

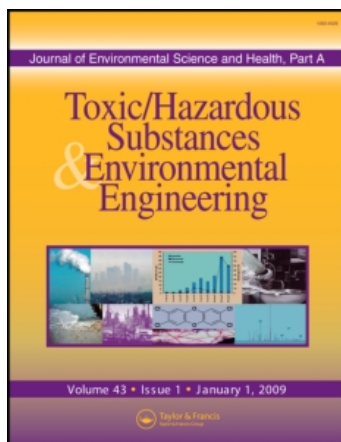
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A Study on Dissolution Properties of the Sludges from Cr(VI) Reduction–Precipitation Processes

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ABSTRACT

In this article, dissolution characteristics of Cr(VI) reduction–precipitation sludges in the solutions containing mineral acids, organic complexing materials or both are examined. For this purpose, the effects of pH, concentration of complex forming agent and contact time on dissolution of metals from two different sludges obtained by using sodium sulphite and ferrous sulphate as reducing agents are studied. In addition, pollution potentials of the sludges are determined by applying the toxicity tests of TCLP, SPLP, USEPA-1979, and USEPA-1980. It was found that pH, contact time, concentration and type of complex forming substances are effective parameters on dissolution of metals from the sludges. In mineral acid solutions at pH 3, especially in the presence of organic complexing substances, chromium leached out from hydroxide sludges exceeds the concentration limits of USEPA for hazardous wastes. The amounts of chromium dissolved in the citric and ascorbic acid solutions and the amount of iron dissolved in the EDTA solution were found to be higher than in the other test solutions. Also, TCLP test shows that chromium hydroxide sludge obtained from sulphite reduction–precipitation process of Cr(VI) is a potential hazardous solid. According to the results of this study, considering the probable presence of complexing agents in the disposal sites, toxicity test methods should be modified.

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Key Words: Chromium; Dissolution; Heavy metal; Metal hydroxide sludges; SPLP; TCLP; Toxicity test.

INTRODUCTION

Since heavy metals and their compounds are widely used in many industrial processes, the wastewaters discharged from these processes may contain heavy metal ions. Conventionally, heavy metal bearing wastewaters are treated by precipitation technique that utilizes the hydroxide precipitation method. In these processes, a voluminous metal hydroxide sludge formed is discharged.

Most of the heavy metals have great ecological significance due to their toxic effects to animals and human beings. For that reason, most of the sludges containing heavy metals are generally considered to be a hazardous waste by the majority of authorities.^[1,2] The main environmental impact of such sludges is the risk of redissolving of heavy metals. The amount of heavy metals to be released from the sludges depends on the site conditions such as pH, temperature, and presence of complex forming substances and microorganisms. Some natural occurrences may alter the site conditions that may affect solubilization properties of wastes. Particularly, the low-molecular-weight organic acids that have complex forming effects on metals may be in contact with those sludges. These acids are secreted into the soil by plant roots and are also generated during decay of organic substances such as residues of animals and plants, fungus and organisms.^[3,4] It has been reported that the concentration of these acids are in the range of 10^{-2} – 5.10^{-4} M in soil solutions.^[3,5,6] These acids may increase the mobility of the heavy metals in the soil and water ecosystems by forming soluble complexes. Some published articles about the soils and anaerobically treated sludges report that heavy metals in these materials are released into the water by influence of microorganisms and complex forming organic substances present.^[7–9]

Another factor affecting the dissolution of heavy metals in wastes is acid rains. It is well known that sulphur and nitrogen oxides are the primary reasons of acid rains.^[10] Acidic precipitations cause a decrease in the pH of water and soil below their natural values and may thus accelerate the dissolution of the waste contacted with. As a consequence, it can be stated that leaching behavior of heavy metals from sludges discharged to the nature can dynamically change depending on the environmental conditions.

In order to determine the toxicity of solid wastes, some leaching tests have been developed by various authorities. In this context, some tests such as Toxicity Characterization Leaching Procedure (TCLP), Synthetic Precipitation Leaching Procedure (SPLP), Equilibrium Leach Test (ELT) and some others have been recommended by USEPA. These tests are based on determining the concentrations of particular toxic constituents leached out from a solid waste. If the concentration of the toxic components released from a solid waste is over the toxicity limits, the waste is considered as hazardous.

