

## Hexavalent chromium removal by ferrochromium slag

Mehmet Erdem<sup>a</sup>, H. Soner Altundoğan<sup>b</sup>, M. Deniz Turan<sup>b</sup>, Fikret Tümen<sup>b,\*</sup>

<sup>a</sup> Department of Environmental Engineering, Firat University, 23279 Elazığ, Turkey

<sup>b</sup> Department of Chemical Engineering, Firat University, 23279 Elazığ, Turkey

Received 17 March 2005; received in revised form 20 June 2005; accepted 23 June 2005

Available online 10 August 2005

### Abstract

The aim of this study is to demonstrate the potential of Cr(VI) generation during jigging operation applied for ferrochrome recovery from slag. The Cr(VI) concentrations of water contacted with ferrochromium slag (W/FS = 10) in a closed cycle after 50 batches were found as 0.61 mg/l. Also, reduction of Cr(VI) to Cr(III) and a subsequent precipitation of Cr(III) by using ferrochrome slag (FS) in a model solution has been aimed. The effects of amount of acid, contact time, FS dosage, initial Cr(VI) concentration and temperature on the Cr(VI) reduction have been studied through the batch runs. The amount of acid has been found to be the most effective parameter affecting the Cr(VI) reduction. A 10 g/l FS dosage and 3.5 ml/l H<sub>2</sub>SO<sub>4</sub> (5 M) are sufficient to reduce all Cr(VI) in the model solution containing 10 mg/l Cr(VI) and for contact time of 60 min at 25 °C. In reduced solutions, precipitation of metal ions has been studied by using extra FS. A 60 g/l dosage of fresh FS can precipitate all Cr(III) and Fe ions in the reduced solution. Thus, it has been demonstrated that the treatment of jigging water stream to be generated in a ferrochrome plant containing Cr(VI) can be accomplished by using ferrochromium slag and sulphuric acid. Also, it has been determined that solid residues of the process are environmentally stable by applying TCLP test.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Hexavalent chromium; Reduction; Ferrochromium slag; Heavy metal removal; TCLP

### 1. Introduction

Ferrochromium is a master alloy of iron and chromium, containing 45–80% Cr and various amounts of Fe, C and other elements. Ferrochromium is produced pyrometallurgically by carbothermic reduction of chromite ore (FeO·Cr<sub>2</sub>O<sub>3</sub>). The main slag additives used are quartzite and aluminium oxide containing materials to compensate for the high magnesium content in certain ores, and magnesium and calcium oxide containing materials for aluminium rich ores. The ferrochromium slags consist mainly of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and MgO in different phases such as spinel, MgO·Al<sub>2</sub>O<sub>3</sub>, and forsterite, MgO·SiO<sub>2</sub>, but also smaller amounts of CaO, chromium and iron oxides and metal fragments. The chromium content in slags is 2–12%, in oxide and metal form. The slag/metal

amount ratio in smelting varies from 1.0 to 1.8, depending on raw materials [1].

Slag is discarded as a waste material in enormous quantities during the ferrochrome production. A relatively small percentage of this material finds application, but the vast majority of material generated each year is held in dumps and as land disposing costs increase, new disposal options are needed. As an alternative to land disposal, considering chemically inert and safe, slag has been used as construction materials and aggregate due to its excellent technical material properties [2–4].

Alternatively, reclaiming ferrochromium metal entrapped in slag seems to be economic. In order to recover metal, slag has been crushed and subjected to wet magnetic and gravimetric methods [1,5]. All of these might be good ideas, however, slags can contain high levels of extractable toxic elements which could pose environmental problem. In a study dealing with the process water of metal recovery from slag, it has been reported that Cr has been detected as chromate in

\* Corresponding author. Tel.: +90 424 2370000/3643; fax: +90 424 2415526.

E-mail address: ftumen@firat.edu.tr (F. Tümen).

the processing water, which may create chromium pollution [6]. In another study, it has been reported that milling practice of ferrochromium slag could alter the oxidation state of chromium and cause the threat of Cr(VI) releasing [7]. On the other hand, it has been indicated that other solid wastes such as bag filter dust or its sludge produced during the ferrochromium production contain high levels of soluble hexavalent chromium [8–11]. Since these materials are considered as hazardous pollutants, their fixation and stabilization characteristics have also been studied [12–15]. The production of ferrochromium and stainless steel has been mentioned among the greatest contributors to atmospheric emission of chromium [16]. These facts show that ferrochromium production is a source of Cr(VI) pollution which can threaten the environment.

