Effect of NaCl on Cr(VI) Reduction by Granular Zero Valent Iron (ZVI) in Aqueous Solutions

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This study examined the effect of NaCl on the removal of Cr(VI) by ZVI in aqueous solutions and proposes a potential mechanism of Cr(VI) removal by ZVI in aqueous solutions with NaCl. A series of batch tests was conducted on ZVI using 100 mg/L Cr(VI) solutions at an initial pH of 3 at various NaCl concentrations. The NaCl in aqueous solutions improved the removal efficiency for Cr(VI) by ZVI. Fe(III)-Cr(VI) (oxy)hydroxides were precipitated both on the ZVI surface and in the solution via the reduction reactions of Cr(VI) to Cr(III) in the presence of NaCl. The increase in the Cr(VI) removal efficiency in the solutions with NaCl was attributed to the Cl⁻ ions, which accumulate at the anodic sites of ZVI, thereby enhancing ZVI oxidation and colloidal particle formation. In the NaCl solutions, small grains were initially precipitated on the ZVI surface, via relatively fast reactions. The subsequent slowing of these reactions resulted in the precipitation of large grains on the ZVI surface and colloidal particles in the solutions.

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1. Introduction

Cr(VI) has been increasingly used to inhibit metal corrosion in the metal plating industry. Wastewater containing the Cr(VI) compounds, chromate (CrO₄²⁻) and dichromate (Cr₂O₇²⁻) can be released from the metal plating industry and thus contaminate groundwater by the delivery of Cr₂O₇²⁻ and CrO₄²⁻ as these ions are soluble in water, not biodegradable, mobile and toxic. Groundwater thus contaminated must be treated.

Cr(VI) in aqueous solutions can be reduced to Cr(III), which is less mobile and toxic than Cr(VI), by coupling with oxidation of reducing agents. Sodium metabisulfite,¹) hydrogen sulfide,²) divalent iron,³)⁵)⁷) Fe(II)-bearing minerals,⁸) zero valent iron (ZVI),⁹)¹⁷) and organic compounds¹⁸) can be used as the reducing agents. Cr(III) in aqueous solutions can precipitate as Cr(OH)₃ in the pH range between 8 and 10.

ZVI has been increasingly used in permeable reactive barriers as a reactive medium to treat contaminated groundwater. The reduction of Cr(VI) to Cr(III) by ZVI is described by following reactions.¹⁹)

\[ 3\text{Fe}^0 + 2\text{CrO}_4^{2-} + 16\text{H}^+ \rightarrow 3\text{Fe}^{2+} + 2\text{Cr}^{3+} + 8\text{H}_2\text{O} \] (1)

\[ 3\text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ \rightarrow 3\text{Fe}^{3+} + \text{Cr}^{3+} + 4\text{H}_2\text{O} \] (2)

Reactions (1) and (2) can be combined as follows to give (3).

\[ \text{Fe}^0 + \text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{Cr}^{3+} + 4\text{H}_2\text{O} \] (3)

Fe(II) can also be produced by the reaction between Fe⁰ and H⁺

\[ \text{Fe}^0 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2 \] (4)

Fe(II) produced by reaction (4) can also reduce Cr₂O₇²⁻ by reaction (2).

The production of Cr(III) and Fe(III) can cause precipitation of solid solutions such as CrₓFe₁₋ₓ(OH)₃(s) and CrₓFe₁₋ₓ(OOH)(s), which can constrain the concentration of Cr(III) to less than 10⁻⁶ M in aqueous solutions at pH ranging between 5 and 11.³¹) This precipitation process affects pH according to the following reactions:

\[ (1 - x)\text{Fe}(\text{III}) + x\text{Cr}(\text{III}) + 3\text{H}_2\text{O} \rightarrow \text{Cr}_x\text{Fe}_{1-x}(\text{OOH})_3(s) + 3\text{H}^+ \] (5)

\[ (1 - x)\text{Fe}(\text{III}) + x\text{Cr}(\text{III}) + 2\text{H}_2\text{O} \rightarrow \text{Cr}_x\text{Fe}_{1-x}(\text{OOH})_3(s) + 3\text{H}^+ \] (6)

In general, the rate of Cr₂O₇²⁻ reduction by ZVI is a function of ZVI surface area, Cr(VI) concentration, and pH as follows:

\[ \frac{dC_{\text{Cr(VI)}}}{dt} = -k \cdot A \cdot C_{\text{Cr(VI)}}^n \cdot C_{\text{H}^+}^m \] (7)

where \( k \) is the reaction rate constant and \( A \) is the reactive ZVI surface area. The reduction rate increases with decreasing pH and increasing ZVI surface area. Impregnation of transition metals such as Cu²⁺ on ZVI can also increase the reduction rate by increasing the reactivity of ZVI. In addition, some anions such as Cl⁻ can also affect the rate and extent of the reduction by enhancing iron corrosion.²²,²³) However, few studies have investigated how the colloidal particles formed in aqueous solutions with NaCl affect the Cr(VI) reduction by ZVI.