Many industrial processes including leather tanning, textile, electroplating, wood preservation and power plant discharge Cr(VI), one of the priority metal pollutants, into surface and ground water. It has been indicated that Cr(VI) is toxic,



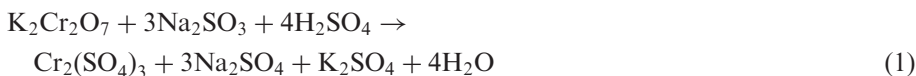
mutagenic and even potential carcinogenic.^[11,12] Thus, wastewaters containing Cr(VI) must be treated to lower its concentration to the allowable limits before discharging into the environment. The conventional treatment method of wastewater containing chromium includes the reduction of Cr(VI) to the trivalent state, followed by precipitation of chromium hydroxide by using a base. Reducing agents commonly used for this purpose are sulphur dioxide, sodium sulphites and ferrous sulphate.^[11,13,14] In this treatment method, called as reduction-chemical precipitation process, a heavy metal bearing sludge is formed. The composition of these sludges change in accordance with reducing agent used in the process. For instance; when iron(II) salts are used as a reducing agent, a large amount of iron introduces in the sludge. In order to determine an appropriate discharge way, it is necessary to know the dissolution behavior of these sludges under the conditions resembling the environment.

In this study, dissolution characteristic of Cr(VI) reduction-precipitation sludges prepared synthetically was investigated. For this purpose, the effects of pH, concentration of complex forming agent and contact time on dissolution of two different sludges obtained by using sodium sulphite and ferrous sulphate as reducing agents were studied. In addition, pollution potentials of the sludges were determined by applying the leaching tests recommended by USEPA.

MATERIALS AND METHODS

Materials

In this study, two different hypothetic sludges prepared in laboratory were used. The first sludge (S1) was prepared by precipitation of Cr(III) in the solution from the Cr(VI) reduction process utilizing sodium sulfite. For this purpose, firstly, Cr(VI) solution in the concentration of 2000 mg-Cr(VI) L⁻¹ was prepared by dissolving K₂Cr₂O₇ in distilled water. The pH of this solution was adjusted to 2 ± 0.1 by using H₂SO₄. A stoichiometric amount of sodium sulphite, calculated from Eq. (1), was added to the Cr(VI) solution and then whole Cr(VI) was reduced by shaking the mixture in the period of 15 min. In order to check the complete reduction of Cr(VI), the final solution was subjected to a color test with 1.5-diphenyl carbazide solution.^[15] The Cr(III) formed was completely precipitated by using NaOH solution at the pH range of 7.5–8.3.



The second sludge (S2) was prepared in the same way by using Cr(III) ions obtained from Cr(VI) reduction process where ferrous sulphate was used. It has been reported that an excess dosage of the theoretical amount of ferrous sulphate (app. 2.5 fold) is required in order to obtain a complete reduction of Cr(VI) according to Eq. (3).^[16] Therefore, 2.5 fold of theoretical amount of ferrous sulphate was used in the Cr(VI) reduction step. Cr(III) and Fe(III) ions in the reduced solutions were coprecipitated



Table 1. The chemicals used in the preparation of the solutions.

Sulphuric acid (98%)	H ₂ SO ₄ , Merck-1.00713
Nitric acid (65%)	HNO ₃ , Merck-1.00443
Citric acid (99%)	C ₆ H ₈ O ₇ ·H ₂ O, Merck-242
Tartaric acid (99.5%)	C ₄ H ₆ O ₆ , Merck-802
Oxalic acid (99.5%)	C ₂ H ₂ O ₄ ·2H ₂ O, Riedel-de Haën-33506
Ascorbic acid (99%)	C ₆ H ₈ O ₆ , Aldrich-25,556-4
Acetic acid (100%)	CH ₃ COOH, Merck-56
EDTA (di sodium salt)	C ₁₀ H ₁₄ O ₈ Na ₂ Pan Reac
Humic acid (sodium salt)	Aldrich-H 1,675-2
Sodium hydroxide	NaOH, Merck, 1.06462

at the same conditions mentioned above for S1.



S1 and S2 sludges were decanted and then filtered by suction. The obtained cakes were slurried in plentiful distilled water, filtered and dried at 25°C for three days and then ground in a mortar.

In the dissolution experiments, sulphuric, sulphuric+nitric, citric, tartaric, oxalic, ascorbic and acetic acids and EDTA (di sodium salt) solutions having the concentrations of 10⁻² M with initial pH values of 3, 4, and 5 (±0.1) were used as dissolution agents. In a group of experiments, dissolution runs were carried out in 10⁻², 10⁻³, and 10⁻⁴ M solutions containing the same organic substances and humic acid (sodium salt) without any pH adjustment. The solutions were prepared from the compounds given in Table 1. When it was necessary, H₂SO₄ and NaOH solutions in various concentrations were used to adjust the pH of solutions.

