Reduction of hexavalent chromium by pyrite-rich andesite in different anionic solutions

Jae Gon Kim · Pil-Kyun Jung · Hi-Soo Moon · Chul-Min Chon

Abstract Introduction of Cr(VI) to the environment has been of environmental concern due to its toxicity and mobility. In treatment processes for wastewater, groundwater, and soil contaminated with Cr(VI), the reduction of Cr(VI) to Cr(III) and the subsequent precipitation of insoluble Cr(III) compounds are generally employed. Finely ground, hydrothermally altered andesite containing 11.8% of pyrite reacted with Cr(VI) solutions (0 to 400 mg l^{-1}) in the presence of dissolved oxygen and 0.01 to 0.1 M of KCl, K_2SO_4, and KH_2PO_4. Before and after the reaction, the morphology of the pyrite was also examined with a scanning electron microscope. The altered andesite was an effective Cr reductant in KCl and K_2SO_4 solutions, but KH_2PO_4 decreased the Cr(VI) reduction capacity of the altered andesite. The higher the initial concentration of Cr(VI), the more Cr(VI) reduced to Cr(III) in KCl and K_2SO_4 solutions, but no relationship between the initial concentration of Cr(VI) and the amount of reduced Cr(VI) in KH_2PO_4 solutions was observed. The final solution pH for KCl and K_2SO_4 increased with an increasing initial concentration of Cr(VI). For KH_2PO_4, the pH was not significantly changed by changing the initial concentration of Cr(VI), but it did increase with an increasing KH_2PO_4 concentration. A concentration of aqueous ferrous iron [Fe(II)] nonstoichiometrically decreased with an increasing amount of reduced Cr. The changes in solution pH and concentrations of Fe(II) and Cr(VI) indicate that the reduction of Cr(VI), both at solid-solution interface and in solution, occurred simultaneously. Pyrite had relatively smooth surfaces and sharp edges before the Cr reduction, but showed rough surfaces, dissolution pits on surfaces, and smoothed edges after the Cr reduction.

Keywords Matrix solution · Solution pH · Aqueous iron · Micromorphology

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Introduction

Chromium has been used in various industrial processes and introduced into the environment, including via electroplating, leather tanning, cooling with water, pulp and pigment producing, and ore and petroleum refining. Toxicity and mobility of Cr in the earth-surface environment are dependent on its oxidation state (Elderfield 1970). Chromium is present in the surface environment in two thermodynamically stable oxidation states, Cr(III) and Cr(VI). Trivalent Cr is relatively innocuous and immobile in the surface environment. However, Cr(VI) is more toxic and mobile than Cr(III) (Bartlett and James 1988) and is also a class A human carcinogen (Katz and Salem 1993). Hexavalent Cr is one of the most frequently encountered contaminants of wastewater, groundwater, and soil. The reduction of Cr(VI) to Cr(III) and the formation of insoluble Cr(III) precipitate are essential steps in the treatment of water and soil contaminated with Cr(VI). For Cr(VI) reduction to occur, a suitable redox couple having a compatible electron symmetry to allow electron exchange must be present (Patterson and others 1997). Ferrous iron (Buerge and Hug 1997), metallic iron (Gould 1982), sulfide (Patterson and others 1997), and organic matter (Wittbroadt and Palmer 1995; Deng and Stone 1996) have been reported as Cr reductants in the treatment process. Among these reductants, water soluble Fe(II) compounds, such as $FeSO_4$, are the most commonly used reagents (Eary and Rai 1988). After the reduction process, the adjustment of pH with NaOH is generally employed for the precipitation of insoluble Cr(III) solid.

Ferrous iron-bearing minerals such as pyrite, biotite, augite, hornblede, and siderite, reduce Cr(VI) to Cr(III) as minerals undergo dissolution to release ferrous iron into

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solution or as Cr(VI) adsorbs on a surface to allow direct contact with Fe(II) (White and Yee 1985; Eary and Rai 1989; Blowes and others 1997; Ilton and others 1997). The effectiveness of natural aqueous Fe(II) in Cr(VI) reduction has also been shown in forested wetland soils (Masscheleyn and others 1992), and in the sand and gravel of a suboxic aquifer (Anderson and others 1994).

