



# Cr(VI) reduction in aqueous solutions by using copper smelter slag

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## Abstract

The ability of Copper Smelter Slag (CSS) to reduce Cr(VI) in aqueous solutions has been investigated. The extent of reduction is dependent on the amounts of acid and reductant, contact time, Cr(VI) concentration, temperature of the solution and particle size of CSS. The amount of acid is the most important variable affecting the reduction process. When twice the amount of acid required with respect to Cr(VI) was used, Cr(VI) in 100 ml solution (100 mg/l) was completely reduced in a contact period less than 5 min by a 10 g/l dosage of CSS. Reduction efficiency increased with increase in temperature of solution, showing that the process is endothermic. Reduced chromium, and iron and other metals dissolved from CSS were effectively precipitated by using NaOH or calcinated carbonatation sludge from sugar plant. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Copper smelter slag; Carbonatation sludge; Cr(VI) reduction; Chromium removal

## 1. Introduction

It is known that chromium belongs to a heavy metal group of very high pollution potential. In aqueous systems, it is found in both trivalent and hexavalent forms; the latter is of particular concern due to its higher toxicity and carcinogenic effect. The major sources of Cr(VI) are electroplating, tanning, wood preservation and preparation of chromate compounds. It is also discharged from cooling tower blowdowns.

Removal of Cr(VI) from wastewaters usually consists of a two stage process, first, the reduction of Cr(VI) to Cr(III) and, second, precipitation of the Cr(III) [1–4]. The standard reduction treatment technique is to adjust pH to 3.0 or below with sulphuric acid, and convert the Cr(VI) to Cr(III) with a chemical reducing agent such as sulphur dioxide, various sulphite compounds or ferrous sulphate [2]. Several reports describe the use of solid iron sources such as magnetite [5], iron sulphides [6,7] and metallic iron [8–12] as a Cr(VI) reducing agent in aqueous solutions.

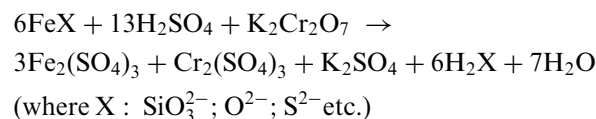
Iron silicate slag formed during the matte smelting stage of copper production is an alternate Fe(II) source. The use of smelter slag in the Cr(VI) reduction process

appears to be attractive because of its low-cost. The aim of this study is to investigate the CSS capability to reduce Cr(VI) in the aqueous system.

## 2. Experimental

Reverberatory slag of the Etibank Ergani Copper Plant, Elazığ-Turkey, was used in the study. The slag in the form of granules was ground and sieved to obtain various fractions. A representative slag sample was analyzed by atomic absorption spectrophotometer (Perkin–Elmer 370) utilizing the lithium metaborate fusion-nitric acid dissolution route [13]. The chemical composition of the slag is given in Table 1. XRD analysis showed that the slag was in amorphous form.

First, it was assumed that all iron in the slag was in Fe(II) form and the following reaction would take place in the reduction process.



(1)

From the standpoint of the presence of excess iron originating from slag placed in a reaction vessel, the amount of acid calculated based on chromium according

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Table 1  
Chemical analysis of slag

Constituent	Amount	Constituent	Amount
Fe	39.65%	Cu	1.01%
SiO <sub>2</sub>	31.94%	Co	1040 mg/kg
CaO	3.95%	Mn	420 mg/kg
MgO	2.82%	Ni	150 mg/kg
Al <sub>2</sub> O <sub>3</sub>	2.40%	Zn	7220 mg/kg

to Eq. (1) was named as '1 stoichiometric acid'. Experimental dichromate solutions in various Cr(VI) and acid concentrations were prepared by combining 10 g/l stock Cr(VI) solution and sulphuric acid for predetermined conditions.

