

The reduction of hexavalent chromium by sulphite in wastewater

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Abstract

The reduction of hexavalent chromium, Cr(VI), in unbuffered aqueous solution by sulphite was investigated as a function of pH, possible dosage and contact time required to reach equilibrium. Dissolved $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ served as the aqueous source of Cr(VI). The rate of the reaction between Cr(VI) and sulphite exhibited a very strong dependence on the pH of the reaction mixture, with a decrease in reaction rate with an increase in pH from 2.0 to 5.0. For a $5.0 \times 10^{-4} \text{ mol-dm}^{-3}$ Cr(VI) solution ($\sim 26 \text{ mg/l}$) a sulphite concentration of at least 5 times the initial Cr(VI) concentration was needed for complete reduction in this pH range. Above pH 6 very large concentrations of sulphite were needed to reduce Cr(VI) effectively. To check the industrial relevance of the results, baghouse dust from a ferrochromium plant was leached to serve as a model source of industrial wastewater containing aqueous Cr(VI), for conducting various comparative experiments. The results clearly indicated that sulphite would be a suitable reductant for Cr(VI) in wastewater under specific conditions ($2.0 \leq \text{pH}_{\text{initial}} \leq 5.0$ and $[\text{sulphite}] = 5 \times [\text{Cr(VI)}]_{\text{initial}}$).

Introduction

It is estimated that South Africa holds approximately 72% of the world's chromium reserves. Currently South Africa is the largest chromite and ferrochromium, as well as the sixth largest stainless steel producing country in the world (Mintek, 1994). It is suggested that by the year 2000 this industry will export products to the value of \$6.2 billion, which is approaching that of gold exports, which is estimated at \$7.1 billion (Robinson, 1996).

Although chromium has found many useful applications, the impact of the chromium industry on the local environment is extensive, complicated and not fully quantified. Landfill disposal of waste containing chromium compounds is common practice arising from industrial chromium production as well as chromium utilising industries (Gericke, 1995). Contaminated landfill sites and industrial effluents are likely to contain only trivalent chromium, Cr(III), and hexavalent chromium, Cr(VI). Divalent chromium, Cr(II), is fairly unstable and is rapidly oxidised to Cr(III). Elemental chromium, Cr(O), is also oxidised to Cr(III) unless it is made passive by superficial oxidation.

Trivalent chromium is considered a trace nutrient for human and animals alike (Wong and Trevors, 1988). The low solubility of Cr(III) solid phases (mostly Cr_2O_3 and Cr(OH)_3) is likely to be the major reason why Cr(III) generally makes up a small percentage of the total chromium concentration in polluted groundwater (Calder, 1988). Mobilisation of the Cr(OH)_3 precipitate is slow, unless enhanced by dissolution in strong acidic environments or complexation with organics (Rai et al., 1987). Oxidation of Cr(III) is mostly achieved through MnO_2 , which acts as a catalyst in the oxidation of chromium(III) (Rai et al., 1989).

In contrast, hexavalent chromium is considered toxic and carcinogenic (Yassi and Nieboer, 1988). There are no significant solubility constraints in groundwater for Cr(VI) (Rai et al., 1989). When Cr(VI) is transported by groundwater, it may be transformed to and precipitated as Cr(III). However, the reducing capability of

a soil is limited to the amounts of reductant (organics, Fe(II), sulfides, etc.) present. Hence excessive chromium loading on soil might not only upset, but destroy, the natural balance, giving way to Cr(VI) formation, even if the original load was exclusively Cr(III). Due to the toxicity and carcinogenicity of Cr(VI), the U.S. E.P.A. has set a drinking water limit for chromium of 0.05 mg/l (Calder, 1988). As a result, removing chromium(VI) from industrial wastewater has become necessary in order to avoid contamination of natural water and raw water used for public supply.

According to Lin and Vesilind (1995), removing Cr(VI) by chemical reduction from industrial wastewater involves a two-step process: reduction of hexavalent chromium under acidic conditions (usually pH 2 to 3) and the precipitation of trivalent chromium as hydroxyl species. The most commonly used reducing agents are gaseous sulphur dioxide, sodium sulphite, sodium metabisulphite and ferrous sulphate (Lin and Vesilind, 1995; Conner, 1990). Sodium dithionate has also been identified as a useful reducing agent for Cr(VI) (Pal and Yost, 1995).