Pyrite (FeS_2) is a common mineral associated with hydrothermally altered rock, sulfide ore, and mangrove soil. It has been used in industrial processes such as production of sulfuric acid. However, it has also caused environmental problems, such as acidification of soil and surface water, with its oxidation. Currently, pyrite is considered industrial waste rather than a valuable ore mineral. The inverse utilization of the oxidative dissolution of pyrite in wastewater treatment and agriculture has been studied. Pyrite was an effective reductant for Cr(VI) to Cr(III) in wastewater treatment (Zouboulis and others 1995). Finely ground, pyrite-containing material also effectively reduced disease in young rice plants, producing acid as it was oxidized (Yun and others 1991).

The reduction of Cr(VI) to Cr(III) by iron sulfide is favored by a lower pH, a high initial Cr(VI) concentration, and a high ratio of surface area to solution volume (Zouboulis and others 1995; Patterson and others 1997). In the reduction of Cr(VI) by amorphous iron sulfide under oxygen-free and slightly acidic to alkaline conditions, Cr reduction occurred dominantly at solid-solution interface; this resulted in precipitation of $Cr_{0.75}Fe_{0.25}(OH)_3$ on the surface (Patterson and others 1997). The reduction reaction was nonstoichiometric. There was an increase in solution pH and no significant change in concentration of aqueous Fe(II) with an increasing amount of reduced Cr.

The reduction of Cr(VI) to Cr(III) by aqueous Fe(II) in the presence of dissolved oxygen, SO_4^{2-}, ClO_4^-, Cl^-, F^-, and NO_3^- was a stoichiometric reaction at pH<10 but more than 3 mol of Fe(II) were needed for the reduction of 1 mol of Cr at pH>10 (Eary and Rai 1988). In the presence of dissolved oxygen and phosphate, the Cr reduction by aqueous Fe(II) is stoichiometric at pH<6 but it is not stoichiometric at pH>6. The solution pH decreases due to the precipitation of $(Fe_{0.75}Cr_{0.25})(OH)_3$ under slightly acidic and alkaline conditions.

Chemical treatment using Fe(II) for wastewater, groundwater, and soil contaminated with Cr(VI) is known as a high-cost method. Pyrite is known as a cost-effective Cr reductant (Zouboulis and others 1995). However, the effectiveness of pyrite as a Cr reductant under various conditions is still under evaluation. Soil solution, groundwater, and wastewater generally contain various dissolved ions. The effect of common ions on the reduction of Cr(VI) to Cr(III) by pyrite is not available in the current literature in this field. The objectives of this study were (1) to examine the Cr reduction capacity of a hydrothermally altered pyrite-rich andesite as a cost effective reductant, and (2) to examine the effect of different anionic species (Cl^-, SO_4^{-2}, and PO_4^{-3}), which are common in soil, groundwater, and wastewater, on the reduction of Cr(VI) to Cr(III) by this hydrothermally altered pyrite-rich andesite in the presence of dissolved oxygen.

Materials and method

Hydrothermally altered, pyrite-rich andesite as reductant

Fresh, hydrothermally altered pyrite-rich andesite was collected from Yangsan-ci, Kyongsangnam-do, Korea and stored in a refrigerator at 4 °C. The andesite was formed and hydrothermally altered by volcanic activity during the Mesozoic (KIGAM 1962). The sampling site had been laid out for a residential area with a golf course and the altered andesite consequently exposed to the atmosphere. The subsequent oxidation of pyrite resulted in an acidification of soil and surface water there.

For chemical and mineralogical analysis, the bulk sample was ground with a ceramic agate and pestle to pass a 50 μm sieve and then air-dried. Total sulfur (S) content of the altered andesite was determined with an IR carbon and sulfur analyzer (Leco Co.). For mineralogical composition, the ground sample was analyzed by X-ray using a MAC Science MXP 18A Rint-2500 X-ray diffractometer. Morphology and particle size of pyrite before and after Cr(VI) reduction were examined with a Hitachi S-570 scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS).

The bulk altered andesite sample was ground with a ceramic agate and pestle to pass a 2-mm sieve and then additionally ground with a Spectromill ball pestle impact grinder (Chemplex Industries Inc., Stuart, FL, USA) for 3 min for the Cr-reduction experiment. The specific surface area of the finely ground sample was determined with an ethylene glycol monoether (EGME) method (Carter and others 1986).

