

## Equilibria and Kinetics of Cr(VI) Reduction 심층 지하에서의 육가 크롬 환원

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### 요약/Abstract

환원은 심층 지하처분되는 Cr(VI)의 양을 줄이는데 중요한 수단 중의 하나이다. 이 반응은 pH와 온도에 따라 민감하게 작용하며, 지하심층 처분장의 낮은 pH와 높은 온도는 토양 유기질, 높은 염소이온 농도와 더불어 Cr(VI)의 환원에 좋은 환경을 제공한다. 본 연구에서는 다양한 환경 조건에 따른 토양 유기질과 염소이온에 의한 Cr(VI)의 환원이 조사되었다. aquifer와 aquitard 샘플은 각각 미국 루이지애나주 세인트 버나드군과 세인트 찰스군의 심층 처분장에서 채취되었다. 본 연구에서는 심층처분장을 대표하는 pH(-0.81~2.0), 온도(50°C와 70°C), 염소이온 농도(0, 0.26, 0.52 몰)를 이용하였다.

Reduction is one of the important mechanisms in decreasing the amount of Cr(VI) in wastewater and this reaction is quite dependent on pH and temperature. Either soil organic materials, or a high inorganic salt concentration with elevated temperature and low pH will provide a good condition for the reduction of Cr(VI) to Cr(III) in deep well injection zones.

Chromate reduction by soil organic materials and chloride ion in various environment conditions is investigated. Aquifer and aquitard formation samples have been obtained from a deep well in St. Bernard Parish, and St. Charles Parish, LA, U.S.A., respectively. For this study, pH ranging from -0.81 to 2.0, temperature 50°C and 70°C, and chloride concentration 0 M, 0.26 M and 0.52 M are used to represent the actual conditions in deep well injection zones.

## INTRODUCTION

The Louisiana Department of Natural Resources has shown that chromium contaminated wastewater is a significant portion of the wastes being deep well injected, occupying 20 % of total wastewater disposed of through deep well injection practices in Louisiana, U.S.A. (Jacobus et al., 1985). As part of an overall study on the fate and transport of chromium upon deep well injection, this paper addresses the equilibria and kinetics of chromium reduction in deep well injection zones.

Many investigators reported the behavior of Cr(VI) and Cr(III) and removal techniques using different kinds of mechanisms. The two major removal pathways are adsorption and reduction. Zachara et al. (1987) studied chromate ( $\text{CrO}_4^{2-}$ ) adsorption on amorphous iron oxyhydroxide. They found that anionic and nonionic co-solute such as  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{SiO}_4$  respectively reduced chromate adsorption through a combination of competitive and electrostatic effects, but cations such as  $\text{K}^+$ ,  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$  did not show appreciable influence. Stollenwerk and Grove (1985a) showed the quantity of Cr(VI) adsorbed varied with the type and concentration of other anions in solution. They found that a mixture of 50% ( $\text{H}_2\text{PO}_4^- + \text{HPO}_4^{2-}$ ) inhibited adsorption of Cr(VI) to a great extent. Griffin et al. (1977) showed that adsorption of Cr(VI) by two different types of clay increased with the decrease of pH in the range of 9 to 1.

James and Bartlett (1983a) investigated the

effect of dissolved organic carbon on the reduction of Cr(VI) at different pH and the effect of sulfate and phosphate on Cr(VI) adsorption. Hyun and Field (1989) showed the effect of chloride ion on the attenuation mechanisms of Cr(VI), temperature effect, and the role of organic chemicals coinjected in the reduction of Cr(VI). The mechanism of Cr(VI) reduction by chloride ion oxidation is similar to the interference caused by chlorides in the chemical oxygen demand (COD) test of a wastewater. The environment in the COD reaction vessel is similar to that in deep well injection zones with respect to high temperature and low pH. Cripps and Jenkins (1964) suggested that an ion pair form with mercury ion ( $\text{HgCl}_2^\circ$ ) before any chloride reacts with  $\text{K}_2\text{Cr}_2\text{O}_7$ , prevents the interference by chloride ion.

