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Reduction of Chromium(VI) by Iron(II) Hydroxide in Alkaline Solution

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Iron(II) hydroxide stoichiometrically reduces CrO_4^{2-} to chromium(III) in alkaline solutions of pH 8 or above. This reduction was finished in less than one minute even at 5 °C. Although chromium(III) dissolves as CrO_2^- above pH 9.5, it did not dissolve in the presence of iron(III) hydroxide which had resulted from the oxidation of iron(II) hydroxide.

This paper reports a fundamental study on the removal of chromium(VI) from wastewaters. In the two-step process[1,2] used at present, chromium(VI) is first reduced to chromium(III) with sulfur dioxide, sodium bisulfite, or iron(II) sulfate below pH 3, and is then precipitated as chromium(III) hydroxide at pH 7.0—8.5 with sodium hydroxide or lime. The first step is always carried out at this low pH because there is a belief that the reduction of chromium(VI) is fast below pH 3 and very slow at pH 4—10.[3]

Recently, we have developed a new process for the chemical treatment of wastewaters which permits simultaneous removal of hazardous metals. In this process, chromium(VI) is reduced by iron(II) at pH 10. A plant for the treatment of laboratory wastewaters was constructed using the new process at the University of Osaka Prefecture and has been in continuous operation since August 1974. Chromium(VI), with a maximum value in influent of 8.2 ppm, is removed to below the detection limit of 0.2 ppm[4] as are the other hazardous metals.

The reduction of chromium(VI) by iron(II) has been studied below pH 7[5,6] and at pH 6.8—7.8,[7] but it has not been studied at pH of 8 or above, at which iron(II) is precipitated as iron(II) hydroxide. In this paper, we report on the heterogeneous reduction of chromium(VI) by iron(II) hydroxide in order to explain the successful treatment of chromium(VI) at the wastewater treatment plant described above.

Experimental

Reagents. All reagents were of analytical-reagent grade. Water was doubly distilled, the second distillation being carried out from alkaline permanganate in an all-Pyrex still. Stock solution of 0.20 mol dm^{-3} chromium(VI) was prepared by dissolving potassium dichromate which had been dried for two hours at 105 °C in redistilled water. Stock solution of 1.00 mol dm^{-3} iron(II) was prepared by dissolving iron(II) sulfate in 0.2 mol dm^{-3} sulfuric acid. When more than 1.0% of the 1.00 mol dm^{-3} iron(II) had been oxidized by oxygen in the air, a stock solution of iron(II) was freshly prepared.

Apparatus. The pHs of the solutions were measured with a Horiba Model F-7DE pH meter. Total iron and total chromium in the solution were determined by atomic absorption spectroscopy using a Nippon Jarrel-Ash Model AA-1W. A Shimadzu Model UV-200 spectrophotometer was used to determine chromium(VI).

Procedure. A solution containing an appropriate amount of 0.2 mol dm^{-3} chromium(VI) solution was adjusted with sodium hydroxide to a pH of 8 or above. Another solution containing an appropriate amount of 1.00 mol dm^{-3} iron(II) solution was similarly adjusted to the same pH. Both solutions were mixed, and stirred at 25 °C. At 0, 2, 5, 10, 20, and 30 min, samples of the resultant mixture were put through glass filters (3G4). Glass filters were used in preference to filter paper, because paper reduced part of the chromium(VI) to chromium(III).

Chromium(VI) in alkaline solution absorbs in the ultraviolet at 370 nm, but chromium(III) does not absorb at this wavelength, so chromium(VI) in the filtrate can be selectively determined in the presence of chromium(III). Total chromium in the filtrate was determined by an atomic absorption method using ammonium perchlorate as a releasing agent to remove interference from other metals and anions.[8]

Futhermore, the reduction of chromium(VI) by iron(II) hydroxide was examined in a nitrogen atmosphere. Commercial nitrogen gas contains traces of oxygen, so this oxygen was removed by passage of the nitrogen gas through an impinger containing an iron(II) hydroxide suspension. With this system, only 1.0% of 500 ppm iron(II) was oxidized after stirring for 30 min at pH 10.