Thus, the present study objective was to investigate the effect of colloidal particle formation in the presence of NaCl on the Cr(VI) reduction by ZVI particles in aqueous solutions. Batch tests were conducted to evaluate the rate and extent of Cr(VI) reduction by ZVI particles in aqueous solutions at various NaCl concentrations.

2. Materials and Methods

Granular ZVI (Kanto Chemical) with a particle size ranging between 0.1 and 0.75 mm was used in this study without pretreatment. Sodium chromate tetrahydrate (Junsei Chemical) and hydrochloric acid (Matsunoen Chemical) were used for preparing Cr(VI) solutions and for adjusting...
pH, respectively. Deionized (DI) water was used for preparing all aqueous solutions.

A series of batch tests was conducted on granular ZVI using aqueous solutions with an initial Cr(VI) concentration of 100 mg/L at an initial pH of 3.0 to determine the extent for Cr(VI) reduction. The tests were conducted at various NaCl concentrations ranging between 0 and 0.4 M and ZVI dosages ranging between 2 and 20 g/L.

Various amounts of granular ZVI (0.1–1.0 g) were placed in 50 ml-polypropylene copolymer centrifugal tubes with Cr(VI) solutions. The tubes were then spun for various reaction times ranging between 10 min to 100 h, using a rotator shaker at 60 rpm and 25°C. At the designated sampling time, the pH of the solution was measured immediately using a pH meter. A portion of the suspension was collected and stored in a polypropylene bottle. One milliliter of the suspension was collected from top of the suspension in the polypropylene bottle.

The turbidity of the suspension was determined to estimate the concentration of colloidal particles in the suspension because red colored colloidal particles were produced in solutions with NaCl. Almost no ZVI particles were contained in the suspension because the ZVI particles sank much faster than the colloidal particles due to their higher density and larger size. The suspension was diluted 10 to 1 using DI water. The turbidity of the diluted suspension was measured using a turbidimeter (HANA micron). The remained suspension was filtered through 0.45 µm filter paper and then stored in a polypropylene bottle for chemical analysis. The Cr(VI) concentration of the filtrate was measured by a colorimetric method using a HACH colorimeter.

Colloidal particles were obtained by the filtration. The reacted ZVI particles, which had settled due to their high density, were also collected at the bottom of the centrifugal tube. The colloidal particles were dried in an oven at 70°C, whereas the reacted ZVI particles were dried in a vacuum desiccator to prevent their further oxidation. The dried colloidal particles and reacted ZVI particles were analyzed using scanning electron microscope (SEM) with energy dispersive X-ray spectrocope (EDX) to evaluate their morphology and chemical composition.

3. Results and Discussion

3.1 Effect of NaCl concentration

The temporal variations of Cr(VI) concentration and pH, shown in Fig. 1, were comparable, regardless of the NaCl concentration and ZVI dosage. Significant changes in the Cr(VI) concentration and pH were observed within 10 h because of the reduction of Cr(VI) to Cr(III) by ZVI particles according to reactions (1) and (2). The subsequent slow changes in Cr(VI) concentration and pH between 10 and 50 h were probably due to the formation of a protective rust film that prevented ZVI from further corrosion according to reactions (5) and (6). After 50 h, almost no changes in the Cr(VI) concentration and pH occurred because the ZVI surface was almost fully covered by the protective rust film.

The Cr(VI) concentration after 50 h of reaction at the ZVI dosage of 2 g/L decreased significantly from 80 to 50 mg/L as the NaCl concentration was increased from 0.004 to 0.04 M, but subsequently decreased slightly from 50 to 40 mg/L as the NaCl concentration was increased from 0.04 to 0.8 M (Fig. 2(a)). The results of pH as a function of the NaCl concentration were similar to those of the Cr(VI) concentration (Fig. 2(b)). These results indicate that the NaCl concentration may positively affect the Cr(VI) reduction by enhancing the iron corrosion.