Stollenwerk and Grove (1985b) investigated the reduction of Cr(VI) in water samples acidified for preservation. They found the occurrence of reduction by dissolved organic matter, even at 4 °C. They found also that the rate of reduction of Cr(VI) increased with increase of nitrite produced from aged nitric acid, dissolved organic carbon, hydrogen ion ( $\text{H}^+$ ), and temperature. The reduction by inorganic substances such as ferrous ion is also possible in shallow subsurface environments (Eary and Rai, 1988).

The objective of this study is to investigate how environmental factors such as temperature, pH, soil organic material, and chloride ion can affect the reduction rate of Cr(VI).

## MATERIALS AND METHODS

Two core samples were obtained from injection zone of existing wells in Louisiana. A sample of shale was obtained from the St. Bernard injection well. Sand sample was collected from the drilling of the St. Charles injection well. Both well samples were crushed with pestle and mortar and were washed with deionized water until the chloride ion in decanted water was not detected, using the silver nitrate titration technique (APHA et al., 1985). Then the prewashed formation materials (shale and sand) were dried at  $102 \pm 1^\circ\text{C}$  in a drying oven and were ground to pass through a No. 100 sieve. The injection zone formation materials were then stored in a desiccator until use.

In case of the experiment at pH  $-0.62$ , 83 ml of deionized water, and 7 ml of concentrated nitric acid ( $\text{HNO}_3$ ) were mixed with 2 g of dry shale or sand and shaken at  $50^\circ\text{C}$  for 24 hours in 250 ml Erlenmeyer flasks adapted with a septum port. Twenty four hours at  $50^\circ\text{C}$  has been shown to be adequate to reach a stabilized pH (Fink, 1987). Each flask then received 10ml of  $\text{K}_2\text{CrO}_4$  solution (1mg/ml of Cr(VI)).

The flasks were purged with purified nitrogen gas to remove all traces of oxygen and then sealed. The flasks were then shaken in a water bath (120 rpm). At various intervals, 2 ml of solution was taken by syringe through the septum port and centrifuged (Eppendorf Microcentrifuge Model #5415), maintaining 14,000 G force for 20 min. The use of a septum and syringe to withdraw samples from the fla-

skis prevented escape of chlorine gas ( $\text{Cl}_2$ ), which would consequently trigger the further reduction of Cr(VI). 1 ml of supernatant was used to analyze the Cr(VI) concentration. Fresh nitric acid was used and always kept in a dark cabinet to prevent nitrite reduction of chromium.

Temperature was controlled at  $50^\circ\text{C}$  and  $70^\circ\text{C}$  to observe temperature dependency. Sodium chloride concentrations were maintained at 0, 0.26, and 0.52 mole. The pH effect was investigated at four values (2, 0,  $-0.62$ , and  $-0.81$ ). Only at pH 2 was there a slight pH change after 24 hour stabilization. 1 N and 0.1 N  $\text{HNO}_3$  or NaOH were added to maintain pH 2 before reduction experiments were initiated. During the experiments pH did not change more than  $\pm 0.2$  from pH 2.

Cr(VI) was analyzed by measuring the pink color complex developed between 1, 5-diphenylcarbazide and Cr(VI) ion in an acidified solution (APHA et al., 1985). Absorbance was measured at 540 nm with a Perkin Elmer Lambda 4 Spectrophotometer, using 1 cm cuvette. The minimum detectable concentration was 0.005 mg/l. The amount of soil organic materials (reducing agents in injection zone formation materials) was determined on separate sample aliquots by weight loss after ashing at  $550^\circ\text{C}$  (APHA et al., 1985). Experimental preparations are summarized in Table 1.