Experimental Procedure

Experimental study was organized in two different groups. In first group, dissolution properties of sludges were determined. In second group, toxicity tests were applied.

Dissolution Experiments

The experiments were carried out by using a flask shaker (Clifton) equipped with a temperature controlled water bath. The sludge sample of 0.5 g and a 50 mL solution with desired concentration and pH were mixed in a flask and then shaken by a shaker at 300 cycle min⁻¹ for contact time ranging from 1 to 8 h. All of the experiments were carried out at 25°C.

At the end of predetermined contact period, the reaction mixture was centrifuged at 7000 rpm for 15 min and then the pH of filtrate was measured by



using pH meter (Shot CG 840). The supernatants were acidified with HNO_3 to prevent precipitation and analyzed for chromium and iron.

Toxicity Tests

To determine the pollution potential, S1 and S2 sludges were subjected to TCLP,^[17] SPLP^[18] and two other different extraction procedures^[19,20] (EP1 and EP2, recommended in 1979 and 1980 by USEPA, respectively). These tests are applied as in following.

In TCLP, leaching solution and sludge sample are mixed in a flask at a liquid:solid ratio of 20:1. Two different leaching solutions are used in TCLP depending on acidity of the wastes. Solutions 1 and 2 have the pHs of 4.93 ± 0.05 – 2.88 ± 0.05 , respectively. In order to decide which leaching solution to be used, pHs of the samples are measured. For this purpose, a solid sample of 5.0 g is mixed with the distilled water of 96.5 mL in a 250 mL beaker covered with a watch glass. That is stirred with a magnetic stirrer for 5 min and then pH of the sample is measured by using a pH meter. If the pH is less than 5, solution 1 is used. If the pH is greater than 5, it is added 3.5 mL of 1 N HCl in the beaker, covered with a watch glass, heated the slurry to 50°C on a hotplate and hold at that temperature for 10 min. Then, it is cooled to room temperature and measured the pH. If the pH is now less than 5, solution 1 is used. Otherwise, solution 2 is used as the leaching solution. According to the procedure, the mixture liquid:solid ratio of which 20:1 is prepared and agitated at 30 ± 2 rpm, $22 \pm 3^\circ\text{C}$ for 18 ± 2 h and then filtered. The extract is analyzed for metals. In this study, since the pHs of the samples are less than 5, the solution 1 was used throughout the tests.

In SPLP, the leaching solution pH of which is adjusted to 4.2 by a mixture of 60% (wt wt⁻¹) H_2SO_4 (98%) and 40% HNO_3 (65%) (wt wt⁻¹) is used. Liquid:solid ratio and other operational conditions are the same with those in TCLP.

In EP1, 2 g of dried solid sample is dispersed in 200 mL of distilled water and pH is adjusted to 5.0 ± 0.2 by addition of NaOH or HCl. The mixtures are subjected to continuous shaking. The pH is measured and adjusted to 5.0 ± 0.2 for every 24 h. When two consecutive measurements are obtained as 5.0 ± 0.2 , the procedure is stopped and the suspensions are allowed to settle for 24 h. The supernatant is then filtered and the metal concentration is determined.

In EP2, 100 g-dried solid is placed in a 2.5 L jar containing 1600 mL distilled water. Then pH is adjusted to 5.0 ± 0.2 by using 0.5 N acetic acid. The mixture is stirred with a mechanical stirrer at 100 rpm for 24 h. During the stirring period, the pH is kept at 5.0 ± 0.2 by addition of 0.5 N acetic acid. At the end of the 24 h extraction period, total liquid volume is filled up to 2000 mL with distilled water. EP2 test was subjected to S1 and S2 at the same conditions but initial amounts of liquid and solid were proportionally taken in a smaller scale than given in the procedure.

Methods of Analysis

Mineralogical composition of S1 and S2 sludges was determined by X-ray diffractometer (Siemens, D-5000). In order to determine the chemical composition,



S1 and S2 sludges were dissolved in nitric acid solution and then the concentrations of iron and chromium were determined by using atomic absorption spectrophotometer (Perkin Elmer 370).

The concentration of metals in the solutions obtained from dissolution study and leaching tests procedures was determined by atomic absorption spectrophotometer using flame atomization technique.^[21]

The experiments were regularly performed in duplicate and the mean values were considered. A group of experiments were repeated in a number of times to ascertain the reproducibility of the results and it was observed that the experimental results were found to vary within $\pm 5\%$.

RESULTS AND DISCUSSION

Chemical compositions of S1 and S2 are presented in Table 2. As a metallic constituents, S1 contains 39.64% Cr, while S2 contains 6.32% Cr and 42.5% Fe. XRD analysis showed that both of the samples were in amorphous form.