Experimental procedure for Cr(VI) reduction

A mixture of 3 g of the finely ground altered andesite and 30 ml of Cr(VI) solution with different concentrations of anions was placed in a 40 ml polyethylene centrifuge tube where the concentration of Cr(VI) ranged from 0 to 400 mg l^{-1} prepared with $K_2Cr_2O_7$ and the matrix solutions were 0.01 M, 0.05 M, and 0.1 M of KCl, K_2SO_4, and KH_2PO_4. The mixture was shaken with a rotation shaker for 72 hours. After the reaction, the solution pH was measured with an Orion 720A pH meter. Then, the mixture was centrifuged at 3,000 rpm for 10 min. After centrifugation, the supernatant was collected and concentrations of Cr(VI) (Bartlett and James 1996), Fe(II) (Loeppert and Inskeep 1996) and total Fe (Loeppert and Inskeep 1996) in the supernatant were determined with chromagen methods. For the determination of Cr(VI) concentration, 1 ml of s-diphenylcarbizide (DPC) reagent and 8 ml of supernatant were reacted to develop color for 20 min and then the color was compared with a standard at 540 nm wavelength using a SHIMADZU UV-160 PC spectrophotometer. The DPC reagent was prepared by adding 120 ml of 85% H_3PO_4, diluted with 280 ml distilled water, to 0.38 g of DPC previously dissolved in 100 ml of ethanol. For the concentration of total aqueous Fe, 6 ml of supernatant, 1 ml of 10% $NH_2OH•HCl$, and 1 ml of 1,10-phenanthroline reagent were mixed and then 2 ml of

5 M $NH_4C_2H_3O_2$ was added to the mixture. The solution was thoroughly mixed and set for 10 min for color development. The color was compared with a standard at 510 nm wavelength using the spectrophotometer. The 1,10-phenanthroline reagent was prepared by dissolving 0.30 g of 1,10-phenanthroline monohydrate in 30 ml of distilled water and heating at 80 °C and then by diluting to 100 ml with distilled water. The procedure for the determination of the concentration of aqueous Fe(II) was basically the same as that for the concentration of total aqueous Fe. $NH_2OH{\bullet}HCl$, a reductant, was not used for aqueous Fe(II).

To determine adsorbed Cr(VI), another set of samples was prepared with the same method described above. After reaction for 72 h, 1 M KH_2PO_4 was added to the mixtures to give 0.05 M KH_2PO_4 of phosphate and the mixture was additionally shaken for 10 min. For the 0.05 M KH_2PO_4 and 0.1 M KH_2PO_4, the additional treatment was not conducted. Then, the mixtures were centrifuged at 3,000 rpm for 10 min and the supernatants were collected for the determination of Cr(VI) concentration. The concentration of Cr(VI), which was the sum of adsorbed and solution phases, was determined with the chromagen method described above. The amount of adsorbed Cr(VI) on solid particles was calculated by subtracting the solution phase of Cr(VI) determined without the phosphate treatment for Cr(VI) determination described above from the sum of solution and adsorbed phases. All tests were conducted with duplicate samples. All chemicals used in this study were reagent grade. The mixtures should contain dissolved oxygen as they were exposed to air during preparation and no other treatment was conducted for the removal of dissolved oxygen.

Results

The specific surface area of the finely ground altered andesite was 0.6 $m^2\ g^{-1}$. The andesite contained 11.8% of pyrite (FeS_2), which was calculated based on 6.5% of total S content, assuming that all sulfur existed as pyrite (FeS_2). The pyrite content, determined with a semiquantitative analysis using an X-ray diffraction pattern (Chung 1974), was 11.0%; this is close to the value determined based on the chemical data. The major mineral components of the altered andesite were quartz, illite, and pyrite (Fig. 1). Pyrite had high crystallinity indicated by the sharp XRD peaks. The pyrite in the finely ground andesite had particles sizes of 0.3 to 150 μm as determined under SEM. Most of the unreduced Cr(VI) remained as aqueous chromium after the reaction period (less than 10% as adsorbed form). However, there was no differentiation between the solution phase and the sum of solution and adsorbed phases of Cr(VI) for 0.05 M and 0.1 M of KH_2PO_4. The data for Cr(VI) reported in this paper represent the total Cr(VI) including both solution and adsorbed phases. The Cr reduction capacity of the altered andesite was not affected by KCl and K_2SO_4, but KH_2PO_4 reduced the Cr reduction capacity (Fig. 2). As the concentration of KH_2PO_4 increased, smaller amounts of Cr(VI) reduced to Cr(III) at the same initial concentration of Cr(VI). The higher the initial concentration of Cr(VI), the more it was reduced to Cr(III) by the altered andesite in KCl and K_2SO_4 solutions. However, the amount of Cr reduced by the altered andesite having the same concentration of KH_2PO_4 did not show any relationship to initial concentration of Cr(VI). All (100%) of the Cr(VI) was reduced to Cr(III) for 50 to 200 mg l^{-1} of initial concentration of Cr(VI), and about 80% for 400 mg l^{-1} in both KCl and K_2SO_4 solutions (Fig. 3). For KH_2PO_4 solutions, 2 to 54% of the Cr(VI) reduced to Cr(III) depending on the concentrations of Cr(VI) and KH_2PO_4. The amount of