## RESULTS AND DISCUSSION

Formation Effect : Figure 1 shows that shale

Table 1 Experimental Preparations

Experiment	NaCl	Temp.	pH	Formation
Formation	0 Mole	70 °C	-0.62	Shale
Effect	0.26 Mole			Sand
Temp.	0.26 Mole	50 °C	-0.62	Shale
Effect		70 °C	-0.81	
NaCl	0 Mole	50 °C	0.0	Shale
Effect	0.26 Mole	70 °C		
	0.52 Mole			
pH Effect	0 Mole	50 °C	2.0	Sand
	0.26 Mole		-0.62	
			-0.81	

sample containing 1.3% (w/w) organic materials produces 100% reduction of Cr(VI) at 70 °C in 24 hours ( $k \sim 3.97 \times 10^{-2} \text{ hr}^{-1}$ ). In the experiment with sand sample containing 0.5% organic materials, the reaction period to reach 100% was extended to 48 hours ( $k \sim 2.47 \times$

$10^{-2} \text{ hr}^{-1}$ ). When the temperature was high enough, both experiments showed complete reduction of Cr(VI). When chloride ion was involved in the reduction of Cr(VI), the reactions on both injection zone formation materials showed the same rate of reaction ( $k \sim 2.1 \times 10^{-2} \text{ hr}^{-1}$ ). In case of shale, the reduction rate constant was decreased from  $3.97 \times 10^{-2}$  to  $2.1 \times 10^{-2} \text{ hr}^{-1}$ , while the time to reach equilibrium was extended from 24 to 48 hours. Meanwhile, the reduction rate constant was decreased slightly from  $2.47 \times 10^{-2}$  to  $2.1 \times 10^{-2} \text{ hr}^{-1}$  in case of sand, whose organic material content is only 0.5%. This implies that the chloride ion hinders Cr(VI) reduction by soil organic materials and the reduction rate is governed mainly by the oxidation of chloride ion. Consequently, the amount of soil organic materials is no longer important as far as deep well injection zone

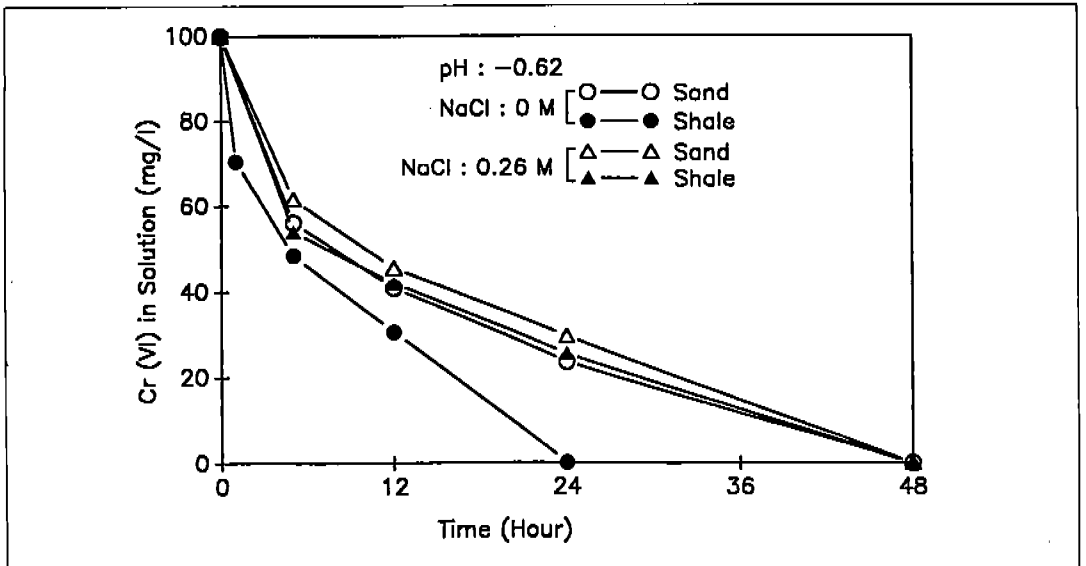


Fig. 1 Formation Effect on Reduction at 70 °C

is concerned, where the concentration of chloride ion is high enough.