The Cr(VI) reduction experiments were carried out in 150 ml glass flasks into which 100 ml of acidic dichromate solutions were placed. A weighed amount of slag was added to the solutions. The flasks were capped tightly, immersed in a temperature controlled water bath and then shaken mechanically at the rate of  $500 \pm 50$  cycle/min for a contact period varying from 5 to 240 min. At the end of the predetermined shaking period, flask contents were filtered and final pH of the solution was measured. Cr(VI) was determined spectrophotometrically by using the diphenyl carbazide method [14]. A portion of filtrate was acidified by nitric acid and retained for analyses of metals released from CSS. All experiments were performed with the -200 mesh (-74  $\mu$ m) slag fraction, except those relating to the effect of particle size on the reduction. In addition, the reduction capacity of CSS was determined by treating successively the 1.0 g CSS with 100 ml solution of 100 mg Cr(VI)/l and 1.5 stoichiometric acid content for 45 min until its reduction efficiency was dropped under a value of 10%.

The amount of Fe, Cu, Co, Mn and Zn dissolved from slag and total Cr [Cr(VI) plus Cr(III)] were measured by atomic absorption spectrophotometer [15]. In addition, for some experiments, silica in the filtrate was determined gravimetrically [16].

The experiments were performed in duplicate and the results were found to vary within  $\pm 5\%$ .

### 3. Results and discussion

#### 3.1. Effects of copper smelter slag (CSS) dosage, acid content and contact time

Fig. 1 shows Cr(VI) reduction by copper smelter slag (CSS) of various dosages as a function of contact time for an initial concentration of 100 mg/l Cr(VI) in the presence of 1.0, 1.5 and 2.0 stoichiometric amounts of sulphuric acid. In this figure, the molar ratio, [dissolved iron]/[reduced Cr(VI)], is also presented. As seen from

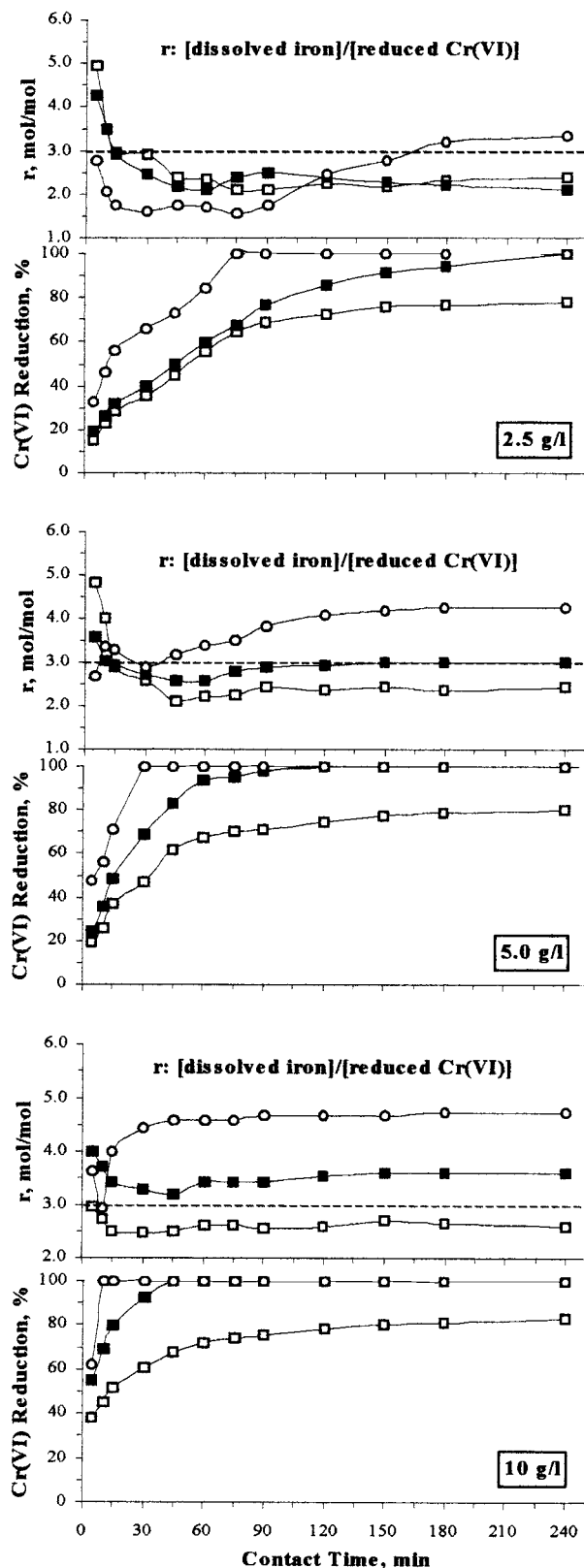


Fig. 1. The variation of Cr(VI) reduction and molar ratio of dissolved iron to reduced Cr(VI) with contact time at different CSS dosages and acid contents [Initial Cr(VI) concn.: 100 mg/l; Temp.: 25°C; Particle size: -200 mesh;  $\square$  1.0,  $\blacksquare$  1.5 and  $\circ$  2.0 stoichiometric amount of acid].