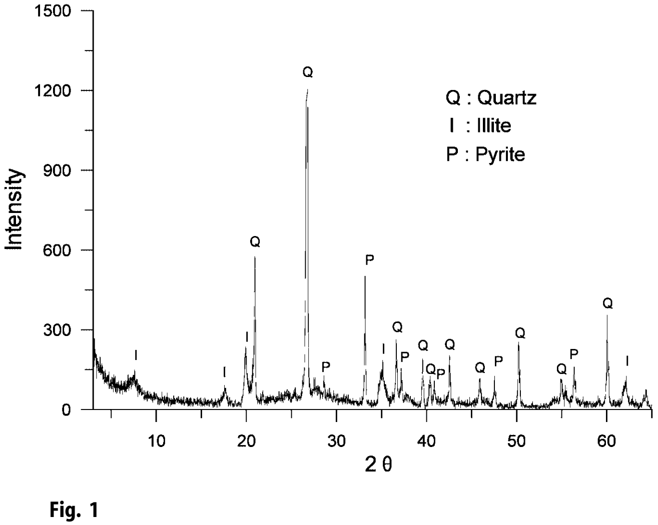

Fig. 1
The XRD pattern of bulk altered andesite sample shows quartz, illite, and pyrite as major mineral components

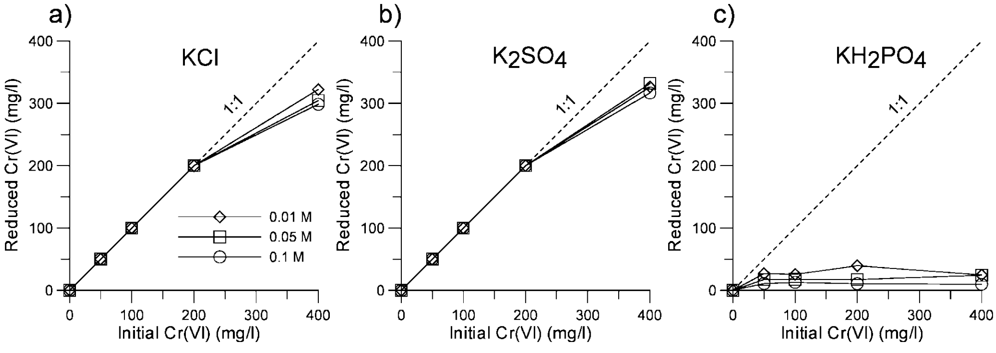

Fig. 2a–c
Amounts of reduced Cr by the altered andesite and initial Cr(VI) concentration show a positive relationship for **a** KCl and **b** K_2SO_4 but no relationship for **c** KH_2PO_4. The higher the concentration of KH_2PO_4, the smaller the fraction of initial Cr(VI) reduced to Cr(III)

Cr(VI) reduced to Cr(III) by the altered andesite decreased with increasing concentration of KH_2PO_4 at the same initial concentration of Cr(VI).

The final solution pH increased significantly as the amount of reduced Cr increased for the KCl and K_2SO_4 solutions (Fig. 4). The concentration of KCl and K_2SO_4 did not have a significant effect on the pH change. However, the final solution pH for KH_2PO_4 was slightly increased by Cr reduction and it increased with increasing concentration of KH_2PO_4 (Fig. 4): pH 3.2 to 3.25 for 0.1 M, pH 2.98 to 3.05 for 0.05 M, and pH 2.78 to 2.85 for 0.01 M.