Results and Discussion

Stoichiometry of Reduction Reaction. In order to determine reduction times of chromium(VI) by iron(II) hydroxide at pH 8.0, 10.0, and 11.6, the remaining chromium(VI) in the mixture of a suspension containing iron(II) hydroxide and a solution containing chromium(VI) at the same pH was determined at appropriate time intervals. The sampling and filtering process took two minutes and so the first two minutes of the reaction could not be examined. Within this limitation, Table 1 shows that pHs in this range have no effect on the rate of reduction of chromium(VI) by iron(II) hydroxide in a nitrogen atmosphere. In all of these cases, the reduction of chromium(VI) finished in less than two minutes. In the experimental

Table 1. Effect of pH on reduction of Cr(VI) by iron(II) hydroxide[a)]

Time/min	Remaining concentration of Cr(VI)/ppm		
	pH 8.0	pH 10.0	pH 11.6
0	100	100	100
2	24.5	30.2	32.1
5	25.2	30.8	31.8
10	24.1	31.2	31.6
20	24.9	30.4	32.3

a) Initial concentration of iron(II) and chromium(VI) are 224 ppm and 100 ppm, respectively. Experiments were carried out at 25±1 °C in a nitrogen atmosphere.

conditions of Table 1, 30.9 ppm chromium(VI) should have remained in solution if the reduction proceeded at a stoichiometric 3:1 molar ratio of iron(II) to chromium(VI) according to the following equation:

$$3\mathrm{Fe(II)} + \mathrm{Cr(VI)} \longrightarrow 3\mathrm{Fe(III)} + \mathrm{Cr(III)}. \qquad (1)$$

The reduction proceeded stoichiometrically at pH 10.0 and 11.6, but the concentration of chromium(VI) remaining at pH 8.0 was less than the predicted value. It appears that a little of the remaining chromium(VI) was adsorbed at pH 8.0 on iron(III) hydroxide which was the oxidized product of iron(II) hydroxide.[9)]

The reduction of chromium(VI) by iron(II) hydroxide was also examined using air instead of nitrogen. In this case, the reduction was also completed in less than two minutes.

To elucidate the stoichiometry of this reduction, the chromium(VI) remaining in the solution after 30 min was determined when various concentrations of iron(II) hydroxide were added to 100 ppm of chromium(VI). Figure 1 shows that the remaining chromium(VI) decreases with increasing iron(II) hydroxide and, in a nitrogen atmosphere, coincides with the curve estimated from the stoichiometry at a 3:1 molar ratio of iron(II) to chromium(VI). On the other hand, experimental data obtained in the presence of air deviated from the stoichiometric curve. In this case, dissolved oxygen competed with the chromium(VI) for the available iron(II) hydroxide.[10)] This competition made iron(II) hydroxide unavailable for the reaction with chromium(VI), thereby increasing the concentration of chromium(VI) remaining.

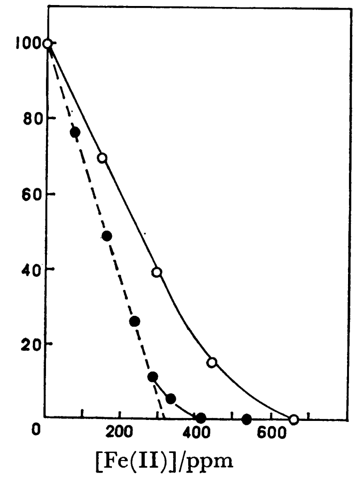

Fig. 1. Relation between remaining concentration of Cr(VI) and concentration of added Fe(II). Experiments were carried out at pH 10.3 (25 °C) in air(○) and in a nitrogen atmosphere(●). Stoichiometric curve is (----).

Chemical Species Taking Part in the Reduction. Chromium(VI) exists in solution as various species as shown in the following equilibria:

$$\begin{array}{lll} & \mathrm{p}K & \\ \mathrm{Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^-} & 1.5, & (2) \\ \mathrm{HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+} & 6.5. & (3) \end{array}$$

These equilibrium constants were taken from Sillén and Martell.[11)]

Chromium(VI) is present as $\mathrm{CrO_4^{2-}}$ in alkaline solution of pH 8 or above as in Eq. 3. On the other hand, iron(II) hydrolyzes to produce iron(II) hydroxide above pH 8. From our results and from thermodynamic considerations, it seems that iron(II) hydroxide reduces $\mathrm{CrO_4^{2-}}$ by the following reaction:

$$\begin{aligned} &\mathrm{3Fe(OH)_2 + CrO_4^{2-} + 4H_2O} \longrightarrow \\ &\qquad \mathrm{3Fe(OH)_3 + Cr(OH)_3 + 2OH^-}. \qquad (4) \end{aligned}$$

This reaction indicates that, for every mole of iron(II) hydroxide oxidized, 2/3 mol of hydroxide ion is produced, and in fact, when a suspension of iron(II) hydroxide and a chromium(VI) solution adjusted to same pH were mixed, the pH of the mixture was increased. Therefore, we tried to determine the rate of reduction by following this change of pH. The pH of each mixture became constant immediately after mixing at 5—8 °C. It takes about one minute to mix the solution completely. Thus, the reduction of chromium(VI) by iron(II) hydroxide proceeds in less than one minute in alkaline solutions even at these low temperatures.