the figure, the amount of Cr(VI) reduced increases depending upon the contact time and amount of acid. As expected, for a constant initial Cr(VI) concentration, an increase in the dosage of reductant will cause the reduction of Cr(VI) to be completed in a shorter time. But, in the solutions containing 1 stoichiometric acid, Cr(VI) could not be completely reduced even for a long period of 240 min and further dosage of 10 g/l. However, the complete Cr(VI) is reduced in a short period of time by increasing the acid content. For example, when the stoichiometric amount of acid was increased from 1.5 to 2.0, the required time for completion of reduction decreased from 240 to 75 min for a CSS dosage of 2.5 g/l. On the other hand, for further dosages of 5 and 10 g/l, the reduction times corresponding to 1.5 and 2.0 stoichiometric acid contents were determined as 120 and 30 min; 45 and 10 min, respectively.

The results show that the  $[\text{dissolved iron}]/[\text{reduced Cr(VI)}]$  molar ratios calculated for contact times less than 15 min are usually higher than their theoretical molar ratio of 3.0 (dashed line in figure). The values of molar ratios from the results using 1.0 and 1.5 acid contents became nearly constant after a contact time of 45 min. However, in the case of 2 stoichiometric acid, the values of molar ratios increased over the theoretical value depending upon contact time. This situation can be attributed to the presence of excessive amount of acid and iron (from CSS) with respect to the stoichiometric amount of Cr(VI) because iron will continue dissolving from the CSS after the entire Cr(VI) was reduced.

### 3.2. Effect of Cr(VI) concentration

The effect of initial concentration on the reduction process was studied by combining Cr(VI) solutions of various initial concentrations and acid contents with 10 g CSS/l dosage at 25°C for 30 min. The results obtained are given in Fig. 2.

The reduction extent of Cr(VI) in the solutions containing 2.0 stoichiometric amount of acid was 100%, but under less acidic conditions (1.0 and 1.5 stoichiometric acid content), the Cr(VI) was not completely reduced. As seen, the reduction percentage of Cr(VI) is, to a large extent, dependent on acid content. Since the amount of acid to be added to the working solutions is calculated with respect to Cr(VI) content, to increase the initial Cr(VI) concentration necessitates increasing the acid content of the solution. Therefore, the reduction yield of Cr(VI) in the solution containing 25 mg Cr(VI)/l is lower due to the fact that the amount of acid is not sufficient to dissolve the iron from CSS. The reduction percentage of Cr(VI) does not show a significant change by increasing the initial concentration of Cr(VI) for 1.0 and 1.5 stoichiometric acid contents. However, the amount of reduced Cr(VI) per gram CSS increases with increasing initial concentration.

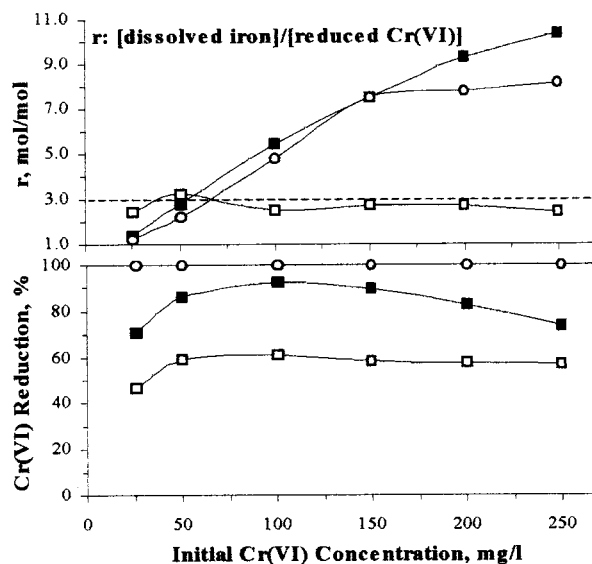


Fig. 2. The variation of Cr(VI) reduction and molar ratio of dissolved iron to reduced Cr(VI) with initial concentration at different acid content [contact time: 30 min; CSS dosage: 10 g/l; Temp.: 25°C; Particle size:  $-200$  mesh;  $\square$  1.0,  $\blacksquare$  1.5 and  $\circ$  2.0 stoichiometric amount of acid].