The capacity of the ferrous ion to reduce Cr(VI) has been investigated in relative detail (Sedlak and Chan, 1997; Buerge and Hug, 1997; Fendorf and Li, 1996; Lin and Vesilind, 1995; Eary and Rai, 1988; 1989). Some investigations have also been conducted on the reduction of Cr(VI) by sulphite (Wawrzenczyk and Cyfert, 1994; Haight et al., 1965; Brandt and Elding, 1998). However, the use of buffers and the relatively small pH range in which these studies were carried out, make their results less applicable for industrial applications. In this paper the suitability of sulphite as a reductant for Cr(VI) in an unbuffered systems, over a wide pH range ($2.0 \leq \text{pH} \leq 8.0$), is reported. The results therefore give a good indication of the industrial applicability of sulphite for this purpose.

Materials and methods

Materials

Analytical grade reagents with the highest purity level were bought from the different suppliers and used without any further purification. Sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) (UniLab) was used as

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the aqueous source of Cr(VI). Sodium sulphite (Na_2SO_3) (*Merck*), and sodium metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$) (*BDH*) were used as the sulphite sources. The pH of reactant solutions was adjusted prior to mixing with stock solutions of sodium hydroxide (NaOH) (*Merck*) and/or perchloric acid (HClO_4) (*BDH*), the ionic strength of all solutions was kept constant at $0.1 \text{ mol}\cdot\text{dm}^{-3}$ by adding calculated volumes of a stock solution of sodium perchlorate ($\text{NaClO}_4\cdot\text{H}_2\text{O}$) (*Merck*) to the reactant solutions. Millipore milli-Q deionised water ($18 \text{ M}\Omega\cdot\text{cm}^{-1}$) was used to make up all solutions.

Baghouse dust from a ferrochromium plant, leached with milli-Q water, served as a model source of industrial wastewater containing aqueous Cr(VI). During the leaching procedure 1 g of baghouse dust and 10 ml of water was stirred for 15 min. The solution was thereafter filtered by using a nylon Millipore filter ($0.2 \mu\text{m}$ pore size) and diluted as required.

Methods

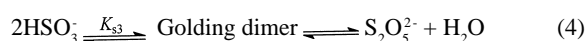
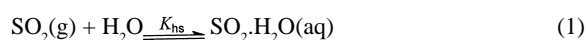
A variety of analytical methods can be employed to determine the chromium concentration in aqueous solution (Vogel, 1989). The most commonly used techniques are ion chromatography, atomic absorption and colorimetric methods, whereas titrimetric and gravimetric techniques have become less favourable since they are tedious and less accurate at low concentrations. Due to its relative ease of use and the fact that concentration changes can be monitored as they take place, the direct photometric absorption measurement method was chosen as the standard procedure to monitor the aqueous concentration of Cr(VI).

All kinetic experiments were carried out on a Pharmacia Biotech Ultraspec 3000 spectrophotometer or a SX-17MV Stopped-Flow spectrophotometer from Applied Photophysics. The temperature of all reagent mixtures was kept constant at $25.0^\circ \pm 0.5^\circ\text{C}$. The pH of the various reagents and reaction mixtures was measured with a Hanna Instruments (HI) 9318 pH meter, fitted with an HI 1131 pH electrode and an HI 7669/2 temperature sensor.

A limited number of atomic absorption (AA) determinations were done, to analyse aqueous solutions leached out of baghouse dust from a ferrochromium plant. For this purpose a Varian SpectAA-250 Plus spectrometer was used. Scanning electron micrographs of the baghouse dust were obtained with a Cambridge Stereoscan 250 scanning electron microscope, using carbon tape to bond the dust onto the metal mounting plates.

Results and discussion

If $\text{SO}_2(\text{g})$ is dissolved in water, the following equilibria exist:



with values of $K_{\text{hs}} = 1.24 \text{ mol}\cdot\text{dm}^{-3}\cdot\text{atm}^{-1}$ at 25°C and $I = 1.0 \text{ mol}\cdot\text{dm}^{-3}$ (Van Eldik and Harris, 1980), $K_{\text{s1}} = 1.29 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$ at 25°C (Maahs, 1982), $K_{\text{s2}} = 6.014 \times 10^{-8} \text{ mol}\cdot\text{dm}^{-3}$ at 25°C (Maahs, 1982) and $K_{\text{s3}} = 7.6 \times 10^{-2} \text{ dm}^3\cdot\text{mol}^{-1}$ at 25°C (Bourne et al., 1974) reported in literature. These equilibria and equilibrium constants are also valid for aqueous sulphite or bisulphite solutions. Independent of the source (dissolved SO_2 , sulphite or bisulphite), the total concentration of dissolved sulphur in the 4+ oxidation state

is referred to as S(IV). Since concentrations of $\text{S}_2\text{O}_5^{2-}$ in dilute aqueous solutions are very low, S(IV) can be defined as:

$$[\text{S(IV)}] = [\text{SO}_2\cdot\text{H}_2\text{O}(\text{aq})] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}] \quad (5)$$

In contrast to the term ‘‘sulphite’’, ‘‘S(IV)’’ can be used in a more general sense, since it does not depend on reaction conditions. In this paper all the results will therefore be discussed in terms of S(IV) and not sulphite.