Chromium contamination of soil and water is a significant problem since hexavalent form of chromium is highly toxic, mutagenic and potentially carcinogenic to living organisms [17,18]. The most stable oxidation states of chromium are Cr(III) and Cr(VI) in aqueous systems. The trivalent chromium is quite immobile in the water environment because of limited solubility of its hydroxide, which is readily formed in the pH range of natural waters. Because of the benign character of Cr(III), detoxification and immobilisation processes of Cr(VI) is based on its reduction to Cr(III). Conventionally, the reduction of Cr(VI) is performed by using SO<sub>2</sub> and sulphite salts and ferrous sulphate in the treatment processes practised [19–22].

For hexavalent chromium treatment of ferrochromium recovery process water, FeSO<sub>4</sub> reduction and coke adsorption processes have been applied as a model solution [6]. In the mentioned study, chromium reduction properties of ferrochromium slag have also been found out. This fact brings to mind the idea that the treatment of jigging water containing Cr(VI) may be accomplished by using ferrochromium slag. It is worthy to investigate Cr(VI) reduction by using ferrochromium slag which contains iron and chromium mostly in metallic state as reductants. Further, oxide and silicate matrix of slag may partly adsorb chromates. Additionally, after reduction, in a following step another portion of slag may be used to neutralize the reduced solution in order to precipitate Cr(III) formed. That this waste has no cost and is readily available material in the ferrochromium plant may constitute an advantage. With economic point of view, in our earlier works, we have studied Cr(VI) reduction by some solid reductants such as copper smelter slag [23], steel wool [24], pyrite [25], synthetic iron sulphide [26] and siderite [27] which are cheap materials.

In this study, the use of ferrochrome slag for the reduction of Cr(VI) in the outlet water of ferrochrome reclaiming process was explored. For this purpose, firstly, chromium dissolution from ferrochromium slag contacted with water was tested. Then, amounts of sulphuric acid and ferrochromium slag on the reduction of Cr(VI) in a hypothetical model outlet water were studied.

## 2. Materials and methods

### 2.1. Material

#### 2.1.1. Ferrochromium slag

Ferrochrome slag (FS) samples were provided from Elazığ Ferrochrome Plant of Etiholding (Turkey). FS was crushed to <1.2 mm (16 mesh). A portion of crushed FS sample was grinded and screened from a 200 mesh (75 μm) screen. Both FS samples (<16 and <200 mesh) were used for obtaining model outlet water of jigging. Less than 75 μm fraction (<200 mesh) of FS was used for Cr(VI) reduction study. The XRF analysis of FS sample was given in Table 1.

#### 2.1.2. Cr(VI) solutions

A 1 g/l Cr(VI) stock solution was prepared by using K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. All working solutions in different concentrations were prepared by diluting the stock solution with distilled water.

### 2.2. Methods

#### 2.2.1. Model of jigging outlet water

A 5 l of tap water was mixed with 500 g of crushed original FS sample [W/FS ratio (w/w) = 10]. This mixture was reciprocally shaken for 2 h. The water was separated from solid by decanting. The water obtained at washing operation was mixed with a fresh portion of FS in the ratio of 10. This mixture was shaken for 2 h. A 50 ml water sample was pipetted at the end of each fifth batch. This procedure was sequentially repeated 50 times by keeping the W/FS ratio of 10 and contact time of 2 h. Water samples drawn at every fifth stage were subjected to pH measurements and Cr(VI), total Cr and Fe analyses. This test was also repeated for grinded FS sample.

#### 2.2.2. Hypothesis of reduction process

Our preliminary tests showed that Cr(VI) could be reduced in the aqueous solution by slag in acidic conditions. The reduction of hexavalent chromium by metallic components of slag in acidic solutions can be expressed by following equation:

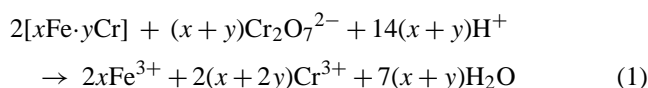
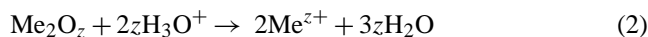


Table 1  
Chemical composition of ferrochromium slag (FS) sample

Constituent	%
Fe	1.40
Cr	5.20
SiO <sub>2</sub>	28.89
Al <sub>2</sub> O <sub>3</sub>	29.64
MgO	31.51
CaO	0.50

where  $x$  and  $y$  are stoichiometric coefficients. It must be denoted that the amount of acid to be used in reduction process is the most important parameter because of the fact that the basic components of slag can also consume acid by simultaneous reaction depicted by Eq. (2):



where Me is a metal i.e. Ca, Mg, Al or others present in oxide form and  $z$  is a stoichiometric coefficient depending on oxidation state of metal.