Figure 2 shows the pH effect on the adsorption of Cr(VI) by shale and sand formation materials. Initial concentration of Cr(VI) was 20 mg/l. As seen in the figure, the shale adsorbs Cr(VI) slightly (11%) only at pH 2, but not below pH 2. The speciation of Cr(VI) at different pH accounts for this dependency of adsorption on pH. Bichromate ( $\text{HCrO}_4^-$ ) is predominant in the pH range of 1.5 to 6.5, and as pH decreases in this range, the increased positive surface charge of the clay attracts more anions. At pH less than 1.5, chromic acid ( $\text{H}_2\text{CrO}_4$ ) is predominant, and is less preferentially adsorbed. Mayer and Shick (1981) reported that the adsorption of Cr(III) to clay surface could control the reduction rate of Cr(VI). However, the Cr(III) ion reduced from Cr(VI)

is not adsorbed at pH 2 to the surface of clay components in shale, and most of Cr(III) remains in the soil solution (Huang and Wu, 1977; Griffin et al., 1977). Thus, adsorption cannot control the reduction rate at pH 2 in this study, though the adsorption is possible at pH 2. No adsorption is shown at any pH, even at 2, when sand formation material is used. This is due to the small specific surface area and the small electrostatic potential at the surface of the sand.

Temp. Effect : Figure 3 shows the temperature effect on reduction at pH -0.62 and -0.81. At pH -0.62, when the temperature was 50 °C, the time to reach equilibrium took more than 100 hours and only 60% of Cr(VI) in solution was reduced. However, at 70 °C, the time to reach equilibrium was reduced to 50 hours and 100% reduction was possible. Once