While the change of molar ratios with the initial concentration of Cr(VI) is almost constant around the theoretical molar ratio for 1.0 stoichiometric amount of acid, those of 1.5 and 2.0 stoichiometric acid have an increase. This situation stems from the increase in the amount of dissolved iron due to excessive amount of acid added to the solution to obtain stoichiometric amount of acid suitable with respect to Cr(VI).

### 3.3. Effect of temperature

Fig. 3 shows the change in amount of Cr(VI) reduced and total chromium in the supernatant and molar ratios of dissolved iron to reduced Cr(VI) with rise in temperature of solution. These results were obtained from the experiments carried out with the 100 ml solution of 100 mg Cr(VI)/l at temperatures ranging from 25 to 80°C. The CSS dosage of 2.5 g/l and 1.0 stoichiometric acid content were used in this series of experiments to see more clearly the effect of temperature on the reduction yield of Cr(VI).

Raising the temperature has a positive effect on the reduction of Cr(VI) by CSS. By increasing the temperature of solution, the amount of Cr(VI) to be reduced increased and the time required to complete the reduction of Cr(VI) was shortened. For example, while the Cr(VI) in the solution is completely reduced at 80 and 65°C within the times of 60 and 120 min, respectively, the reduction process can not be completed at the lower temperatures for a contact period of 240 min.

Consequently, the reduction of Cr(VI) by CSS can be considered as an endothermic reaction.

The concentration of total chromium determined in the supernatant decreased with a rise in temperature of solution and contact time. There is an increasing trend in the final pH of solutions with increased contact time and temperature of solution. The raise in final pH causes the oxidized iron ions to precipitate as ferric hydroxide. Although the entire Cr(VI) was reduced at 80 and 65°C after an adequate contact time, the concentration of total chromium in supernatants under same conditions is not equal to the initial concentration of Cr(VI). These differences between final and initial concentrations of chromium suggest that the chromium may be partially adsorbed by CSS and the ferric hydroxide formed by hydrolysis. The amount of chromium absorbed increased