### 2.2.3. Reduction study

To prepare a working solution in desired Cr(VI) concentration having various amount of acid, appropriate volumes of stock Cr(VI) solution (1000 mg/l) and  $\text{H}_2\text{SO}_4$  solution (5 M) was mixed and made up to 250 ml with distilled water. Predetermined amount of FS was added to the solution prepared. The flask was capped and the mixture was shaken at a rate of 200 rpm. After a predetermined period, a 10 ml sample representing mixture was drawn by automatic pipette. The mixture was filtered by using S&S 589 filter paper. The supernatants were analyzed. Controls without solid were also run in parallel. All experiments were performed in duplicate and the mean values were taken. The values obtained in duplicates were found to vary within  $\pm 5\%$ .

### 2.2.4. Precipitation study

In order to precipitate metal ions in the solution obtained from Cr(VI) reduction study, usability of FS having basic property as a precipitation reagent was tested. For this purpose, different dosages of FS were added to the solutions and mixtures were shaken for 60 min and then they were filtered and analyzed for metal ions.

### 2.2.5. TCLP tests

The toxicity characteristics leaching procedure (TCLP) test method was applied to see the leaching behaviour of chromium from FS and solid residues of reduction and precipitation processes. For this purpose, 100 g of sample was placed in a plastic bottle together with 2000 ml of leach solution, sodium acetate/acetic acid buffer solution, pH of which is 4.93. The mixture was then agitated at 18 rpm for 24 h. The mixture was filtered through a  $0.45 \mu\text{m}$  glass fibre filter and the filtrate obtained was analyzed [28].

### 2.2.6. Methods of analysis

Ferrochromium slag samples were analyzed by XRF spectrometer (Rigaku) in Etiholding Ferrochromium Plant. Model outlet water of ferrochromium concentration process and solutions obtained in reduction study were analyzed by spectrophotometer (Shimadzu UV 1201) using diphenyl carbazide method for Cr(VI), by atomic absorption spectrophotometer (Perkin-Elmer 370) for Fe and total Cr [29]. pH measurements were done by a pH meter (Mettler Delta 350). Standard solutions were prepared by using

analytical chemicals. All dilutions were made by distilled water.

## 3. Results and discussion

### 3.1. Results of TCLP test

Toxicity characteristic leach procedure (TCLP) tests showed that Cr concentration in TCLP extracts obtained from crushed and grinded ferrochromium slag (FS) samples are 0.54 and 0.80 mg/l, respectively, that meet the US EPA limits of 5 mg/l for chromium. This result is in agreement with the results reported by Gericke [9] for various ferrochromium slags. According to TCLP test results, it can be concluded that the ferrochromium slag is not a potential pollutant.

### 3.2. Results of sequential washing of FS

In order to see the concentration value to be achieved after certain batches, the solubilization of chromium from FS was systematically tested by sequential washings in which fresh FS samples were contacted with a same water sample at a water/FS ratio of 10 for 50 batches. The concentrations of Cr(VI) of each fifth extract drawn is shown in Table 2. Cr(VI) and total chromium concentrations of the final extracts have been found in very close range ( $\pm 3\%$ ) that implies the chromium in the extracts exists mostly in hexavalent form. The sequential batch washing experiment applied as a model of ferrochromium reclaiming operation showed that concentration of Cr(VI) increased with batch number. The Cr(VI) concentrations of water contacted with FS in a closed cycle after 50 batches were found as 0.61 and 3.80 mg/l for crushed FS ( $<1.2 \text{ mm}$ ) and grinded FS ( $<75 \mu\text{m}$ ), respectively. These results show that outlet water of jigging operation causes a chromium pollution that it has to be prevented. This fact necessitates that water effluent of jigging must be reused in a closed cycle and final effluent must be treated for Cr(VI) removal. It is a surprising result that a trace amount of chro-

Table 2  
Cr(VI) Concentration and pH of water sequentially contacted with FS

Batch no.	Cr(VI) concentration (mg/l)		pH	
	Crushed FS ( $<1.2 \text{ mm}$ )	Grinded FS ( $<75 \mu\text{m}$ )	Crushed FS ( $<1.2 \text{ mm}$ )	Grinded FS ( $<75 \mu\text{m}$ )
5	<sup>a</sup>	0.41	8.78	9.95
10	0.14	0.76	8.87	10.20
15	0.19	1.20	8.96	10.22
20	0.26	1.52	9.11	10.24
25	0.32	1.87	9.15	10.22
30	0.39	2.29	9.24	10.21
35	0.46	2.73	9.30	10.22
40	0.52	3.12	9.37	10.24
45	0.57	3.46	9.40	10.25
50	0.61	3.80	9.38	10.23

<sup>a</sup> Under detection limit.