Characteristics of Cr(VI)-S(IV) reaction system

Cr(VI) has a strong UV/visible spectrum with a very large molar absorption coefficient of $1550 \text{ mol}^{-1}\cdot\text{dm}^{-3}\cdot\text{cm}^{-1}$ at 350 nm (Wawrzenczyk and Cyfert, 1994). In comparison, the UV/visible spectrum of S(IV) is very weak with low intensity absorption bands at short wavelengths ($\sim 260 \text{ nm}$), visible only at relatively low pH values ($\text{pH} < 3$). Cr(III), formed during the reduction of Cr(VI) with S(IV), also exhibited a UV/visible spectrum, but with a relatively small molar absorption coefficient of $13.5 \text{ mol}^{-1}\cdot\text{dm}^{-3}\cdot\text{cm}^{-1}$ at 350 nm (Wawrzenczyk and Cyfert, 1994). Kinetic experiments were therefore carried out at 350 and 370 nm where the absorption by S(IV) and Cr(III) is negligible.

Effects of pH on Cr(VI) reduction

To determine the effect of pH on the reduction of Cr(VI) by S(IV), a $5.0 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ Cr(VI) solution was treated with S(IV), ranging in concentration from 5 to 15 times the initial Cr(VI) concentration ($[\text{Cr(VI)}]_{\text{initial}}$). To facilitate the comparison of results under different reaction conditions, results are given in terms of the percentage reduction of the $[\text{Cr(VI)}]_{\text{initial}}$ vs. time required. As can be seen from Fig. 1, initial pH of the reaction mixture has a strong and definite effect on reduction times. For $2.0 \leq \text{pH}_{\text{initial}} \leq 6.0$, the time required to achieve 50% reduction of the $[\text{Cr(VI)}]_{\text{initial}}$ ($t_{0.5}$) increased logarithmically with increasing $\text{pH}_{\text{initial}}$.

Under the same reaction conditions the time required to achieve 95% reduction of $[\text{Cr(VI)}]_{\text{initial}}$ ($t_{0.95}$) showed a similar trend, increasing logarithmically with increasing pH, at $2.0 \leq \text{pH}_{\text{initial}} \leq 4.0$ (Fig. 2). A discontinuity is, however, observed at $\text{pH}_{\text{initial}} > 4$ where the time required to reach 95% reduction, is no longer directly logarithmically related to the $\text{pH}_{\text{initial}}$.

At $\text{pH}_{\text{initial}} > 6$ very long reaction times, together with large S(IV) concentrations, were needed to reduce Cr(VI) successfully. For instance at $\text{pH}_{\text{initial}} = 7.0$, with $[\text{S(IV)}] = 15 \times [\text{Cr(VI)}]_{\text{initial}}$, it took 7.4 h to reach a 50% reduction and 15.3 h to reach 95% reduction of $[\text{Cr(VI)}]_{\text{initial}}$. At $\text{pH}_{\text{initial}} = 8.0$, with $[\text{S(IV)}] = 50 \times [\text{Cr(VI)}]_{\text{initial}}$, only 16% reduction of $[\text{Cr(VI)}]_{\text{initial}}$ had occurred after 6 d. No further investigations into the reduction of Cr(VI) by S(IV) were therefore conducted at $\text{pH}_{\text{initial}} \geq 7$.

In order to correlate the above-mentioned results with published data, $t_{0.5} = 0.034 \text{ s}$ was calculated from $k_{\text{obs}} = 20.3 \text{ s}^{-1}$ reported by Wawrzenczyk and Cyfert (1994), at $\text{pH} 1.46$ and $[\text{S(IV)}] = 10 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$. Extrapolation of experimental results ($[\text{S(IV)}] = 7.5 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$) to $\text{pH} 1.46$ yielded $t_{0.5} = 0.030 \text{ s}$.

Looking at the results shown in Figs. 1 and 2, three phenomena warrant explanation: a) what causes the reaction rate to increase at lower pH values; b) why a logarithmic increase in the time required to reach 50% reduction of $[\text{Cr(VI)}]_{\text{initial}}$ was observed for increasing pH ($2.0 \leq \text{pH} \leq 6.0$); and c) why this logarithmic increase only persisted between pH 2 and 4 for the time required to reach 95% reduction of the $[\text{Cr(VI)}]_{\text{initial}}$.