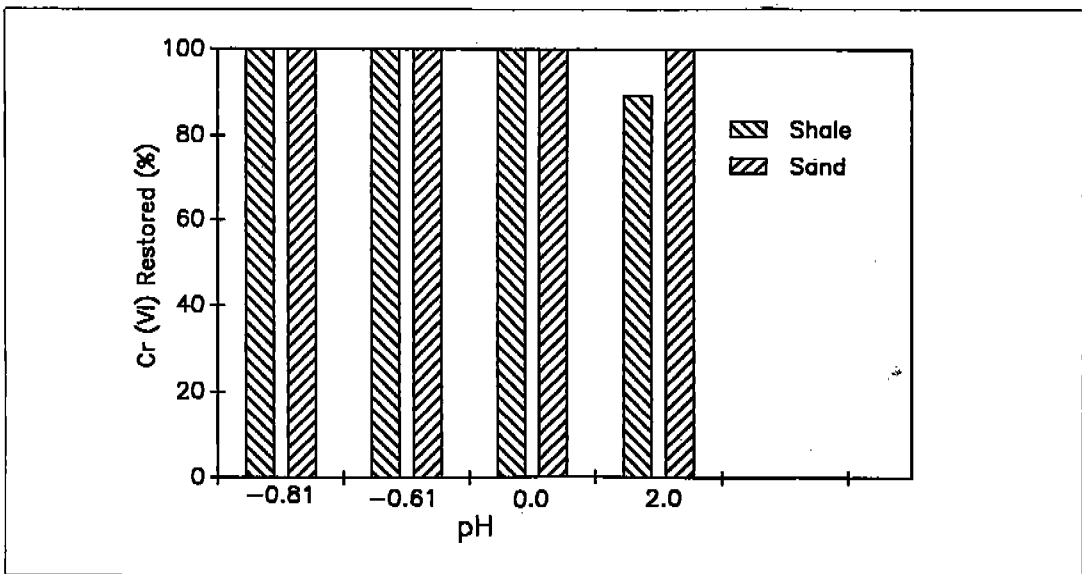


Fig. 2 Cr(VI) Restored after Oxidation

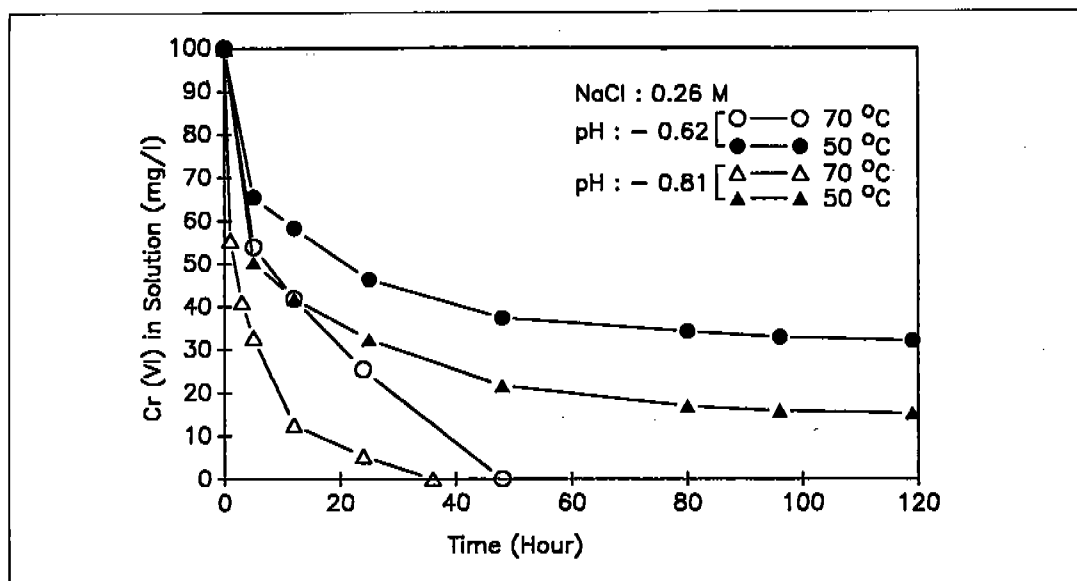


Fig. 3 Temperature Effect on Reduction with Shale

the temperature was high enough, such as 70 °C, even the reduction hindered by the presence of chloride ion could become 100% in 50 hours. The effect of temperature on reduction rate is related to its effect on the reaction rate constant. In most reactions, collisions between reacting species are necessary for chemical reactions to occur. The number of collisions between reacting species can be increased by increasing the temperature. Amacher and Baker (1982) reported that the rate of reduction could be increased by increasing the temperature, but the most dramatic change was produced by lowering the pH of the solution. They attributed this large rate increase to the protons which were one of the reactants in the reduction rate. However, in Figure 3, it was found that when pH was changed from -0.62 to -0.81, the equilibrium concentration of Cr

(VI) changed from 35 mg/l to 20 mg/l. When the temperature was changed from 50 °C to 70 °C, that concentration was decreased from 35mg/l to 0 mg/l. Therefore, the temperature had more dramatic effect in the change of reduction rate in this study.

The activation energy for this reaction could be calculated from the data on Figure 3. The effect of temperature on reaction rate is well presented in Arrhenius empirical rate law (Snoeyink and Jenkins, 1980),

$$k = Ae^{(-E_a/RT)} \quad (1)$$

where A : frequency factor,  $E_a$  : activation energy, R : ideal gas constant and T : temperature in °K. Equation 1 can be linearized as

$$\ln k = \ln A - E_a/(R \times T) \quad (2)$$

Thus, a plot of  $\ln k$  versus  $1/T$  should give a straight line with a slope of  $-E_a/R$  and an intercept on the  $1/T$  axis of  $\ln A/(E_a/R)$ . From the calculation, activation energy at pH  $-0.81$  was  $17.61$  Kcal/mole and at pH  $-0.62$  was  $15.12$  Kcal/mole. These values imply that the temperature dependence of reduction at lower pH is greater than that at higher pH. These values are comparable to  $13.9$  Kcal/mole of activation energy for the reduction of Cr(VI) by fulvic acid at pH  $5.5$  obtained by Amacher and Baker(1982).

**NaCl Effect :** Figure 4 shows the effect of chloride ion on reduction of Cr(VI) to Cr(III). In this experiment, possible reducing agents are only chloride and soil organic materials. The shale from a disposal well in St. Charles Parish contained  $1.3\%$  (w/w) of soil organic materials. When the pH was  $0.0$ , at any concen-

tration of NaCl, equilibrium was reached in 100 hours and never yielded  $100\%$  reduction at  $50^\circ\text{C}$ . When no NaCl was added, soil organic materials were the only reducing agent for Cr(VI), resulting in about  $40\%$  of the Cr(VI) being reduced. Increased Cr(VI) reduction to about  $50\%$  of Cr(VI) was independent of NaCl amount added. From this result, it is concluded that the reduction rate is not a function of the NaCl amount added. This result contradicts that of Mayer and Shick(1981). They found Cr(VI) reduced from a  $1\ \mu\text{M}$  Cr(VI) solution by a  $20\ \mu\text{M}$  gallic acid solution was a function of salinity. However, they believed that Cr(III) reduced from Cr(VI) would become rapidly adsorbed by suspended sediments and this adsorption which was affected by the salinity would control the reduction rate of Cr(VI). However, pH range in this study is far less