Ferrous iron was dominant over ferric iron in all final solutions (Table 1). The concentration of aqueous Fe(III) was below the detection limit of the chromagen method (0.01 mg l^{-1}) for all the initial concentrations of Cr(VI) for KH_2PO_4 and for the highest initial concentration of Cr(VI) for the KCl and K_2SO_4 solutions. The concentrations of Fe(II) in the final solution of KH_2PO_4 were much lower than those of KCl and K_2SO_4. For the KH_2PO_4 solution, Cr reduction apparently reduced the concentration of Fe(II), although its concentration was not influenced by those of KH_2PO_4 and initial Cr(VI) concentrations. The concentration of aqueous Fe(II) decreased with an increasing amount of reduced Cr(VI) in the following ratio: 2.3 mol of Fe(II) for 1 mol of reduced Cr(VI) for KCl, 2.5 mol of Fe(II) for K_2SO_4, and 6.5 mol of Fe(II) for KH_2PO_4 (Fig. 5).

The dominant morphologies of pyrite were cubes without strain and pyritohedrons with relatively smooth surfaces and sharp edges before the reaction (Fig. 6a). However, the reaction with the solutions containing dissolved oxygen and/or Cr(VI) in the presence of anions created dissolution pits on the surfaces and smoothed edges (Fig. 6b–d). The change in the surface characteristics of pyrites caused by the reaction was apparently dependent on the kind of matrix solution present. Nonetheless, the initial concentration of Cr(VI) had no significant effect on the morphological change. More dissolution pits were observed on the surface for the KCl and K_2SO_4 solutions (Fig. 6b, 6c) than for the KH_2PO_4 solution (Fig. 6d). No secondary phases, such as Cr and/or Fe hydroxide, on the surfaces of the pyrite were observed under SEM. The chemical composition of pyrite grains was relatively homogeneous and no heavy metals, such as arsenic, lead, and zinc, were detected as impurity. There was also no chemical differentiation of the pyrite grains made with EDS either before or after the reaction having different kinds of anions and the initial concentration of Cr(VI).

Discussion

Altered andesite as a Cr reductant was a mixture of minerals, including pyrite, illite, and quartz (Fig. 1). Quartz is an inert mineral in Cr reduction. Pyrite and Fe(II)-bearing mica are known to have a Cr reduction capacity (Eary and Rai 1989; Zouboulis and others 1995). The reduction of Cr(VI) to Cr(III) by pyrite may be most significant in this study because illite contains only trace amounts of Fe(II) and thus the Cr reduction capacity of pyrite is much higher than that of illite.

Chloride is an inert ion in adsorption and redox reactions. Sulfate is one of the final products of pyrite oxidation. However, there was no effect on the Cr reduction capacity

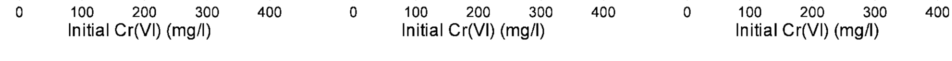

Fig. 3a–c
The high Cr reduction rate caused by the altered andesite for **a** KCl and **b** K_2SO_4, and a low rate appears for **c** KH_2PO_4. The higher the concentration of KH_2PO_4, the lower the rate of Cr reduction

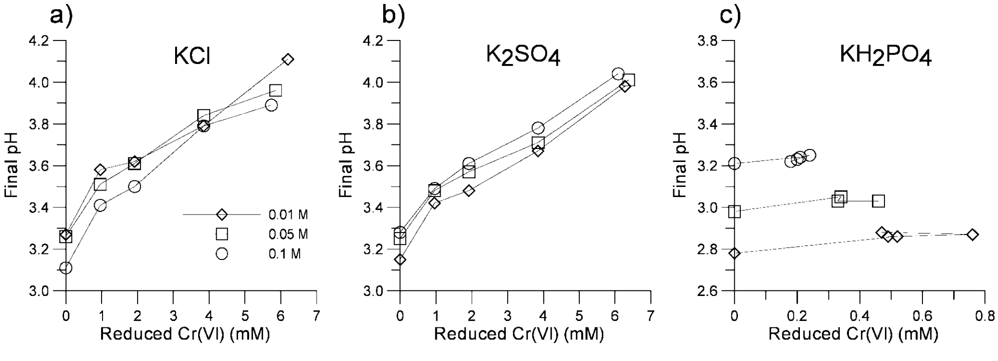

Fig. 4a–c
The final solution pH increased linearly with increasing amount of reduced Cr for **a** KCl and **b** K_2SO_4. **c** The solution pH for KH_2PO_4 slightly increased with Cr reduction, and had higher values at the higher concentration of KH_2PO_4