The results obtained from this study are presented in two sections in the following as dissolution study and toxicity tests.

Results of the Dissolution Study

pH is one of the most important factors affecting metal dissolution in wastes. It is well known that acid rain is one of the major causes of acidity in the ecosystems. Therefore, in the first section, the effect of acidic solutions resembling acid rains on the dissolution of sludges was investigated. For this purpose, the sludges were contacted with acidic solutions (at different initial pHs of 3; 4 and 5 ± 0.1) which their pHs were adjusted with the mixture of sulphuric acid (98%) and nitric acid (65%) (60/40, wt wt⁻¹), and then shaken for contact time in the range of 1–8 h. Results are shown in Table 3.

At the end of the contact period of 8 h, the concentration of chromium released from samples could only be determined for the solution at pH 3. In this case, the concentrations of chromium released from S1 and S2 were determined to be about 5 and 1 mg L⁻¹, respectively. As seen that the media having the pH more than 4 have not a significant dissolving effect. pHs measured at the end of the each contact period were higher than the initial pH values. These differences indicate that S1 and

Table 2. Chemical composition of S1 and S2.

Sample	Loss on drying, (%) (25–105°C)	Loss on ignition, (%) (105–1000°C)	Constituents			
			Cr (%)	Cr ₂ O ₃ (%)	Fe (%)	Fe ₂ O ₃ (%)
S1	21.45	18.42	39.64	57.93	—	—
S2	14.58	11.84	6.32	9.24	42.50	60.71



Table 3. The effect of acid rains on the dissolution properties of S1 and S2.

Initial pH	Contact time (h)	The Concentrations of released metals (mg L ⁻¹)			Final pH	
		Cr		Fe		
		S1	S2	S2	S1	S2
3	1	ND	ND	ND	6.12	5.07
3	2	ND	ND	ND	5.98	5.63
3	4	ND	ND	ND	6.07	5.57
3	8	5	1	2.23	6.19	5.69
4	1				7.09	5.09
4	2				7.10	4.98
4	4	All of the concentrations released metals were under the detectable limits			7.06	5.12
4	8				7.02	5.22
5	1				7.11	5.48
5	2				7.08	6.84
5	4				7.14	6.93
5	8				7.11	6.96

ND: Not detected.

S2 have alkaline characteristics. Thus, it can be stated that the alkalinities of the samples cause the low chromium dissolution by neutralizing the hydrogen ions in the solutions.

On the other hand, it is well known that decaying of biological residues and organisms may contribute to the acidity of soils by generating the organic acids. Both of the organic acids and acid rains affect the pH of the soil solutions. When the solutions containing organic acids contact with wastes, dissolution of heavy metal may be accelerated by complexation effect. To examine this effect, citric, ascorbic, oxalic, tartaric, acetic acids and EDTA (di sodium salt) solutions having 10⁻² M concentration with initial pH values of 3; 4 and 5 were prepared and similar dissolution experiments were performed.

Experimental results showed that the concentration of the metals released from S1 and S2 increased with decreasing pH and increasing contact time (Figs. 1 and 2). For S1 and S2, maximum chromium dissolution was observed in the citric acid solution at initial pH of 3 and at the end of the contact period of 8 h. Under these conditions, the chromium contents of the solutions contacted with S1 and S2 were found to be 8.87 and 4.27 mg L⁻¹, respectively. As seen from these values, the chromium dissolved from S2 is less than that from S1. In the all acetic acid solutions at the predetermined pH ranges investigated, the concentration of metals released from sludges was below the detection limits.

It was observed that the maximum amount of iron leached out from S2 took place in the 10⁻² M EDTA (di sodium salt) solution at pH 3. At the end of contact period of 8 h, the concentration of iron released was found to be about 115 mg L⁻¹. This concentration value corresponds 5.45% of iron in S2, which was excessively