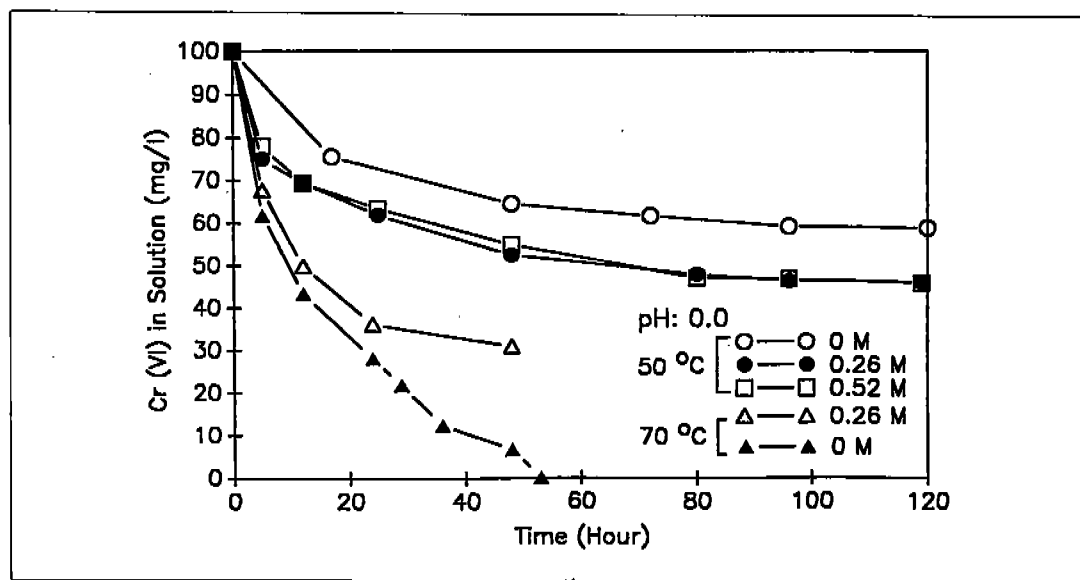


Fig. 4 NaCl Effect on Reduction with Shale

than pH 2, and consequently no adsorption is possible. No adsorption at pH 0.0 or less is due to the formation of chromic acid,  $H_2CrO_4$ , which is predominant below pH 1.5 and is not readily adsorbed (Griffin et al., 1977).

Equilibrium was reached in 60 hours at 70 °C. However, in contrast to the experiment performed at 50 °C, 100% reduction occurred in the absence of NaCl and only 70% reduction occurred when 0.26 M of NaCl was added. It resulted from the hindrance of chloride ion on the reduction of Cr(VI) to Cr(III) by the soil organic materials. As the temperature increased, the reactivity of chloride ion as a reducing agent became predominant in the solution and the chloride ion controlled the reaction rate of reduction. If it is assumed that chloride ion and soil organic materials work independently of each other, the reduction with the addition

of NaCl should be larger than that without NaCl. Therefore, at low temperatures, both soil organic materials and chloride ion were active for the reduction of Cr(VI) and at high temperature, the reactivity of chloride ion was greater than that of soil organic materials.

pH Effect : Figure 5 shows the effect of pH on reduction kinetics. When pH was 2.0, the reduction was less than 10% and was slightly increased when chloride ion was added. However, it was still less than 10% and the time to reach equilibrium was not changed. Even though the pH was decreased, the time to reach equilibrium did not change significantly. James and Bartlett (1983b) observed that the reduction of Cr(VI) increased as pH decreased. This is shown in the figure, when pH changes from 2 to 0 and finally to -0.62 without NaCl. Considering the curves at pH -0.81 and pH