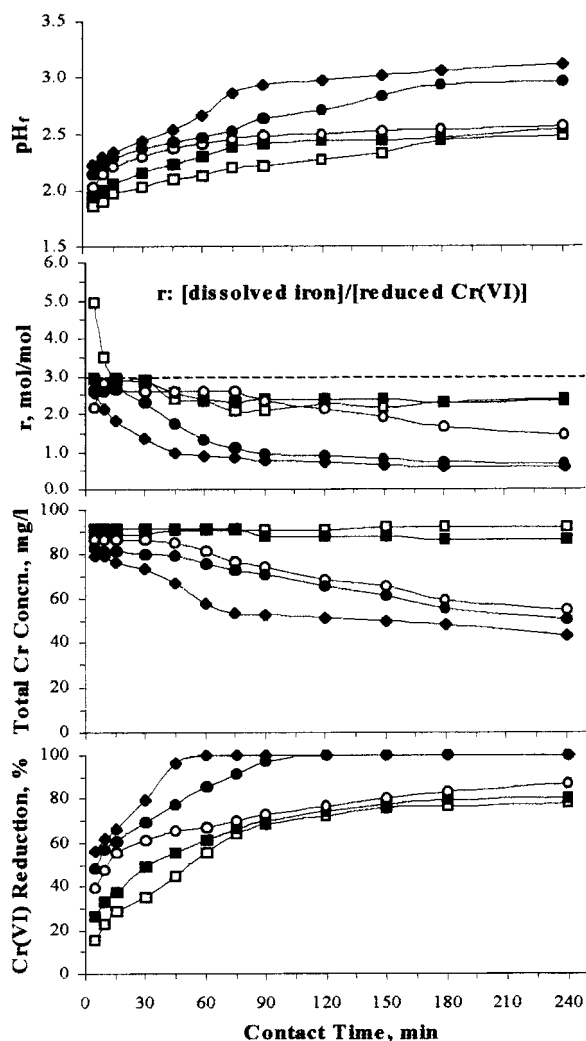


Fig. 3. The variation of Cr(VI) reduction, total chromium concentration and molar ratio of dissolved iron to reduced Cr(VI) with temperature [Initial Cr(VI) concn.: 100 mg/l; acid content: 1.0 stoichiometric amount; CSS dosage: 2.5 g/l; Particle size: -200 mesh; □ 25°C, ■ 35°C, ○ 50°C, ● 65°C, ◆ 80°C].

with increasing temperature of solution, which means that the adsorption process of chromium by CSS is endothermic.

The values of molar ratios calculated for higher temperatures are very low compared to the theoretical molar ratio. The decrease in the values of these increased with rise in temperature and contact time. This is probably due to the removal of dissolved iron ions from solution by precipitation as ferric hydroxide.

### 3.4. Effect of particle size

Fig. 4 shows the effect of CSS particle size on the reduction of Cr(VI). As seen, a decrease in particle size increases reduction yield. Particles smaller than 88  $\mu\text{m}$  (-170 mesh) are able to reduce Cr(VI) completely within a contact time of 45 min for 100 mg/l Cr(VI) solution acidified with  $\text{H}_2\text{SO}_4$  to obtain 1.5 times the theoretical amount of acid. CSS with coarser size possibly requires longer contact time for satisfactory reduction. CSS fractions giving a reduction yield of 100% within 45 min exhibit about 3.0 molar ratios.

### 3.5. Effect of successive reduction

A certain amount of CSS was subjected to successive reduction tests. For this purpose, first reduction test was carried out under the following conditions: 10 g/l CSS dosage; 25°C solution temperature; 45 min shaking time; 100 mg/l Cr(VI) concentration; 1.5 stoichiometric amount of acid; solid, separated by centrifuge of suspension; placed in a new Cr(VI) solution. The reduction test under the same conditions was repeated until the

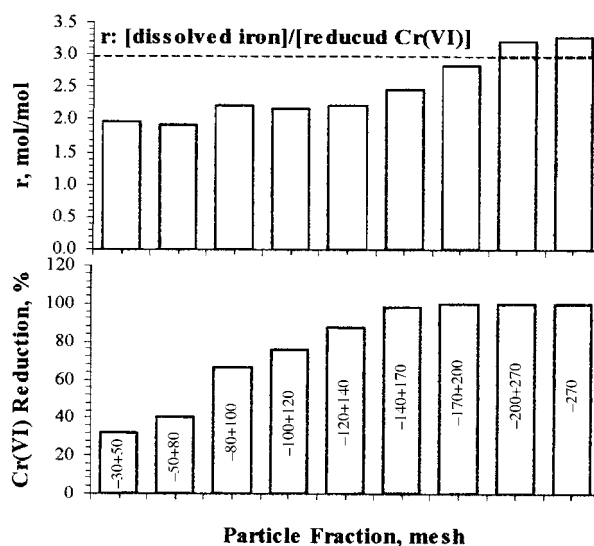


Fig. 4. The variation of Cr(VI) reduction with particle size [initial Cr(VI) concn.: 100 mg/l; acid content: 1.5 stoichiometric amount; CSS dosage: 10 g/l; Temp.: 25°C; contact time: 45 min].

reduction yields of CSS dropped the value lower than 10%. The results from successive reduction studies are given in Fig. 5.

In the first four reductions, the entire Cr(VI) in solution is reduced; thereafter, the Cr(VI) reduction yield decreases. It was found that Cr(VI) reduction yield decreased to 9.92% at the end of the 12th reduction stage. [Dissolved iron]/[reduced Cr(VI)] molar ratios calculated from cumulative values are in the interval of 2.5–3.2. A cumulative calculation shows that the reduction capacity of CSS is 76.5 mg Cr(VI)/g under the conditions mentioned above. In study [7] investigating the reduction of Cr(VI) by pyrite, the reduction capacity of pyrite was reported as 42.56 mg/g in similar conditions. It can be stated that CSS is a more suitable reduction material compared to pyrite.