Table 2 indicates the increase in pH caused by the reduction at various pHs at 5—8 °C, and the theoretical final pH based on Eq. 4. It is thought that the reduction proceeds stoichiometrically according to Eq. 4 since the theoretical pHs agree very closely with the pHs obtained experimentally.

Removal Mechanism of Chromium(VI). The reaction products are chromium(III) hydroxide and iron (III) hydroxide, according to Eq. 4. However, the precipitate formed from reduction in alkaline solution does not seem to be a simple mixture of these hydroxides.

When a suspension of this precipitate at pH 10 was incubated for 30 min, no chromium(III) was detected in its filtrate, while when a suspension (pH 10) of chromium(III) hydroxide was mixed with a suspension (pH 10) of iron(III) hydroxide, the concentration of dissolved chromium(III) increased with

TABLE 2. INCREASE OF pH BY THE REDUCTION OF Cr(VI)

Concn of metals/mmol dm^{-3} a)		pH			Temp/°C
Fe(II)	Cr(VI)	Initial	Final(obsd)	Final(theor.)	
3.0	2.0	9.15	11.28	11.28	8.0
3.0	2.0	9.98	11.25	11.30	5.0
5.0	0.5	10.10	11.32	11.32	7.2
5.0	0.5	11.07	11.20	11.33	5.0

a) Volume: 200 cm^3

time, reaching 0.31 ppm at 30 min as shown in Table 3. Chromium(III) hydroxide redissolves in highly alkaline solutions as shown in curve a of Fig. 2. This redissolution is explained by the formation of CrO_2^-. However, the redissolution of chromium(III) was not observed (curve b of Fig. 2) when sodium hydroxide was added to the acidic solution (pH 2) containing chromium(III) and iron(III). This result shows that chromium(III) is coprecipitated with iron(III) hydroxide. From the results above mentioned, when chromium(VI) was reduced by iron(II) hydroxide in alkaline solution, chromium(III) seems to be incorporated in an undissolved form into iron(III) hydroxide. Therefore, the coprecipitation of chromium (III) with iron(III) hydroxide seems to be the incorporation of chromium(III) into iron(III) hydroxide. This can be explained by the similarity of chemical behavior of iron(III) and chromium(III). Both of them have similar polymerization mechanisms[12,13] and hydrolyze even in acidic solutions,[14] and both ions have the same charge and a similar ion radius.

Table 3. Difference between a mixture of $Fe(OH)_3$ and $Cr(OH)_3$[a] and the precipitate from reduction[b]

Time/min	Dissolved Cr(III)/ppm	
	$Fe(OH)_3$+ $Cr(OH)_3$(pH10)	Precipitate(pH10)
10	0.15	0.05
20	0.22	0.05
30	0.31	0.05

a) Initial concentrations of Fe(III) and Cr(III) are 100 ppm and 50 ppm, respectively. b) According to Eq. 4.

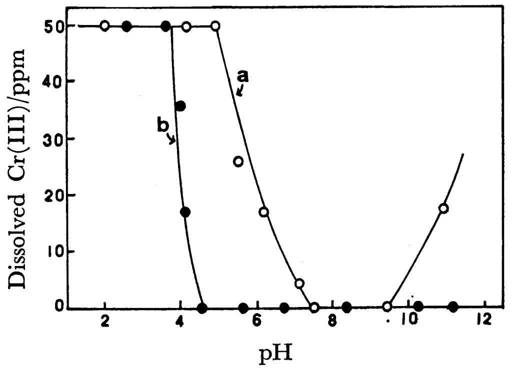

Fig. 2. Precipitation of Cr(III) in the presence of and in the absence of Fe(III).
Initial concentration of Cr(III) and Fe(III) are 50 ppm and 500 ppm, respectively. a; (○) in the absence of Fe(III), b; (●) in the presence of Fe(III).

Conclusion

Iron(II) hydroxide reduces chromium(VI), CrO_4^{2-}, to chromium(III) in less than one minute at pH 8 or above, at 5—8 °C, and at concentrations from 0.5—2.0 mmol dm^{-3}. The chromium(III), concurrently precipitated without adjusting the pH, seems to be incorporated into iron(III) hydroxide which results from the oxidation of iron(II) hydroxide. Thus, iron(II), as iron(II) hydroxide, quickly reduces chromium(VI) even in this heterogeneous system. Therefore, the conventional two-step process mentioned above is not necessary for chromium(VI) removal from wastewaters, since chromium(VI) can be removed, along with other hazardous metals, by iron(II) at pH 8 or above.

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