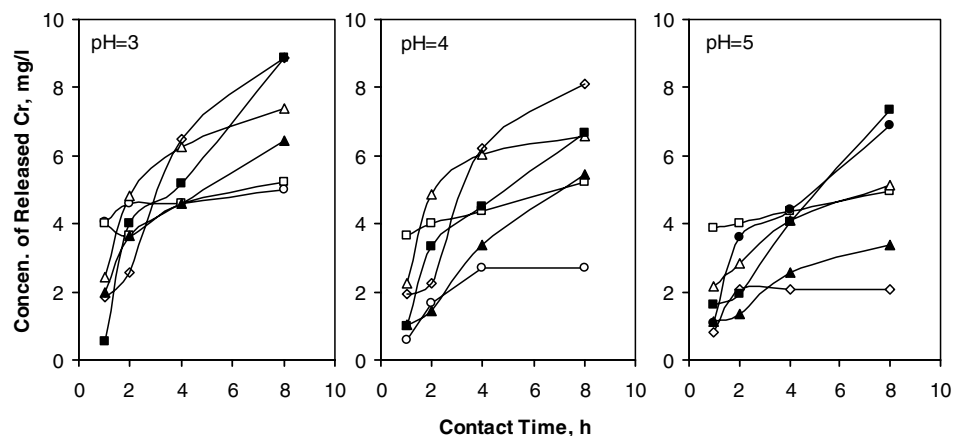


Figure 1. The variation of chromium concentration released from S1 as a function of contact time and pH ($\diamond$: citric acid, $\circ$: H_2SO_4 , $\square$: ascorbic acid, $\triangle$: oxalic acid, $\bullet$: tartaric acid, $\blacksquare$: EDTA-di sodium salt).

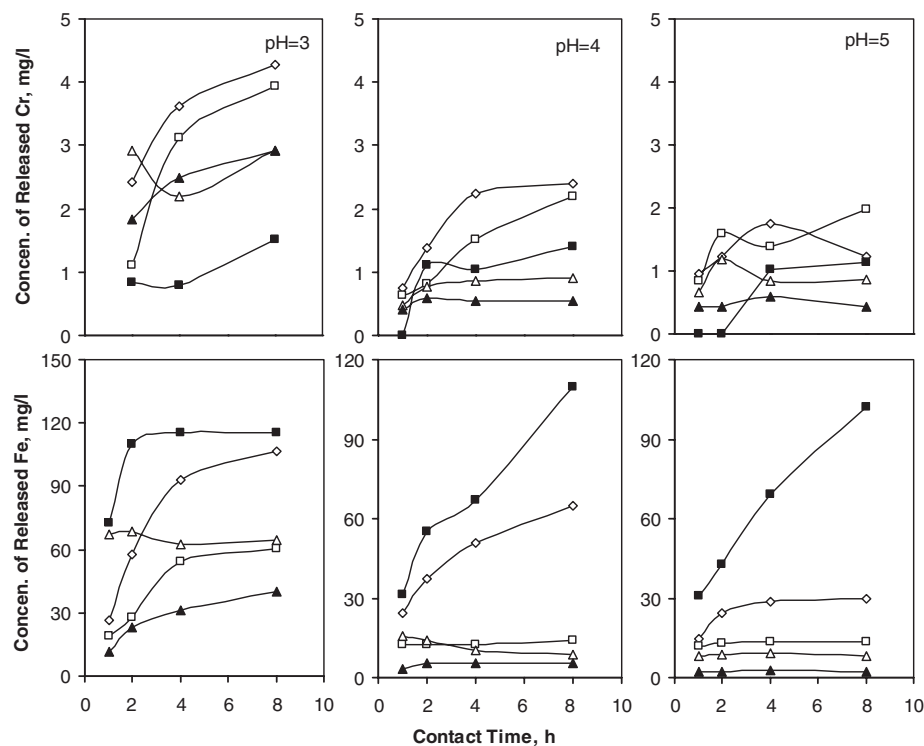


Figure 2. The variation of chromium and iron concentrations released from S2 as a function of contact time and pH ($\diamond$: citric acid, $\circ$: H_2SO_4 , $\square$: ascorbic acid, $\triangle$: oxalic acid, $\bullet$: tartaric acid, $\blacksquare$: EDTA-di sodium salt).



Table 4. The concentrations of chromium released from S1 and S2 and their corresponding dissolution percentages (Concentration: 10^{-2} M; liquid/solid: 100, initial pH: 3, contact time: 8 h).

Solutions	The concentrations of released chromium (mg L^{-1})		The dissolution percentages of chromium	
	S1	S2	S1	S2
Oxalic acid	7.40	2.92	0.37	0.92
Tartaric acid	6.65	2.92	0.33	0.92
Ascorbic acid	5.24	3.94	0.26	1.25
Citric acid	8.87	4.27	0.45	1.35
EDTA-di sodium salt	8.67	1.51	0.43	0.48
Mixed acid ^a	5.00	1.08	0.25	0.34

^aMixed acid: 60% H_2SO_4 -40% HNO_3 .

over the theoretical solubilization value calculated for the final pH of 5.13. Under these conditions, the concentration of iron released into the EDTA solution was about 50 fold higher than that into the mineral acid solution, indicating that the dissolution is mainly controlled by complex formation mechanism.

