ ) (10 g/l slag, standard Cr(VI) solutions in the range 1–4 mg/l, pH = 2, equilibrium time 60 min). *b*, Plot of pseudo second-order-kinetic model ( $R^2 = 0.99$ ) (10 g/l slag, standard Cr(VI) solutions in the range 1–4 mg/l, pH = 2).

**Table 4.** Physical and geotechnical characteristics of ferrochrome slag

| Parameters                                     | Results   |   | Standards to be followed             |       |       |                              |
|--|---|---|--------------------------------------|-------|-------|------------------------------|
| Particle size distribution                     | Gravel (>4.75 mm): 28%;<br>coarse sand (4.75–2.00 mm): 25%;<br>medium sand (2.00–0.425 mm): 30%;<br>fine sand (0.425–0.075 mm): 12%; Silt, 5% |   | IS: 2720 (Part IV) – 1985            |       |       |                              |
| Permeability test                              | Coefficient of permeability: $6.445 \times 10^{-3}$ cm/sec  |   | IS: 2720 (Part XVII) – 1987          |       |       |                              |
| Bulk density                                   | $\gamma$ bulk: 2.02 g/cc at optimum moisture content (OMC) and maximum dry density (MDD)  |   | IS: 2386 (Part III) – 1963           |       |       |                              |
| Water absorption                               | 17.50% (NMC: 1.82%)   |   | IS: 2386 (Part III) – 1963           |       |       |                              |
| Void ratio                                     | $e_0 = 0.515$   |   | IS: 2386 (Part III) – 1963           |       |       |                              |
| Compaction characteristics (Proctor test)      | MDD – 1.78 g/cc; OMC – 13.72%   |   | IS: 2720 (Part III) – 1986           |       |       |                              |
| Shape test (flakiness, elongation, angularity) | Flakiness: 53%; elongation: 8.8%; angularity: size is not available, material size considered: 6.3 mm and above; available max. size 25.0 mm  |   | IS: 2386 (Part I) – 1963             |       |       |                              |
| Crushing value                                 | Crushing: 40.02%  |   | IS: 2386 (Part IV) – 1963            |       |       |                              |
| Specific gravity                               | Specific gravity = 2.79   |   | IS: 2720 Part III Sec 2 – 1980       |       |       |                              |
| pH value                                       | pH = 8.98   |   | IS: 2720 (Part I) – 1983             |       |       |                              |
| Cation exchange capacity                       | 16 meq/100g   |   | IS: 2720-24 (Part XXIV) – 1976       |       |       |                              |
| Direct shear test                              | $c = 0$ and $\phi = 38^\circ$   |   | IS: 2720 (Part XXXIX) – 1977         |       |       |                              |
|  |   |   | Ratio taken 1 : 3<br>(cement : slag) |       |       |                              |
|  | Results on  | Cement taken  |                                      | Limit |       |                              |
| Compressive strength (N/mm <sup>2</sup> )      | 7 days  | OPC 43 Grade  | 29.00                                | 27.67 | 33.00 | IS: 2720 (Part XVI) – 1986   |
| California bearing ratio                       |   |   | 26.40                                |       |       |                              |
|  |   |   | 27.60                                |       |       |                              |
| California bearing ratio                       | Unsoaked  | At 2.50 mm penetration: 23.20%;<br>At 5.00 mm penetration: 21.80% |                                      |       |       | IS: 2720 (Part XVI) – 1986   |
|  | Soaked  | At 2.50 mm penetration: 20.20%;<br>At 5.00 mm penetration: 18.80% |                                      |       |       |                              |
| Abrasive value                                 | Abrasion: 16.30%  |   |                                      |       |       | IS: 2386 (Part IV) – 1963    |
| Impact value                                   | Trial 1: 21.00%; Trial 2: 25.72%  |   |                                      |       |       | IS: 2386 (Part IV) – 1963    |
| Relative density                               | $\gamma_{min}$ : 1.45 g/cc, $\gamma_{max}$ : 1.75 g/cc;<br>Relative density: 1.65 g/cc  |   |                                      |       |       | IS: 2386 (Part III) – 1963   |
| Shear strength (parameters)                    | $c = 0$ and $\phi = 38^\circ$   |   |                                      |       |       | IS: 2720 (Part XXXIX) – 1977 |
| Free swelling index                            | Nil   |   |                                      |       |       | IS: 2720, Part XL            |
| Atterberg limit test                           | Non-plastic material  |   |                                      |       |       | IS: 2720, Part V             |

**Table 5.** Compressive strength of used FeCr slag

| Parameter                                 | Results |              |                                       |         |                              |
|---|---------|--------------|---------------------------------------|---------|------------------------------|
| Compressive strength (N/mm <sup>2</sup> ) | 7 days  | Cement taken | Ration taken 1 : 3<br>(cement : slag) | Average | Limit (as per IS: 8112–1989) |
|   |         | OPC 43 grade | 28.76                                 | 29.40   | 33                           |
|   |         |              | 29.78                                 |         |                              |
|   |         |              | 29.67                                 |         |                              |

All of the parameters were almost in agreement with IS values and so the slag is usable in road making. It has excellent compaction characteristics and swelling index is nil. Only concern is with the specific gravity value which was found marginally higher with respect to the standard value and it should be taken into consideration during design. Another promising result found was that, after reduction reaction used FeCr slag with cement in 3 : 1 ratio, it showed good compressive strength (27 N/mm<sup>2</sup>). It could be used as a construction material if compressive strength is increased to 33 N/mm<sup>2</sup> (Table 5). Lind *et al.*<sup>38</sup> and Ferreira *et al.*<sup>43</sup> showed the use and environmental impact of steel slags as secondary raw material in road construction.

## Conclusion

Valuable utilization of FeCr slag was a challenging task for us. Experimental data inferred that FeCr slag could be utilized as an effective reducing agent of Cr(VI) for chromite mining wastewater. About 99% Cr(VI) removal is accomplished with the help of FeCr slag. The mechanism behind the reduction reaction is *in situ* generation of ferrous sulphate by addition of small amount of oxidizing agent which helps to reduce the hexavalent chromium to trivalent chromium in water. Leaching analysis also supported that the used slag could be utilized as land filling material. Geotechnical data revealed that after reduction, used FeCr slag in combination with cement in 3 : 1 ratio can be used in landfill. This cost-effective system saves high chemical expenditure and can be employed even in remote areas without any basic infrastructure. TCLP data also supported that this waste is non-hazardous.

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ACKNOWLEDGEMENTS. We thank the Research and Development of Tata Steel and the Department of Civil Engineering, Jadavpur University, Kolkata for the help and support.

Received 3 July 2018; revised accepted 28 January 2019

doi: 10.18520/cs/v116/i9/1515-1524