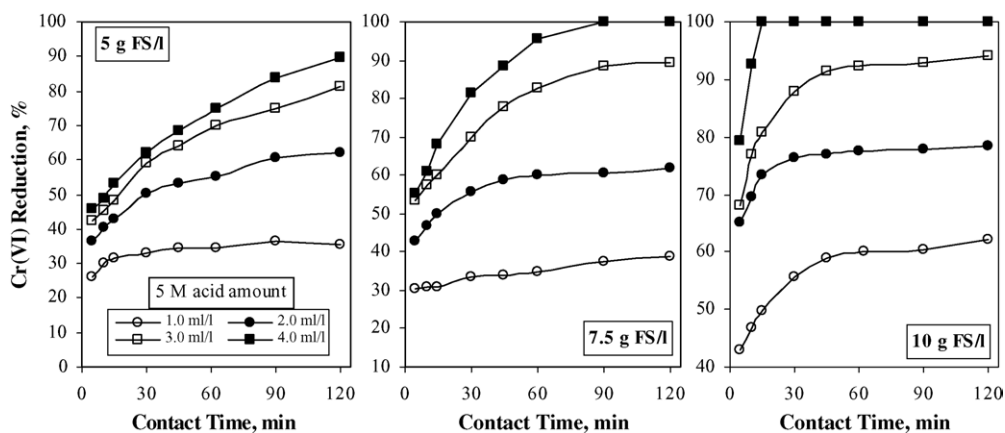


Fig. 1. Effects of acid amount, FS dosage and contact time on the Cr(VI) reduction [initial Cr(VI) concentration: 10 mg/l; temperature: 25 °C; acid concentration: 5 M].

mate compound generates during smelting in spite of strong reductive conditions. However, Beukes and Guest [7] have reported a similar result that has been explained as the milling practice of ferrochromium slag could alter the oxidation state of chromium. In crushing and grinding operations, the atmospheric oxygen and also the heat evolving by the result of friction may cause or contribute to a partial oxidation of metallic or oxidic chromium in FS. That the chromium concentration of the extracts obtained from grinded FS is much

higher than that of crushed FS confirms the results reported by Beukes and Guest [7].

### 3.3. Effects of acid amount, FS dosage and contact time

The reduction of Cr(VI) in the synthetic solutions with ferrochromium slag was systematically investigated under various conditions. In a series of experiments, different amounts of H<sub>2</sub>SO<sub>4</sub> solution (5 M) was added to a 10 mg/l Cr(VI) solu-

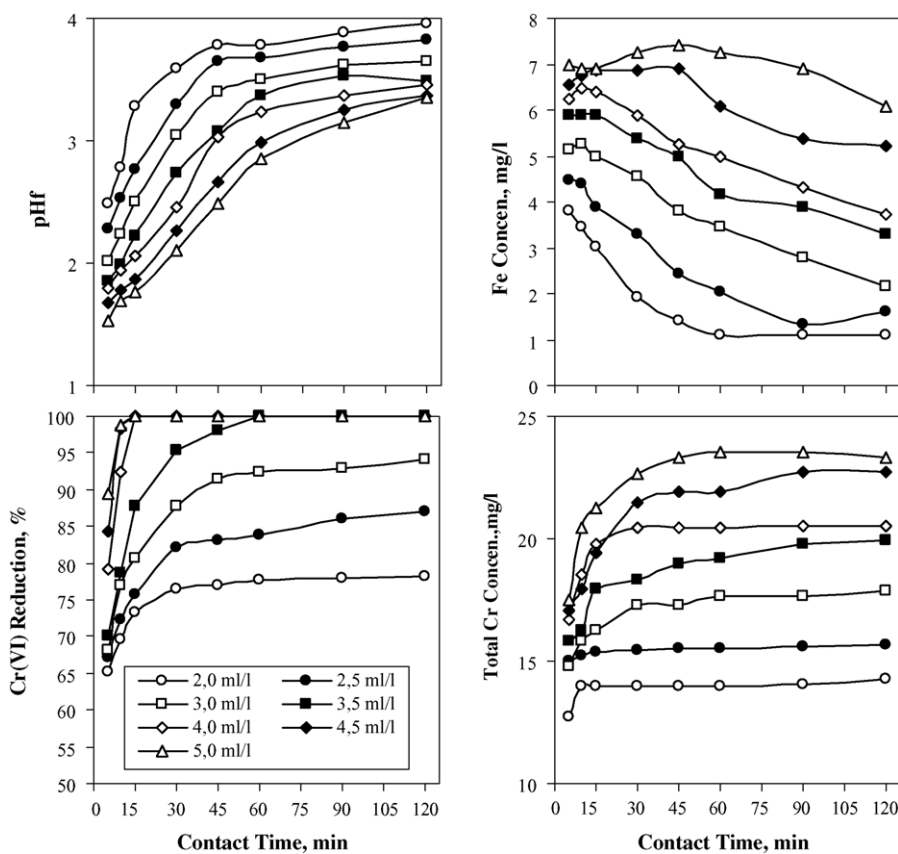


Fig. 2. The variations of Cr(VI) reduction, final pH, Fe and total Cr concentrations with contact time depending on acid amount [initial Cr(VI) concentration: 10 mg/l; FS dosage: 10 g/l; temperature: 25 °C].