Table 1
The concentration of aqueous irons in the final solution after a Cr reduction reaction with the pyrite-rich altered andesite

Initial Cr(VI) (mg/l)	KCL						K_2SO_4						KH_2PO_4					
	0.01 M		0.05 M		0.1 M		0.01 M		0.05 M		0.1 M		0.01 M		0.05 M		0.1 M	
	Fe(II) (mM)	Fe(III) (mM)	Fe(II) (mM)	Fe(III) (mM)	Fe(II) (mM)	Fe(III) (mM)	Fe(II) (mM)	Fe(III) (mM)	Fe(II) (mM)	Fe(III) (mM)	Fe(II) (mM)	Fe(III) (mM)	Fe(II) (mM)	Fe(III) (mM)	Fe(II) (mM)	Fe(III) (mM)	Fe(II) (mM)	Fe(III) (mM)
0	2.22	0.06	2.54	0.19	2.95	0.10	2.45	0.14	2.80	0.15	2.99	0.25	0.07	0.00	0.03	0.00	0.04	0.00
50	1.72	0.08	2.05	0.07	2.08	0.08	1.91	0.17	2.09	0.14	1.95	0.18	0.00	0.00	0.02	0.00	0.02	0.00
100	1.11	0.06	1.28	0.05	1.24	0.05	1.22	0.16	1.33	0.12	1.44	0.06	0.01	0.00	0.00	0.00	0.02	0.00
200	0.49	0.00	0.52	0.02	0.56	0.03	0.63	0.02	0.62	0.05	0.58	0.06	0.01	0.00	0.00	0.00	0.02	0.00
400	0.01	0.00	0.02	0.00	0.00	0.00	0.11	0.00	0.10	0.05	0.07	0.00	0.02	0.00	0.01	0.00	0.02	0.00

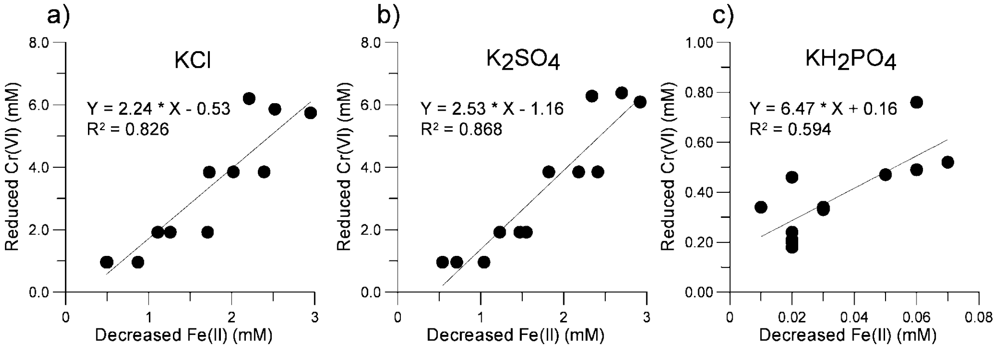

Fig. 5a–c
Amounts of decreased aqueous Fe(II) and Cr(VI) show a non-stoichiometric relationship for all matrix solutions. **a** KCl, **b** K_2SO_4, and **c** KH_2PO_4

of pyrite in this study (Figs. 2 and 3). It was not determined why SO_4^{2-} did not have an effect on the reaction in this experiment since the data on the sulfur in the solution had not been determined. The negative effect of phosphate observed in Cr reduction may be due to the two following possibilities: (1) the acceleration of oxidation of aqueous Fe(II) by dissolved oxygen in the presence of phosphate (Eary and Rai 1988) and (2) iron phosphate ($Fe_3(PO_4)_2$ and $FePO_4$) coating on the surface of pyrite (Nyavor and Egiebor 1995). The acceleration of the oxidation of aqueous Fe(II) by dissolved oxygen caused by phosphate is effective only at pH>6 (Eary and Rai 1988). Therefore, the first possibility above should be ruled out considering the high acidic condition of this experiment. The iron phosphate coating on the surface is, however, a plausible explanation for the negative effect of phosphate on Cr reduction capacity of the altered andesite, despite the fact that the phosphate coating was not detected with the EDS (discussed below).