Red colloidal particles were observed in the suspensions obtained from the batch tests with NaCl. The turbidity of the suspension was measured to estimate the concentration of the colloidal particles. In Fig. 3, the turbidity of the suspensions increased with increasing NaCl concentration, indicating the precipitation of more colloidal particles. These colloidal particles were collected by filtering the suspension and their morphology and chemical composition were analyzed by SEM (EDX) (Fig. 4). The agglomerated colloidal particles were spherical, with a diameter of approximately 2 µm, and primarily consisted of Fe and Cr, suggesting that they were rust particles of Fe(III)–Cr(III) (oxy)hydroxides produced by reactions (5) and (6).

The batch test results suggested that the increased number of colloidal particles in the suspensions might be related to the increase in the Cr(VI) reduction induced by the increasing NaCl concentration. Generally, as a metal in solution is oxidized by oxygen, an increase in aqueous salt concentration increases the distance between the surface of the metal and the sites of rust precipitation.22 The rust, Cr(III)–Fe(III)
(oxy)hydroxides, can be formed either on the surface of the ZVI particles or in the solution, resulting in either a protective film, which can deactivate the ZVI surface, or colloidal particles, which may not affect the reactivity of the surface of ZVI particles. The raised NaCl concentration increased the number of colloidal particles (Fig. 3), leading to more rust precipitation as colloidal particles in the solution. Thus, the raised NaCl concentration may have mitigated the formation of the protective film on the ZVI surface and thereby increased the Cr(VI) removal.

3.2 Effect of ZVI dosage

At the low ZVI dosage of 2 g/L, the increased NaCl concentration increased both the Cr(VI) removal and the turbidity of the suspension induced by the ZVI. On the other hand, at the high ZVI dosage of 20 g/L, the positive effect of the NaCl concentration on the Cr(VI) removal and the turbidity of the suspension was minimized (Figs. 1(a) and 5). At the NaCl concentration of 0.4 M and the ZVI dosage of 20 g/L, Cr(VI) was completely removed from the solution by the reduction of Cr(VI) to Cr(III) after 50 h of reaction, whereas at the ZVI dosage of 2 g/L, approximately 60% of the Cr(VI) was removed from the solution after 50 h of reaction (Fig. 1(a)). However, without NaCl, the Cr(VI) was not completely removed from the solution even at the ZVI dosage of 20 g/L, with approximately 20% of the Cr(VI) remaining (Fig. 1(a)).

The increase in the ZVI dosage decreased the final Cr(VI) concentration at a given initial Cr(VI) concentration (100 mg/L). There is a specific limit of the ZVI dosage for which the Cr(VI) will be completely removed from the solution at any given Cr(VI) concentration. When the ZVI dosage exceeds this specific limit, the Cr(VI) is completely

![Fig. 2 (a) Cr(VI) concentration and (b) pH as a function of the NaCl concentration in solutions with ZVI particles after 50 h of reaction (initial pH = 3, initial Cr(VI) concentration = 100 mg/L, and ZVI dosage = 2 g/L).](image)

![Fig. 3 Suspension turbidity as a function of the NaCl concentration at 50 h of reaction (initial pH = 3, initial Cr(VI) concentration = 100 mg/L, and ZVI dosage = 2 g/L).](image)

![Fig. 4 (a) SEM image and (b) EDX mapping of agglomerated colloidal particles in solutions with 0.4 M NaCl at ZVI dosage of 2 g/L.](image)
removed from the solution and the ZVI surface is not fully oxidized or fully covered with the rust film. On the other hand, when the ZVI dosage is less than the specific limit, the ZVI surface is fully oxidized or fully covered with the rust film, which prevents any further removal of Cr(VI) from the solution.

In the NaCl-free solution, the Cr(VI) was not completely removed from the solution at either of ZVI dosages of 2 or 20 g/L even after 50 h, suggesting that the surface of ZVI particles may have been fully oxidized at both ZVI dosages. In addition, slight change in the solution turbidity occurred during the reaction at any ZVI dosage, indicating almost no colloidal particle formation in the solution (Fig. 5). The increase in turbidity with ZVI dosage at the NaCl concentration of 0.4 M was due to ZVI particles in the solution. The slight increase in the turbidity with ZVI dosage at the NaCl concentration of 0.4 M was due to ZVI particles in the solution. At the ZVI dosage of 20 g/L, the lower turbidity at the NaCl concentration of 0.4 M compared to that at 0 M (Fig. 5) was attributed to coagulation of ZVI particles due to the high ionic strength of the solution.