Table 4 shows the concentration values of chromium released from S1 and S2 in the 10^{-2} M solutions with pH 3. Dissolution percentages calculated from these values are included in the table. Although the concentration of chromium leached out from S1 is higher than that from S2, the dissolution percentage of chromium from S2 is higher than that from S1. This situation is, to a large extend, related to the chromium content of sludge samples.

When these results are compared to those obtained from the first section of this study, it can be seen that the concentration of the metals dissolved in the organic acid solutions is higher than that in the mineral acid solutions having the same pH values. The high dissolution may be due to complex forming effect of organic acids. Similar results were found by Krishnamurti et al.,^[22] who have investigated the kinetics of cadmium release from soils exposed to organic acids. In addition, Lietz and Gallig^[23] have reported that dissolutions of lead, cadmium and zinc from a sediment in the solutions containing complex forming substances were a few fold higher than the values observed for the medium containing no complex forming agent.

Another important factor affecting the dissolution of metals in wastes is the amount of complex forming substances. It has been reported that the concentrations of the organic acids in the soil solution vary in the range of 10^{-2} to 5.10^{-4} M.^[3,5,6] By considering this concentration range, the dissolutions of metals from S1 and S2 were investigated depending on contact time by varying the concentration of complexing material in the range of 10^{-4} - 10^{-2} M. These solutions in various concentrations were used without any pH adjustment in this section of the study. Metal concentrations in the leachates and initial and final pHs are given in Figs. 3 and 4. In the all humic acid (sodium salt) and acetic acid solutions in the concentration ranges examined and the solutions of 10^{-4} M of all other complexing agents, any metals over the detection limits were not detected. Therefore, these variations were not showed in the figures.



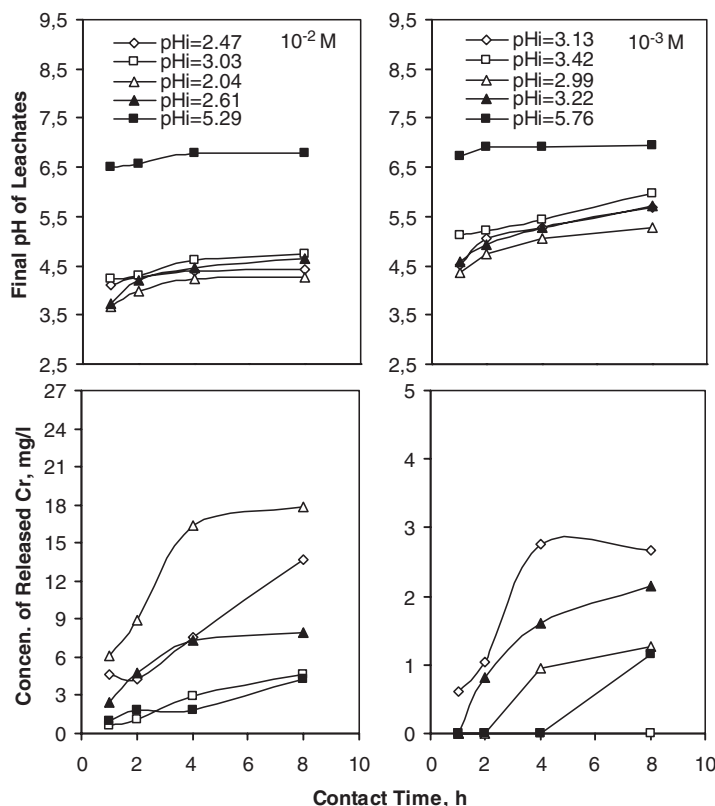


Figure 3. The variation of the chromium concentration released from S1 as a function of contact time and concentration of complex forming substances (◇: citric acid, □: ascorbic acid, △: oxalic acid, ●: tartaric acid, ■: EDTA-di sodium salt).

As seen from Figs. 3 and 4, the concentration of chromium leached out increased with contact time and concentrations of organic acids. Among the solutions containing complex forming substances for the concentration of 10^{-2} M, the maximum chromium dissolution from S1 and S2 was determined to be 0.9% and 5.43%, respectively, for oxalic acid solution. However, the citric acid solution was found to be the most effective medium among the solutions with the concentration of 10^{-3} M. By the considering the initial pH values of all solutions at 10^{-2} M, it can be seen that the oxalic acid solution has the lowest value (2.04). In this case, acid effect may primarily contribute to the dissolution.

Results of the Toxicity Tests

In order to determine the pollution potentials, TCLP, SPLP, USEPA, 1979 and USEPA, 1980 tests were applied to S1 and S2. The concentrations of chromium and iron in the leachates of S1 and S2 are shown in Table 5.