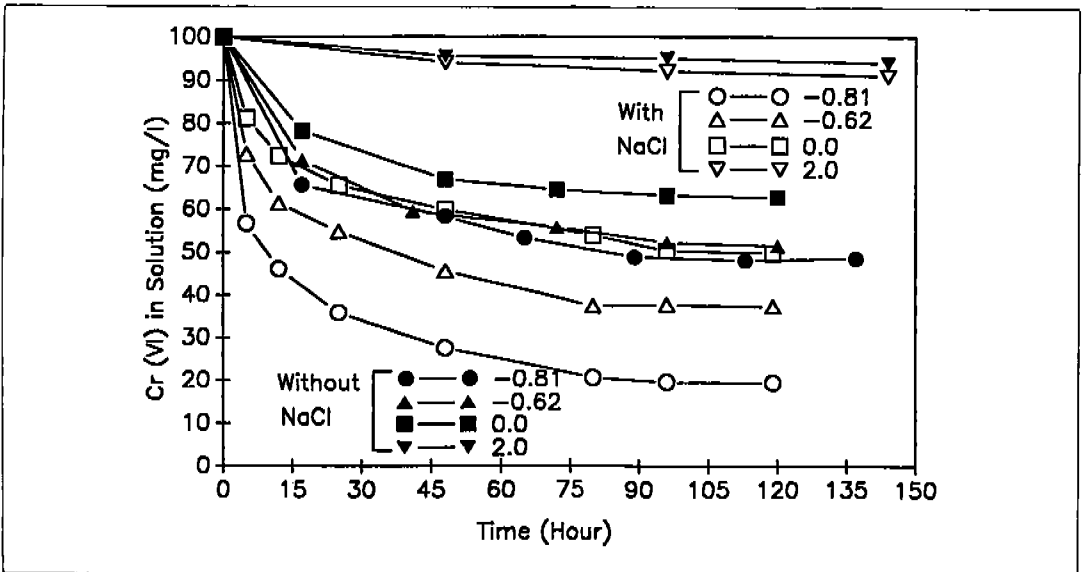


Fig. 5 pH Effect on Reduction with Sand (50°C)



-0.62, it was postulated that once the pH was lower than a certain value, -0.62 here, the reduction rate by soil organic materials was no longer changed with pH. However, when NaCl was added, the contribution of NaCl to the reduction of Cr(VI) was very much sensitive to pH. At pH -0.62, the reduction was equilibrated at about 40 mg/l of Cr(VI) and at pH -0.81, about 20mg/l. Thus, pH change resulted in 20% increase in the reduction of Cr(VI). In Figure 5, the reduction rate was determined to be first order, in which the reaction was a function of Cr(VI) amount remaining in the solution. The reduction rate coefficient 'k' and the determination coefficient 'r<sup>2</sup>' were calculated and are shown in Table 2. The r<sup>2</sup> values in Table 2 support the first order reaction. Amacher and Baker (1982) studied Cr(VI) reduction at the pH range of 1.0 to

Table 2: k and r<sup>2</sup> Values at Different pH

pH	Without NaCl		with NaCl	
	k (sec <sup>-1</sup> )	r <sup>2</sup>	k (sec <sup>-1</sup> )	r <sup>2</sup>
-0.81	3.1×10 <sup>-3</sup>	0.84	7.2×10 <sup>-3</sup>	0.82
-0.62	2.6×10 <sup>-3</sup>	0.79	4.6×10 <sup>-3</sup>	0.85
0.0	1.9×10 <sup>-3</sup>	0.79	2.6×10 <sup>-3</sup>	0.85
2.0	1.7×10 <sup>-4</sup>	0.82	2.8×10 <sup>-4</sup>	0.87

5.5 and in all cases, the reduction rate was first order. Their findings support the above results. In their study, when pH was changed from 5.5 to 1.0, the reaction rate was increased 100 times in magnitude from 0.037 day<sup>-1</sup> to 0.15 hr<sup>-1</sup>. Meanwhile, in this study, when pH was changed from 2 to -0.81, the reduction rate was increased approximately 20 times in magnitude. This study showed a change 5 times lower in the reduction rate. This results from the fact that their study was performed