tion and various FS dosage were tested for Cr(VI) reduction. The results obtained for various contact time are given in Fig. 1. As seen from the figure, increasing FS dosage and the amount of acid increases the reduction percentage of Cr(VI) for a certain contact time. Contact time is another important parameter causing an increase in Cr(VI) reduction. In the presence of 4.0 ml/l 5 M H<sub>2</sub>SO<sub>4</sub>, 5 g/l of FS dosage could reduce Cr(VI) about 90% for a contact time of 120 min, doubling the dosage causes a complete reduction within a short period of 15 min. It is clearly seen that contact time of 60 min is sufficient for an efficient reduction for most of the FS dosages studied.

Because the FS is cheaper material than H<sub>2</sub>SO<sub>4</sub>, for such a process, the amount of H<sub>2</sub>SO<sub>4</sub> must be firstly optimized. For this purpose, 10 g/l FS dosage was selected and the effect of acid amount was studied in the range of 2.0–5.0 ml/l by increasing the amount of H<sub>2</sub>SO<sub>4</sub> (5 M) in 0.5 ml/l increments. In these experiments, final pH was measured and Fe and total Cr were analyzed in the reduced solutions. The results are shown in Fig. 2.

The efficient reductions were obtained for acid amounts more than 3 ml/l. As seen, the more acid amount were used the shortened reduction period were obtained for whole Cr(VI) reduction. For a 100% reduction, 60 min is required with 3.5 ml/l acid (5 M), whereas a contact time of 15 min is sufficient with a 4.0 ml/l acid. Total Cr concentration of reduced

solution are found to be more than 10 mg/l which is initial Cr(VI) concentration. As expected, metallic Cr in FS is oxidized to Cr(III) when it reduces Cr(VI) to Cr(III), and thus, final total Cr concentrations raises to the values more than 20 mg/l. For 2–4 ml/l acid, at the beginning of contact time, Fe concentrations of reduced solutions are estimated in the range of 4–7 mg/l. After a while, a decrease in Fe concentration, on the contrary, an increase in final pH of solutions is observed. This can be explained by the reaction of basic constituents of FS between excess acid present in solution. Consequently, Fe solubilized in the initial period may be converted into hydroxo iron species by hydrolysis as neutralization reactions progress.

From the results, it can be stated that the reduction of Cr(VI) by FS is strongly acid dependent. On the other hand, the basic constituents of FS such as calcium, magnesium and aluminium oxides consume acid. For this reason, excessive acid more than stoichiometry of Eq. (1) may be required.

In order to see the effect of initial Cr(VI) concentration, the solutions containing Cr(VI) in the range of 5–25 mg/l and 3.5 ml/l acid (5 M) was contacted with FS in the dosage of 10 g/l for various periods. The results are given in Fig. 3. It can be seen that a FS dosage of 10 g/l can effectively reduce the Cr(VI) in the concentration of 5 and 10 mg/l in the presence of 3.5 ml/l H<sub>2</sub>SO<sub>4</sub> (5 M). However, for a 15 mg/l Cr(VI), the reduction could not be completed even for a contact time of