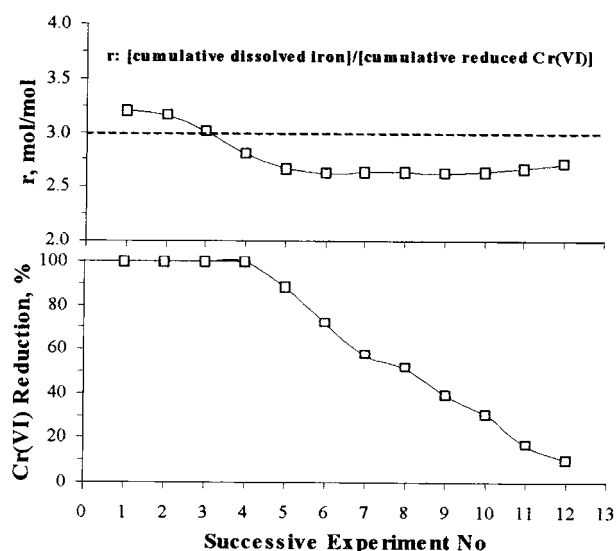


Fig. 5. The results of successive experiments [initial Cr(VI) concn.: 100 mg/l; acid content: 1.5 stoichiometric amount; CSS dosage: 10 g/l; temp.: 25°C; contact time: 45 min; particle size: -200 mesh].

### 3.6. Precipitation study

During the reduction process, metals such as Cu, Zn, and Co, together with Fe go into solution by dissolving from CSS. However, the amounts of these metals are too low to compare to those of iron and chromium in the solution. For example, in the experiments that were carried out by contacting 100 ml Cr(VI) solution [100 mg Cr(VI)/l, 1.5 stoichiometric acid content] with 1 g CSS for 45 min, the concentrations of dissolved Cu, Zn and Co are 16.6, 6.15 and 0.78 mg/l, respectively. The concentration of total chromium at these conditions is determined as 88.05 mg/l. Cr(VI) treatment frequently involves reduction to the Cr(III) form prior to removing the chromium from wastewaters. The reduced chromium is removed by precipitation methods. In this connection, the solution containing these metals in the concentrations mentioned above was subjected to precipitation tests. After the pH of solution was adjusted to 9.0 by using NaOH solution, filtrate was separated. Analysis of the filtrate shows that the concentrations of all metals are under the detection limits.

As alternate and low-cost precipitants such as carbonation sludge of sugar plant and its calcine were also tested for the precipitation of these metals. Results from these experiments were given in Table 2. Metals in reduced solution could be mostly removed by using dried carbonation sludge (DCS) consisting mainly of CaCO<sub>3</sub>. However, even when used in high dosage, such as 10 g/l, these metals remain in solution in significant amounts. On the other hand, by using the calcine produced from DCS at 800°C at the dosage of 2.5 g/l, an effective removal was achieved. In addition, silica dissolved from CSS during the reduction process could be removed in the ratio of 82.1% under these conditions. The positive effect of calcine (CDCS) on the precipitation process can be attributed to its CaO content. A comprehensive study related to the use of such waste

Table 2

Composition of the final solution treated with CSS and result of precipitation experiments

Composition of final solutions <sup>a</sup> (mg/l)	Cr	Fe	Cu	Zn	Co	Mn	Si		
	88.05	343.7	16.59	6.15	0.78	0.38	178.5		
Result of precipitation experiment									
Precipitant	Dosage (g/l)	Final pH	Final concentration (mg/l)						
			Cr	Fe	Cu	Zn	Co	Mn	Si
DCS	2.5	6.01	1.26	10.54	1.42	2.49	0.59	0.27	n.a.
DCS	10.0	10.35	0.47	4.76	1.24	0.19	0.31	0.16	n.a.
CDCS	1.0	5.71	–	5.76	0.95	6.0	0.46	0.12	n.a.
CDCS	2.5	11.34	–	–	–	–	–	–	32.0

<sup>a</sup> Reducing conditions: initial Cr(VI) concn.: 100 mg/l; CSS dosage: 10 g/l; acid content: 1.5 stoichiometric amount; particle size: -200 mesh; Contact time 45 min; temperature 25°C. DCS, dried carbonation sludge of sugar plant; CDCS, dried carbonation sludge calcined at 800°C; n.a.: not analysed.

materials in removing heavy metals from aqueous solution is in progress.