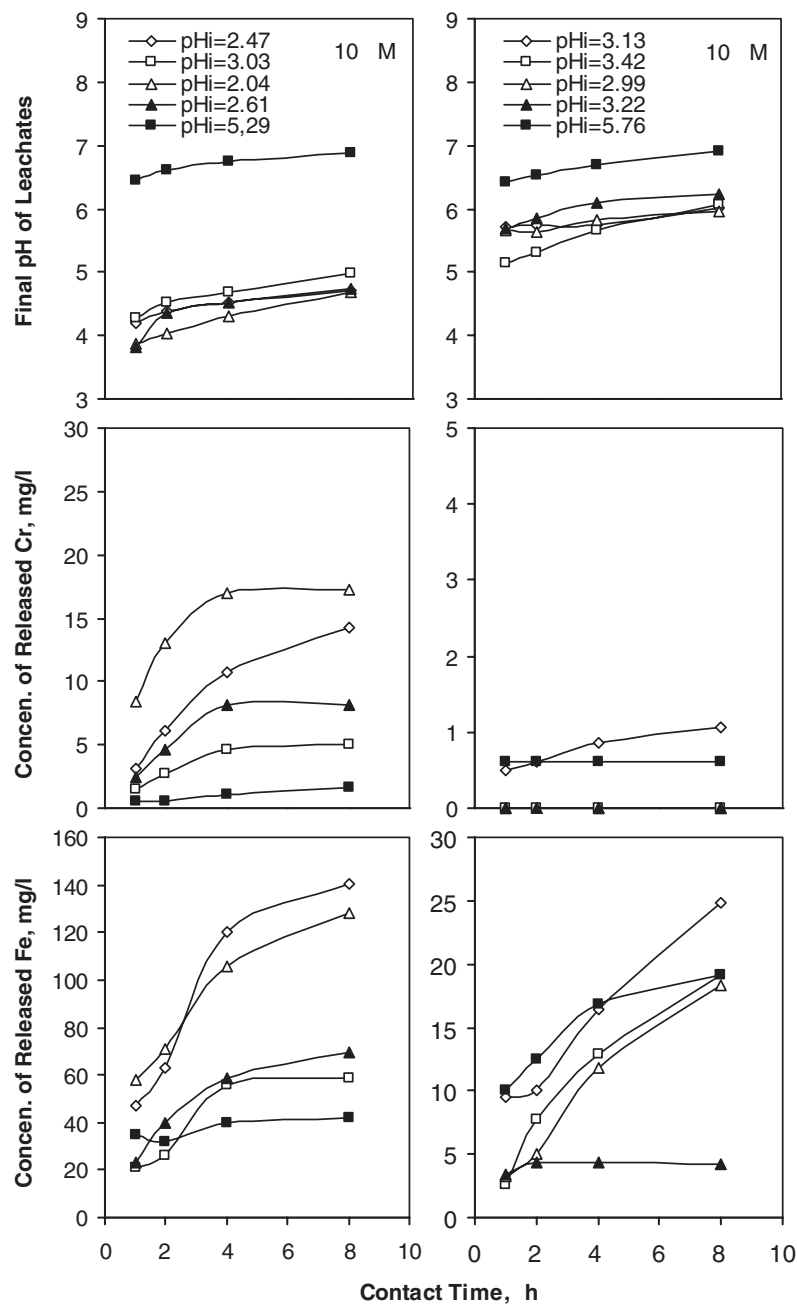


Figure 4. The variation of the chromium and iron concentrations released from S2 as a function of contact time and concentration of complex forming substances (◇: citric acid, □: ascorbic acid, △: oxalic acid, ●: tartaric acid, ■: EDTA-di sodium salt).



Table 5. Leaching tests results applied to S1 and S2.

Sample	Concentrations of metals in extracts (mg L^{-1})							
	TCLP		SPLP		EP1 (1979)		EP2 (1980)	
	Fe	Cr	Fe	Cr	Fe	Cr	Fe	Cr
S1	—	5.75	—	4.26	—	ND	—	ND
S2	ND	ND	ND	ND	ND	ND	ND	ND

ND: Not detected.