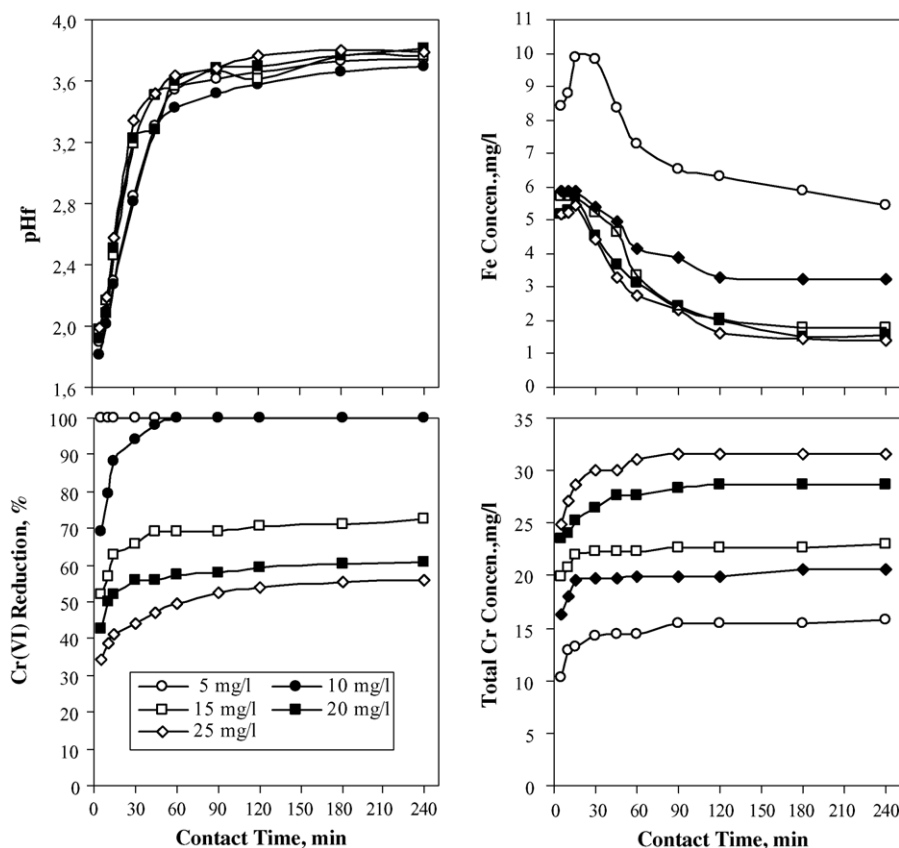


Fig. 3. Effects of Cr(VI) initial concentration and contact time on the Cr(VI) reduction [FS dosage: 10 g/l; acid amount: 3.5 ml/l H<sub>2</sub>SO<sub>4</sub> (5 M); temperature: 25 °C].



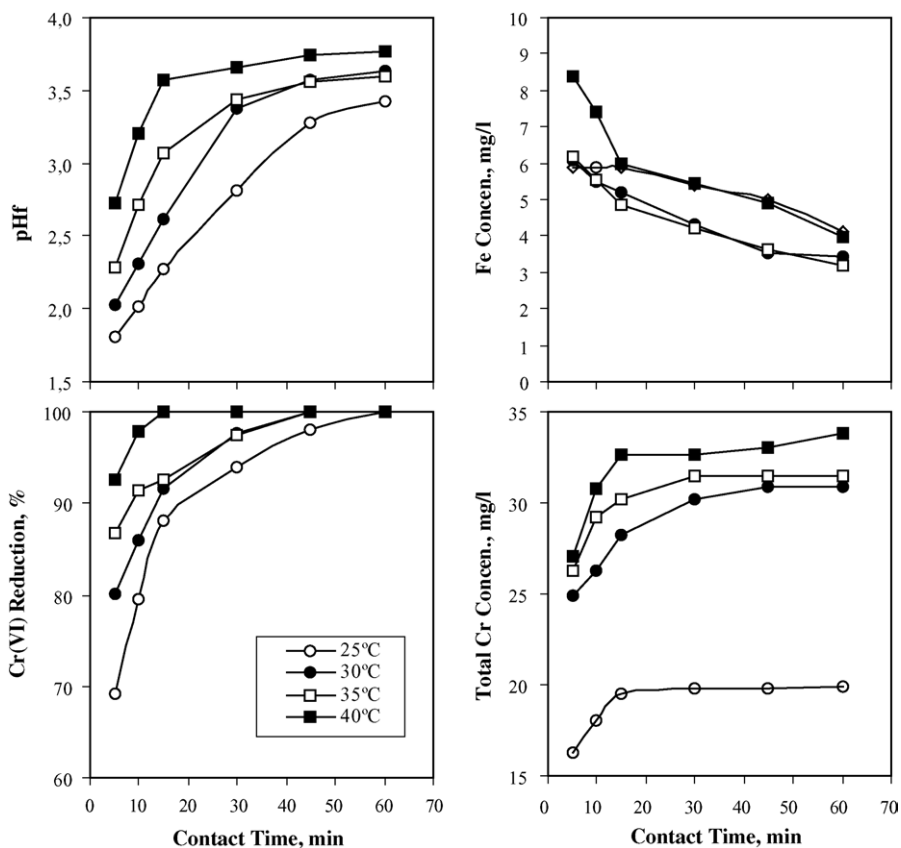


Fig. 4. Effects of temperature and contact time on the Cr(VI) reduction [initial Cr(VI) concentration: 10 mg/l; FS dosage: 10 g/l; acid amount: 3.5 ml/l H<sub>2</sub>SO<sub>4</sub> (5 M)].

240 min. pH of final solutions was measured in the close range of 3.6–3.8. This may show the effect of basic constituents of FS which is present in the same amount (10 g/l) that neutralize the certain amount of acid present (3.5 ml/l) in the solution contacted in the period of 240 min. Reduction reaction rapidly occur in the initial period that the acid is not consumed yet. From Fig. 3, it is clearly seen that reduction reaches to a plateau within a period of 30 min, beyond this point, reduction performs very slowly. Decreasing Fe values are observed and this fact strengthens the hydrolysis idea.