#### 4. Conclusions

The following conclusions may be drawn from this study related to the use of CSS as a reductant for Cr(VI).

The CSS can effectively reduce Cr(VI) from aqueous solution. The reduction efficiency is, to a large extent, dependent on the acid content of solution. When 2.0 stoichiometric acid was used with respect to Cr(VI), the entire Cr(VI) was reduced in a short period of contact time.

The contact time has a positive effect on the reduction process. However, the time required for completion of Cr(VI) reduction changed depending on the conditions applied. The reduction extent of Cr(VI) increased with increasing the temperature of solution. At higher temperatures, the chromium in the supernatant decreased due to its adsorption on the surface of CSS and formed ferric hydroxide.

The reduction efficiency of Cr(VI) increased with decreasing particle size of CSS. CSS with the particle size less than 140 mesh (105  $\mu$ ) can be used to completely reduce Cr(VI) in a 100 ml solution of 100 mg/l within a reasonably short period of contact time.

Successive reduction experiments showed that the entire Cr(VI) in four test solutions of 100 ml [100 mg Cr(VI)/l] was reduced by using 10 g CSS/l and 1.5 stoichiometric acid content. The reduction capacity of CSS has been calculated as 76.5 mg Cr(VI) per g CSS.

All dissolved metal ions in supernatant obtained under certain conditions were precipitated by adjusting the pH of supernatant with NaOH solution to 9.0. By using the calcine of carbonation sludge of sugar plants as a precipitant, heavy metals in the reduced solution could be completely removed. This is also an effective material for precipitating silica dissolved from CSS.

CSS seems to be a suitable material for reduction of Cr(VI) in the aqueous wastes. In addition, the feasibility of the process must be investigated with a separate study.

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#### References

- [1] Sittig M. Pollution Removal Handbook. Noyes Data Corp., England, 1973.
- [2] Patterson JW. Industrial Wastewater Treatment Technology. Stoneham, MA: Butterworths Publishers, 1975.
- [3] Lanouette KH. Heavy Metals Removal. Chemical Engineering Deskbook Issue 73–80, Oct.17, 1977.
- [4] Eckenfelder WW. Industrial Water Pollution Control. New York: Mc Graw Hill Book Co., 1984.
- [5] Anderson JN, Bolto BA, Pawlowski L. A method for chromate removal from cooling tower blowdown water. nuclear and Chemical Waste Management 1984;5:125–9.
- [6] Lancy LE. US Patent 3 294 680, 1966.
- [7] Erdem M, Tümen F. Cr(VI) reduction in aqueous solutions by using pyrite. (In Turkish). Tr J of Engineering and Environmental Science 1996;20:363–9.
- [8] Butler JW. US Patent 3 960 722, 1984.
- [9] Gould J. The kinetics of hexavalent chromium reduction by metallic iron. Water Research 1982;16:871–7.
- [10] Moring JM. US Patent, 4 188 272, 1980.
- [11] Saito T, Tanaka A, Murakami M. Iron powder method for wastewater treatment. Metals and Materials Soc (TMS), Warrendale, PA, USA, pp.91–94, 1993.
- [12] Özer A, Altundoğan HS, Erdem M, Tümen F. Cr(VI) reduction in aqueous solutions by steel wool. Environmental Pollution 1997;97:107–12.
- [13] Bailey NT, Wood SJ. A comparison of two rapid methods for the analysis of copper smelting slags by atomic absorption spectrometry. Anal Chim Acta 1974;69:19–25.
- [14] APHA, Standard Methods for Examination of Water and Wastewater. APHA-AWWA-WPCF, 14th ed., pp. 192–194, 1975.
- [15] Perkin–Elmer. Atomic Absorption Instruction Manual. Perkin–Elmer Corporation, Norwalk, Conn., USA, 1976.
- [16] Vogel AI. Vogel's Textbook of Quantitative Chemical Analyses. Revised by G.H. Jeffery et.al., Longman, London, 5th Ed., 1989.