At the NaCl concentration of 0.4 M, the turbidity decreased up to the ZVI dosage of 12 g/L and then increased slightly (>50 h) (Fig. 5). At the NaCl concentration of 0.4 M at a given initial Cr(VI) concentration (100 mg/L), the ZVI oxidation process can be divided into two stages, surface precipitation stage (SPS) and colloidal precipitation stage (CPS), depending on the aqueous formation of colloidal particles. In SPS (represented by the ZVI dosage ≥12 g/L), Cr(III)–Fe(III) (oxy)hydroxides might be precipitated on the ZVI surface. In CPS (represented by the ZVI dosage ≤12 g/L), Cr(III)–Fe(III) (oxy)hydroxides might be precipitated in the solution as colloidal particles. However, when NaCl concentration is zero, the oxidation process can’t be divided into the two stages because there is little production of colloidal particles during the whole reaction. At the ZVI dosage of 20 g/L, the higher turbidity at the NaCl concentration of 0.4 M compared to that at 0.4 M (Fig. 5) was attributed to less coagulation of ZVI particles due to the low ionic strength of the solution.

### 3.3 SEM observation

The surfaces of the ZVI particles that had reacted with Cr(VI) at various initial conditions were analyzed with SEM to investigate the effects of the NaCl concentration and the ZVI dosage on the precipitation. Figure 6 shows the SEM images of the unreacted ZVI particles (Fig. 6(a)), the colloidal particles formed during reaction between the ZVI particles and 100 mg/L Cr(VI) in the 0.4 M NaCl solution (Fig. 6(b)), and the reacted ZVI particles after reaction with 100 mg/L Cr(VI) at the ZVI dosages of 2 and 20 g/L in the 0 and 0.4 M NaCl solutions (Figs. 6(c)–6(f)).

The precipitates on surface of the reacted ZVI particles were formed after reaction between the unreacted ZVI particles and Cr(VI), regardless of the NaCl concentration and the ZVI dosage. The precipitates were composed of spherical grains that could be classified into two types according to size as either small or large grains. The small grains were too small to be observed in the 104× magnification SEM image (Fig. 6(c)) but were observed in the 105× magnification SEM image (Fig. 6(d)). The size of the small grains was about 20 nm. The surface of the ZVI particles reacted with Cr(VI) at the ZVI dosage of 2 g/L in the NaCl-free solution was mainly covered by the small grains.

The large grains could be observed in the 104× magnification SEM image (Fig. 6(e)). Their size was approximately 200 nm and they were mostly observed on the surface of the ZVI particles reacted with Cr(VI) in the NaCl solution at the low ZVI dosage (2 g/L). The colloidal particles formed in the solution during the reaction between the ZVI particles and Cr(VI) at the low ZVI dosage of 2 g/L in the 0.4 M NaCl solution were classified as large grains. The colloidal particles collected from the suspension were spherical with a diameter of approximately 200 nm (Fig. 6(b)). The EDX results revealed Cr, Fe and O elements on the surface of the colloidal particles (Fig. 4), suggesting that the colloidal particles might be Cr(III)–Fe(III) (oxy)-hydroxides. These results indicated that large grains were precipitated in the NaCl solution than in the NaCl-free solution. However, at the high ZVI dosage (20 g/L) the small grains were mainly observed on the ZVI particle surface, and large grains were seldom observed even in the 0.4 M NaCl solution (Fig. 6(f)).

### 3.4 Potential mechanism of colloidal particle formation in the presence of NaCl

The process of precipitation in the presence of NaCl could be explained based on the SEM results. In general, when ZVI particles are oxidized in the NaCl-free solution, their surface can be separated into anodic and cathodic sites.23 In the reaction between ZVI particles and Cr(VI) ions, ZVI particles lose electrons and are oxidized to Fe(II) ions at anodic sites.9 The Fe(II) ions are produced at the ZVI anodic sites. Cr(VI) ions capture the electrons and are reduced to Cr(III). The Fe(II) ions also reduce Cr(VI) to Cr(III) and are then oxidized to Fe(III) ions. During the reaction, Cr(VI) ions accumulate at the anodic sites because of the electromagnetic attraction force. Thus, Fe(II) ions, which are produced from the anodic
sites, reduce Cr(VI) ions and are then oxidized to Fe(III) ions at the anodic sites. Cr(III)–Fe(III) (oxy)hydroxides are precipitated on the ZVI surface, thus generating a protective film that prevents further oxidation. As a result, Fe(III)–Cr(III) (oxy)hydroxides are precipitated only on the ZVI surface in the NaCl-free solution, which was confirmed by the experimental results. Almost no colloidal particles were produced during the reaction between the ZVI particles and Cr(VI) ions in the NaCl-free solution or at very low NaCl concentration (Fig. 5). In addition the small grains were only observed on the ZVI surface in the NaCl-free solution at ZVI dosage of 2 g/L (Fig. 6(d)).