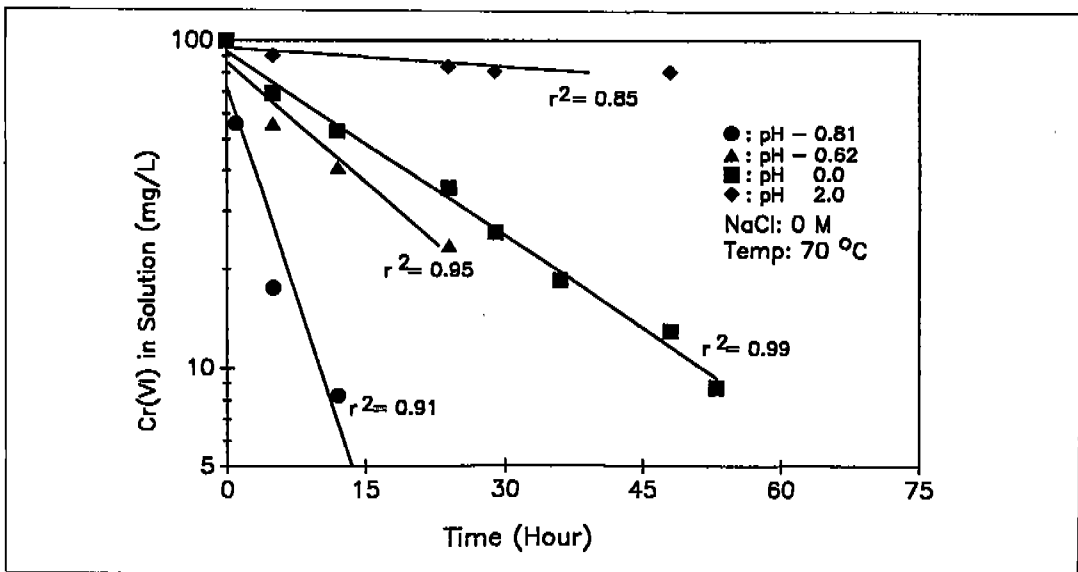


Fig. 6 Regression Analysis for Sand Formation

at high pH ranges where the reduction rate was more sensitive.

Figure 6 shows the linearity of the reduction reaction at different pH values. When the reaction is first order, the plot of  $\log \text{Cr(VI)}$  concentration versus time shows a linear relationship. At low pH values (less than 0), the determination coefficient,  $r^2$ , was higher than 0.9 and at relatively high pH such as 2, the  $r^2$  was slightly less than 0.9. Therefore, overall reaction rate can be concluded to be first order over the pH values examined here. Though the equilibrium  $\text{Cr(VI)}$  concentration at different pH was not shown on Figure 6, it is important to note that not all reactions showed a 100% reduction (some reactions showed less than 10% reduction).

## CONCLUSIONS

When temperature is moderate, such as 50 °C, both soil organic materials and chloride ion contribute to the reduction of  $\text{Cr(VI)}$ . However, as the temperature increases, the reactivity of chloride ion for  $\text{Cr(VI)}$  reduction becomes predominant, and chloride ion controls the reduction rate, which is slower than that by soil organic materials. Temperature affects both time and extent of the reduction. When temperature is high enough, such as 70 °C, 100% reduction occurs in just half the time of reduction at 50 °C. Using the Arrhenius' Law, the activation energy can be calculated, when the reduction rate constants are determined at more than two different temperature.

As the pH is decreased, more  $\text{Cr(VI)}$  is reduced from the soil solution. However, 100% reduction is not obtained at low temperatures, no matter what pH the deep well injection zones commonly have. In the pH range of this study, all the reduction reactions were found to be first order.

When no chloride ion is present, the amount of soil organic materials plays an important role in the reduction of  $\text{Cr(VI)}$ . When the soil organic materials increase from one to another injection zone formation material, the reaction time is reduced and the rate constant is also increased. However, when chloride ion is present, the role of soil organic materials is suppressed by chloride ion and this ion controls the reduction rate.

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