The effect of temperature on the reduction of Cr(VI) by FS is shown in Fig. 4. As seen, temperature has a positive effect on the reduction. For example, the reduction is accomplished within about 15 min of contact time at 40 °C, whereas 60 min is required for a completed reduction of Cr(VI) in the initial concentration of 10 mg/l at 25 °C. Fe concentration decreases in similar trend with increasing temperature and contact time.

By using FS, precipitation experiments were run in reduced solutions. In these tests, firstly, 10 mg/l Cr(VI) solutions were reduced by a 10 g/l FS at the conditions of 3.5 ml/l H<sub>2</sub>SO<sub>4</sub> (5 M), 25 °C and 60 min. At the end of the reduction, a weighed amount of fresh FS was added to the reduced solution and contacted by shaking for another period of 60 min. pH measurements and metal analyses were done in final solutions. The results are shown in Fig. 5. It can be stated that FS

can precipitate Cr(III) and Fe ions in the solution. As seen from figure, an increase in FS dosage results an increase in final pH and a decrease in Cr(III) and Fe concentrations. A 40 g/l FS dosage could precipitate almost all Cr and Fe ions in the solution. In this dosage, final pH of solution was measured as over 6.

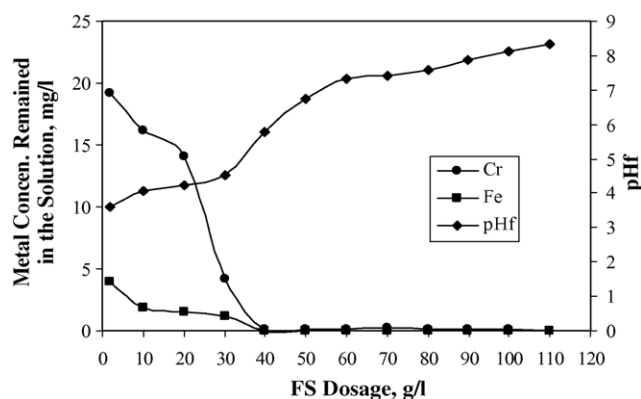


Fig. 5. Effect of FS dosage on the Cr(III) and iron precipitation in the reduced solution. [The reduced solution was obtained by contacting the 10 mg/l Cr(VI) solution with FS (10 g/l) for 60 min in the 3.5 ml/l acid presence at 25 °C. In this solution, initial total Cr concentration was 20.4 mg/l and iron concentration was about 6 mg/l.]

Finally, TCLP tests conducted for the solid residues, contain Cr(III) and Fe(III), from reduction and precipitation processes showed that concentrations of the chromium dissolved from both samples are 0.40 and 0.75 mg/l, respectively, which are well below the 5 mg/l limit for TCLP specified by USEPA. Therefore, it can be noted that the solid wastes remained in the reduction–precipitation process applied are environmentally stable.

#### 4. Conclusions

This study has shown that the outlet water of jigging operation applied for ferrochromium reclamation from slag may contain Cr(VI) in significant level. This investigation has demonstrated that the reduction of Cr(VI) and the precipitation of Cr(III) and Fe ions formed can be accomplished by using fine ferrochromium slag (FS). The reduction of Cr(VI) by FS is strongly governed by the amount of acid. Consequently, it can be stated that the use of ferrochromium slag for the removal of Cr(VI) from jigging water may be a cost-effective alternative. For this process, H<sub>2</sub>SO<sub>4</sub> is solely material to be provided.

#### Acknowledgements

The authors gratefully acknowledge the analytical support of Etiholding which was the owner of Elazığ Ferrochrome Plant in 2002 year. We express our thanks to the student Ümit Karagöz for his help in conducting the experiments.