Phosphate is known to form insoluble iron phosphate compounds such as $Fe_3(PO_4)_2$ and $FePO_4$ and this has been utilized in controlling acid mine drainage (Nyavor and Egieber 1995). Iron phosphate coatings on the surface of pyrite may form a physical barrier which reduces the accessibility of oxygen and Cr(VI) to the pyrite surface and reduces the concentration of aqueous Fe(II) and Fe(III). Therefore, the iron phosphate coating on the surface resulted in a decrease in the oxidative dissolution of pyrite by dissolved oxygen and in the reduction rate of Cr(VI) to Cr(III) at the solid-solution interface and in solution. The decreased oxidative dissolution of pyrite by phosphate coatings resulted in both a higher solution pH and a lower rate of Cr reduction with a higher concentration of KH_2PO_4 (Figs. 2, 3, and 4). The lower concentration of aqueous Fe for the KH_2PO_4 solution compared to the KCl and K_2SO_4 solutions was probably due to the consumption of iron during the precipitation of iron phosphate.

The possible reactions involved in this experiment are the following.

Oxidation of pyrite by dissolved oxygen:

$$FeS_2 + 7/2O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ \tag{1}$$

$$Fe^{2+} + 1/4O_2 + H^+ = Fe^{3+} + 1/2H_2O \tag{2}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{3}$$

Reduction of Cr(VI) to Cr(III) by Fe(II) at the pyrite-solution interface and in solution under oxygen-free conditions:

$$3Fe^{2+}_{(\text{pyrite or solution})} + HCrO_4^- + 6H^+ = 3Fe^{3+}_{(\text{pyrite or solution})} + CrOH_2^+ + 3H_2O \tag{4}$$

The oxidation of pyrite by dissolved oxygen produces aqueous Fe(II) and H^+ [see Eqs. (1) and (3) above],and the reduction of Cr(VI) to Cr(III) at both pyrite-solution interface and in solution neutralizes H^+ and oxidizes Fe(II) to Fe(III) (Eq. 4). When Cr(VI) reduces by Fe(II), 3 mol of Fe(II) need to reduce 1 mol of Cr(VI) to Cr(III) (Eq. 4). As discussed above, when the reduction reaction of Cr(VI) to Cr(III) occurs only at the iron sulfide-solution interface under oxygen-free conditions and there are no change in Fe(II) concentration of the reacting solution and an increase in solution pH at initial pH 5 to 8 (Patterson and others 1997). The reduction of Cr(VI) to Cr(III) by aqueous Fe(II) is characterized by a stoichiometric relationship between the decreased amount of aqueous Fe(II) and the reduced amount of Cr(VI) [3Fe(II):1Cr(VI)] and an increase in solution pH at initial pH 3.5 to 11 (Eary and Rai 1988). In this experiment, the nonstoichiometric relationship between amounts of reduced Cr(VI) and decreased aqueous Fe(II) in solution by Cr reduction (Fig. 5), the positive relationship between the amount of reduced Cr and solution pH (Fig. 4), and the low pH value of final solution without Cr ($3.4>\text{pH}$) suggest that the Cr reduction observed was a complicated reaction involving the oxidative dissolution of pyrite by dissolved oxygen and the reduction of Cr(VI) to Cr(III) at the solid-solution interface and in solution.

The rough surface, dissolution pits on the surface, and smoothed edges of pyrite after the reaction may be the result of oxidative dissolution of pyrite caused by both dissolved oxygen and Cr(VI) (Fig. 6). The precipitation of Cr(III) and Fe(III) hydroxide was not reported in the process of Cr reduction by aqueous Fe(II) and FeS in previous studies (Eary and Rai 1988; Patterson and others 1997). However, no observation of such secondary compound in this study may be due to the acidic condition ($\text{pH}<4.1$) of the experiment. As discussed above, the formation of an iron phosphate coating on the surface was expected, but there was no indication of this occurring according to the EDS data. The iron phosphate coating on the surface was probably too thin to be detected with the EDS equipped at SEM.

Conclusion

The finely ground hydrothermally altered pyrite-rich andesite was an effective Cr(VI) reductant in KCl and K_2SO_4 solutions. The Cr(VI) reduction to Cr(III) by pyrite was not influenced by KCl and K_2SO_4. Phosphate (KH_2PO_4) lowered the Cr(VI) reduction capacity of the altered andesite. The reduction of Cr(VI) to Cr(III) by pyrite in the presence of dissolved oxygen involved both reaction at solid-solution interface and in solution. This was indicated by the nonstoichiometric relationship between the amounts of reduced Cr(VI) and decreased aqueous Fe(II), and by the increase in the final solution pH which corresponded to the increase in the amount of reduced Cr. Hydrothermally altered pyrite-rich andesite can be utilized as a reductant for treatment of wastewater and groundwater contaminated with Cr(VI) as long as the effect of anions, such as phosphate, is carefully considered.