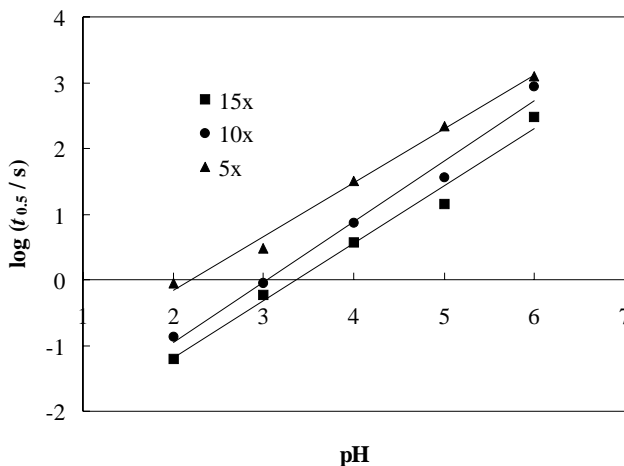


Figure 1

Time required to reach 50% reduction of the initial $[Cr(VI)] (t_{0.5})$
 $[Cr(VI)]_{initial} = 5.0 \times 10^{-4} \text{ mol-dm}^{-3}$; $[S(IV)] = 5, 10 \text{ and } 15 \times$
 $[Cr(VI)]_{initial}$; $I = 0.1 \text{ mol-dm}^{-3}$; $T = 25.0 \pm 0.5^\circ\text{C}$

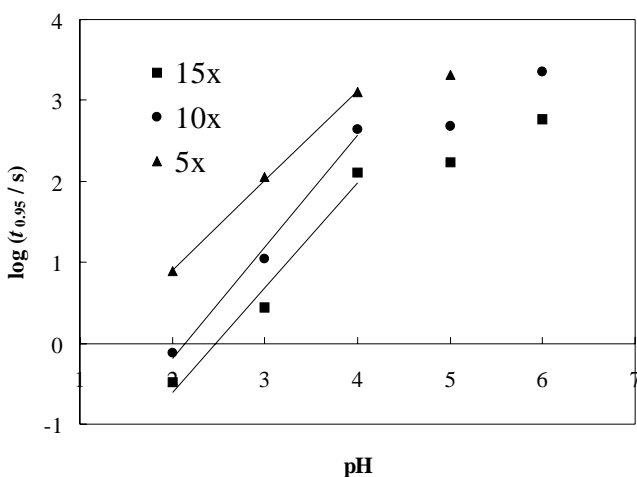


Figure 2

Time required to reach 95% reduction of the initial $[Cr(VI)] (t_{0.95})$
 $[Cr(VI)]_{initial} = 5.0 \times 10^{-4} \text{ mol-dm}^{-3}$; $[S(IV)] = 5, 10 \text{ and } 15 \times$
 $[Cr(VI)]_{initial}$; $I = 0.1 \text{ mol-dm}^{-3}$; $T = 25.0 \pm 0.5^\circ\text{C}$

- a) In order to explain the increase in reaction rate with decreasing pH, one needs to take into account the speciation of both Cr(VI) and S(IV) under these conditions. The Eh-pH diagram shown in Fig. 3 (Rai et al., 1989) provides a generalised depiction of the major aqueous chromium species and redox stabilities under conditions of chemical equilibrium. The dominant Cr(VI) species are $HCrO_4^-$ at pH 1-6 and CrO_4^{2-} at pH > 6. Chromium(VI) also forms other species, such as $HCr_2O_7^-$ and $Cr_2O_7^{2-}$. However, their formation requires Cr(VI) concentrations $> 10^{-2} \text{ mol-dm}^{-3}$ (Baes and Mesmer, 1976). The increase in reaction rate with decreasing pH can therefore probably be attributed to $HCrO_4^-$ which is reduced more easily than CrO_4^{2-} (see redox stabilities Fig. 3). By looking at the speciation of S(IV) (shown in Fig. 4) it is also quite apparent that the increase in reaction rate with decreasing pH, observed for the Cr(VI)-S(IV) reaction, correlates with the increase in concentration of $SO_2 \cdot H_2O(aq)$ at lower pH values. The possibility that