On the other hand, in the NaCl solution with a higher Cl⁻ concentration than Cr(VI) concentration, the Cr(VI) ions are initially oxidized on the ZVI surface, resulting in fast Cr(VI) removal and small Cr(III)–Fe(III) (oxy)hydroxide particles. After the ZVI surface is primarily covered by small Cr(III)–Fe(III) (oxy)hydroxide particles, gaps between the small particles can appear in the ZVI surface in the NaCl solution due to the accumulation of Cl⁻ ions at the ZVI anodic sites. The Fe(II) ions can move away from the ZVI surface by diffusion through the gaps and react with the Cr(VI) ions in the solutions, thereby generating precipitates of Fe(III)–Cr(III) (oxy)hydroxides in the solution as colloidal particles and on the ZVI surface. The Cr(III)–Fe(III) (oxy)hydroxide particles grow slowly, resulting in large particles due to slow diffusion of Fe(II) ions from the ZVI surface to the solution through the gaps. The precipitates of Fe(III)–Cr(III) (oxy)hydroxides can also become the colloidal particles by being detached from ZVI particles. Migration of Cr(VI) ions from the solution to the ZVI surface also becomes a diffusion-dominated process through the gaps. The length and tortuosity of the diffusion pathways through the gaps between the small precipitates from the solution to the reactive ZVI surface increase as the reaction proceeds due to continuous oxidation and dissolution of the ZVI surface inside the gaps. In addition, if the diffusion flux of Fe(II) ions is larger than that of Cr(VI) ions, the precipitation should occur on the interface between the hydroxide layer and the solution layer. On the other hand, if diffusion fluxes of Fe(II) and Cr(VI) ions are comparable, the precipitation should occur inside the gap in the hydroxide layer. Thus, the growth rate of the Cr(III)–Fe(III) (oxy)hydroxides on the surface is probably slow, resulting in large particles because the growth
rate may be controlled by the diffusion rate of Cr(VI) ions delivery between the solution and the ZVI surface through the gaps.

This explanation is supported by the experimental results. In the 0.4 M NaCl solution at the high ZVI dosage (20 g/L), the small grains were observed primarily on the ZVI surface (Fig. 6(f)), suggesting that the small grains were formed in the SPS of the reaction between the ZVI particles and Cr(VI). The large grains were observed on the surface of the ZVI particles reacted with Cr(VI) in the 0.4 M NaCl solution at the low ZVI dosage of 2 g/L, which represents CPS of the reaction between the ZVI particles and Cr(VI). The colloidal particles classified as large grains were also observed in the solution during the reaction between the ZVI particles and Cr(VI) at the low ZVI dosage of 2 g/L in the 0.4 M NaCl solution.

4. Conclusions

The Cr(VI) removal process by ZVI particles in solutions with or without NaCl can be divided into the two stages: SPS and CPS. During the SPS, the Cr(VI) ions are mainly reduced on the ZVI surface, resulting in fast Cr(VI) removal and small Cr(III)–Fe(III) (oxy)hydroxide particles on the ZVI surface. The SPS occurs with the solution, regardless of the presence or absence of NaCl. After the ZVI surface is primarily covered by small Cr(III)–Fe(III) (oxy)hydroxide particles, gaps between the small particles can appear in the ZVI surface in the NaCl solution at the low ZVI dosage due to the accumulation of Cl⁻ ions at the ZVI anodic sites. During CPS, Cr(III)–Fe(III) (oxy)hydroxide particles are precipitated in the solution by the reaction between the Cr(VI) and Fe(II) ions delivered by diffusion through the gaps from the ZVI surface. The Cr(III)–Fe(III) (oxy)hydroxide particles grow slowly, resulting in large particles due to slow diffusion of Fe(II) ions from the ZVI surface to the solution through the gaps. The CPS occurs primarily in NaCl solutions, resulting in the enhanced removal efficiency for Cr(VI) by ZVI provided that the ZVI dosage doesn’t exceed the specific limit for complete removal of Cr(VI) in the solution without NaCl at a given Cr(VI) concentration.

This proposed mechanism is supported by the following two experimental results: (1) the colloidal particles were only formed in the NaCl solution at the low ZVI dosage and (2) the colloidal particles formed in the NaCl solution at the low ZVI dosage were larger than those precipitated on the ZVI surface in the NaCl-free solution or in the NaCl solution at the high ZVI dosage.

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REFERENCES