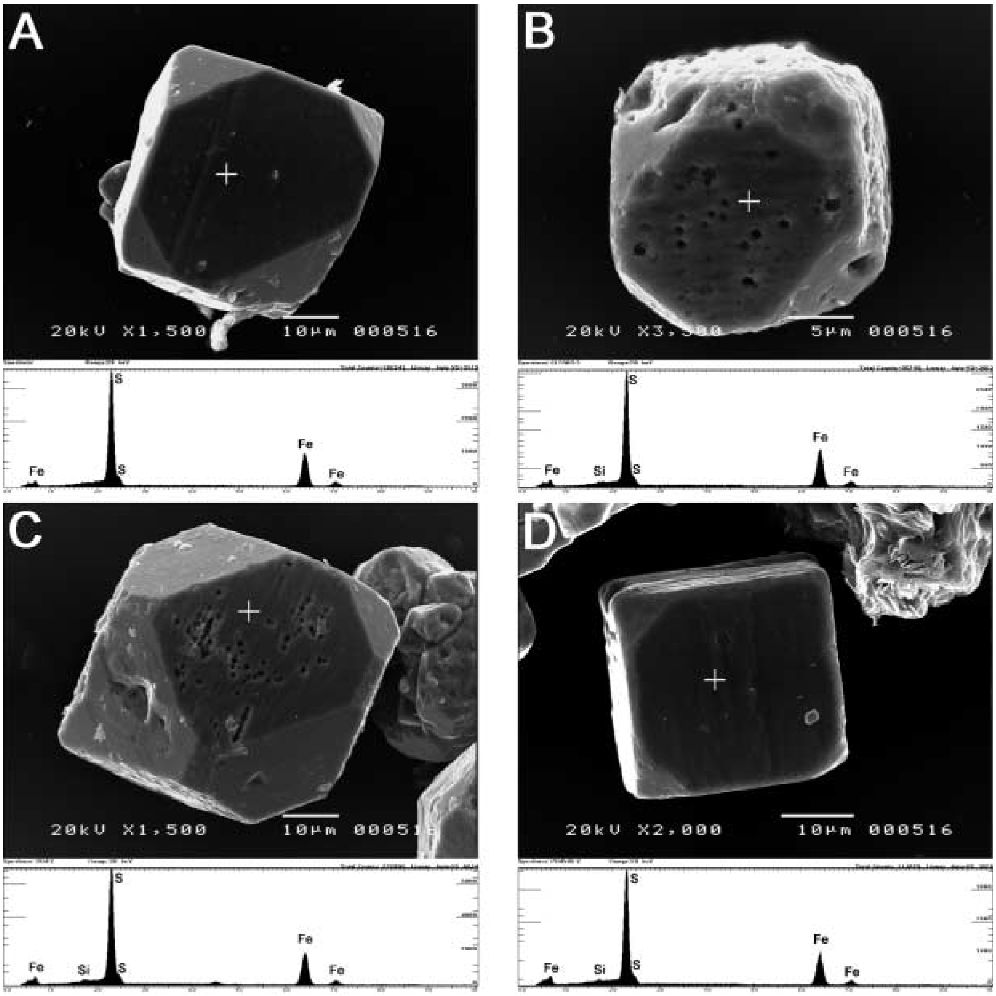

Fig. 6A–D
SEM micrographs of pyrite from the altered andesite show relatively smooth surfaces and sharp edges before Cr(VI) reduction (**A**), dissolution pits on the surface, rough surfaces, and smoothed edges after Cr(VI) reduction for KCl (**B**) and K_2SO_4 (**C**), regardless of the presence of initial Cr(VI), and a relatively smooth surface for KH_2PO_4 (**D**) compared with those of KCl and K_2SO_4. All pyrite grains showed a very similar chemical composition. The *cross bars* indicate the point of EDS analysis

The solution pH suggests that an additional adjustment pH for the precipitation of insoluble Cr(III) solid after the reduction of Cr(VI) to Cr(III) by the hydrothermally altered pyrite-rich andesite is needed for utilization in the treatment of Cr(VI)-containing water.

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