The concentration of chromium leached out from S1 was found to be 5.75 mg L^{-1} , which is over the limit given as 5 mg L^{-1} for TCLP by USEPA. From the results, it can be concluded that S1 is a potential pollutant. On the other hand, it was observed that the concentration of chromium released from S1 and S2 in the solutions obtained from dissolution experiments carried out by using complex forming organic substances also exceed the limit of 5 mg L^{-1} . Particularly, when the dissolution of the metals from samples in different media is compared, it can be seen that the concentrations of chromium released into the mineral acid solution at various pH values are less than those into the solutions containing complex forming agents. For example; while the concentration of chromium dissolved from S1 in the mineral acid solution with initial pH 3 was found to be 5 mg L^{-1} , it was determined to be 8.87 mg L^{-1} in the 10^{-2} M citric acid solution having same initial pH. Final pHs of these solutions were measured to be 6.2 and 4.6, respectively. In the toxicity tests applied, the pH values of the leaching solutions were about 5. Although the final pH values were close to each other, the amounts of the dissolved metals found in dissolution and toxicity tests were different. The concentration values of chromium dissolved from S1 that is over the limit of 5 mg L^{-1} were also observed in the dissolution experiments carried out by oxalic, tartaric, ascorbic acids and EDTA (di sodium salt) solutions. Furthermore, while liquid:solid ratio used in the dissolution tests are the identical with EP1 test, that in toxicity tests is different. When the amounts of chromium released from sludges are compared, it can be seen that for the contact time of 8 h chromium concentrations in all dissolution experiments are over the toxicity limits of 5 mg L^{-1} as that found in EP1 is below the detection limit. For S2, iron exhibits similar dissolution behaviors. From these results, it can be concluded that presence of complexing agent accelerates dissolution of the metals from the hydroxide sludges.

The results obtained from this study give an important knowledge about the environmental characterization of Cr(VI) reduction–precipitation sludges. But, when the composition of leach solutions used in toxicity tests is compared with that of the solutions containing complex forming organic substances, it can be stated that the leaching solutions used in toxicity tests do not resemble the natural liquids in the environment. Furthermore, although it has been reported that the chelated forms of heavy metals are less toxic than unbound ions,^[12] decomposition of these complex ions are possible in the course of time with a change in conditions. In this situation, the toxic ions may reform and release and thus, the toxicity may



continue. Therefore, S1 and S2 can be assumed as hazardous waste for the environment.

The toxicity leaching tests can only give knowledge about elemental solubility as a function of pH and liquid:solid ratio or contact time on metal release. As the composition of the solutions used in leaching tests is not same with those of the natural liquids, except for pH, the actual solubility of metals in the nature may be different from the finding of these tests. The results of present study support this idea as well. Therefore, the leaching tests should resemble the conditions occurred in the nature.

CONCLUSIONS

Dissolution characteristics of Cr(VI) reduction-precipitation sludges obtained by using sodium sulphite (S1) and ferrous sulphate (S2) as reducing agents were studied in different media representing acidic precipitation, containing complex forming substances and both. Also, various toxicity tests recommended by USEPA were applied to the hydroxide sludges. Some of the significant findings are summarized in the following paragraphs.

The amount of metals dissolved from the sludges is strongly dependent on the parameters such as solution pH, contact time, concentration and type of complex forming substances present.

The amount of metals released from the sludges contacted with the solution containing 10^{-2} M complex forming substances increases with decreasing pH and increasing contact time. The maximum dissolution of chromium from both sludges were observed in the citric acid solution with initial pH value of 3 at the end of the contact period of 8 h.

Solubility of the metals in the solutions containing complexing agents in the concentration range of 10^{-4} – 10^{-2} M (without any pH adjustment) increases with increasing concentration of complexing agents. The maximum dissolutions of chromium from S1 and S2 in the 10^{-2} M and 10^{-3} M solutions occurred in the media of oxalic acid and citric acid, respectively. But, the concentrations of chromium in the 10^{-4} M solutions were found to be below the detection limits of analyses.

Metal contents of the solutions containing different organic complexing agents was found to be higher than that in the solutions containing mineral acids at the same initial pH level. Furthermore, increasing acidity in the solutions containing organic substances caused an increase in the dissolution of metals.

According to the results of TCLP, SPLP, USEPA-1979 and USEPA-1980 tests applied, while the concentration of chromium leached out from S1 was found as 5.75 mg L^{-1} , that for S2 was below the detection limit. As the concentration determined for S1 is over the 5 mg L^{-1} being the limit value of TCLP, S1 is a potential pollutant.

In the solutions containing complex forming agents which may be present at the disposal site, most of the concentration values of chromium released from S1 and S2 exceed the limit of 5 mg L^{-1} . From above results, the sludges may be assumed as hazardous waste. Thus, the present toxicity tests should be modified by considering the media containing complexing agents.



As a conclusion, when aqueous solutions containing organic substances contact with metal hydroxide sludges in the disposal sites, toxic metal ions may redissolve and cause pollution in the water and soil ecosystems. To prevent potential hazards of these sludges, they have to be stabilized by using an appropriate method.

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