#### References

- [1] M. Riekkola-Vanhanen, Finnish expert report on best available techniques in ferrochromium production The Finnish Environment, vol. 314, Finnish Environment Institute, Helsinki, 1999, 51 pp.
- [2] S. Igarashi, M. Kawamura, N. Arano, S. Kawaguchi, Alkali reactivity of high carbon ferrochromium slag and its applicability as an aggregate for concrete, in: Proceedings of the 10th International Congress on the Chemistry of Cement, vol. 4, No. iv051, 1997, 4 pp.
- [3] S. Igarashi, M. Kawamura, Arano, S. Kawaguchi, Mechanical properties of mortar containing high-carbon ferrochromium slag as an aggregate, in: Proceedings of the International Conference on Engineering Materials, Ottawa, Canada, 1997, pp. 63–71.
- [4] H. Motz, J. Geiseler, Products of steel slags an opportunity to save natural resources, Waste Manage. 21 (2001) 285.
- [5] H.P. Mashanyare, R.N. Guest, The recovery of ferrochrome slag at Zimaco, Miner. Eng. 10 (1997) 1253.
- [6] G. Coetzer, E.W. Giesekke, R.N. Guest, Hexavalent chromium in the recovery of ferrochromium from slag, Can. Metall. Quart. 36 (1997) 261.
- [7] J.P. Beukes, R.N. Guest, Cr(VI) generation during milling, Miner. Eng. 14 (2001) 423.
- [8] J.P. Beukes, J.J. Pienaar, G. Lachmann, E.W. Giesekke, The reduction of hexavalent chromium by sulphite in wastewater, Water SA 25 (1999) 363.
- [9] W.A. Gericke, Environmental solutions to waste products from ferrochrome production, in: Proceedings of the Eighth International Ferroalloys Congress (INFACON 8), Session A, Beijing, China, June 7–10, 1998, pp. 51–58.
- [10] B. Cohen, J.G. Petrie, Containment of chromium and zinc in ferrochromium flue dusts by cement-based solidification, Can. Metall. Quart. 36 (1997) 251.
- [11] W.A. Gericke, Environmental aspects of ferrochromium production, in: Proceedings of the INFACON 7, Trondheim, Norway, 1995, pp. 131–140.
- [12] J.P. Smit, E.W. Giesekke, R.J. Mogoai, Fixation and stabilisation of Cr(VI) and soluble salts from the ferrochromium industry in cement bricks, in: S.R. Rao, L.M. Amaratunga, G.G. Richards, P.D. Kondos (Eds.), Waste Processing and Recycling in Mineral and Metallurgical Industries III, The Metallurgical Society of CIM, 1998, p. 13.
- [13] E.W. Giesekke, Mineral-based treatment strategies for wastes and effluents, S. Afr. J. Sci. 95 (1999) 367.
- [14] E.W. Giesekke, J.P. Smit, E.A. Viljoen, A.W. Kruger, S.J. Kruger, C.F. Maine, Evaluation of solid-stabilized products made from Cr(VI)-containing ferrochrome bag-filter dust, in: Proceedings of the WASCON 2000, Leeds, UK, May 30–June 2, 2000.
- [15] B.B. Lind, A.-M. Fallman, L.B. Larsson, Environmental impact of ferrochrome slag in road construction, Waste Manage. 21 (2001) 255.
- [16] A.B. Mukherjee, Chromium in the environment of Finland, Sci. Total Environ. 217 (1998) 9.
- [17] A. Leonard, R.R. Lauwerys, Carcinogenicity and mutagenicity of chromium, Mutat. Res./Rev. Genet. Toxicol. 76 (1980) 227.
- [18] J.W. Moore, S. Ramamoorthy, Heavy Metals in Natural Waters, Springer-Verlag, New York, 1983.
- [19] M. Sittig, Pollution Removal Handbook, Noyes Data Corp., UK, 1973.
- [20] J.W. Patterson, Industrial Wastewater Treatment Technology, Butterworths Publishers, Stoneham, MA, 1975.
- [21] W.W. Eckenfelder, Industrial Water Pollution Control, McGraw-Hill Book Co., New York, 1984.
- [22] J. Kotas, Z. Stasicka, Chromium occurrence in the environment and methods of its speciation, Environ. Pollut. 10 (2000) 263.
- [23] B. Kiyak, A. Özer, A. Altundoğan, M. Erdem, F. Tümen, Cr(VI) reduction in aqueous solutions by using copper smelter slag, Waste Manage. 19 (1999) 333.
- [24] A. Özer, H.S. Altundoğan, M. Erdem, F. Tümen, A study on the Cr(VI) removal from aqueous solutions by steel wool, Environ. Pollut. 97 (1997) 107.
- [25] M. Erdem, F. Tümen, Cr(VI) reduction in aqueous solutions by using pyrite, Tr. J. Eng. Environ. Sci. 20 (1996) 363 (in Turkish).
- [26] M. Erdem, H.S. Altundoğan, A. Özer, F. Tümen, Cr(VI) reduction in aqueous solutions by using synthetic iron sulphide, Environ. Technol. 22 (2001) 1213.
- [27] M. Erdem, F. Gür, F. Tümen, Cr(VI) reduction in aqueous solutions by siderite, J. Hazard. Mater. 113 (1–3) (2004) 217.
- [28] USEPA, Toxicity characterisation leaching procedure (TCLP), EPA Method 1311, Washington, USA, 1990.
- [29] APHA, AWWA, WPCF, Standard Methods for Examination of Water and Wastewater, 17th ed., American Public Health Association/Port City Press, Washington, DC, 1989.