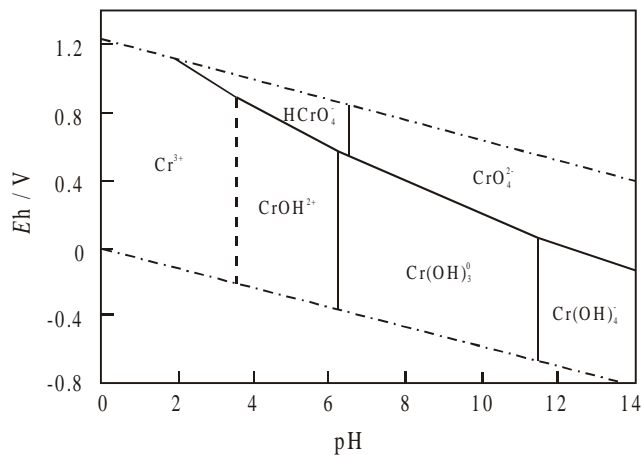


Figure 3

Eh-pH diagram for aqueous chromium species
(Rai et al., 1989)

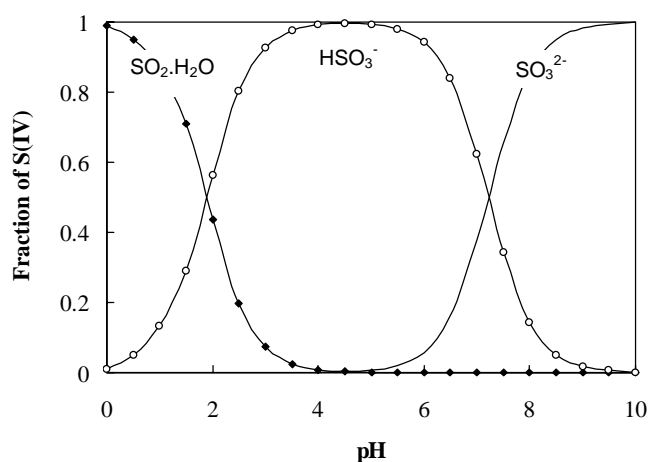


Figure 4

Distribution curve of different S(IV) species as a function of pH, at concentrations relevant to this investigation ($\sim 10^{-3} \text{ mol-dm}^{-3}$)

- $SO_2 \cdot H_2O(aq)$ might be the most reactive S(IV) species in this process must therefore also not be overlooked. In fact Haight et al. (1965) postulated a reaction mechanism for the reduction of Cr(VI) by S(IV) in which $SO_2 \cdot H_2O(aq)$ took part in the rate-determining step, while Wawrzenczyk and Cyfert (1994) suggested that both $SO_2 \cdot H_2O(aq)$ and HSO_3^- took part in two separate rate-determining steps. This can, however, not be used as conclusive evidence for the reactivity patterns of S(IV), since both of these studies were conducted over a very small pH range at low pH values.
- b) A logarithmic increase in time required to reach a certain percentage reduction of the $[Cr(VI)]_{initial}$, for increasing pH, can be explained if the Cr(VI)-S(IV) reaction system's rate law has a first-order dependence on the $[H^+]$. For example a simple rate law might be:

$$\frac{-d[Cr(VI)]}{dt} = k[H^+][Cr(VI)][S(IV)] \quad (6)$$

This can be simplified to:

$$\frac{-d[\text{Cr(VI)}]}{dt} = k'[\text{Cr(VI)}] \quad (7)$$

$$\text{with } k' = k[\text{H}^+][\text{S(IV)}] \quad (8)$$

The half life, $t_{0.5}$, for a first-order reaction is given by:

$$t_{0.5} = \frac{\ln 2}{k'} \quad (9)$$

Which means that:

$$t_{0.5} \propto \frac{1}{[\text{H}^+]}, \text{ since } k' \propto [\text{H}^+] \quad (10)$$

Therefore:

$$\log(t_{0.5}) \propto \log\left(\frac{1}{[\text{H}^+]}\right) = \text{pH} \quad (11)$$

In the same way $\log(t_{0.95}) \propto \text{pH}$. The logarithmic increase in time required to reach a 50% reduction of the $[\text{Cr(VI)}]_{\text{initial}}$, for increasing pH, can therefore be explained by the fact that the Cr(VI)-S(IV) reaction system's rate law has a first order dependence on the $[\text{H}^+]$. As long as the pH remains constant, this direct relationship will remain.

c) During this investigation, unbuffered reaction mixtures were used. Any drift in pH, due to the formation of reaction products, would obviously influence the reduction rate. To investigate this possibility, some initial and final pH values, at a fixed $[\text{Cr(VI)}]_{\text{initial}}$ and $[\text{S(IV)}]$, were measured (Table 1). From these results it is clear that there is a slightly upward drift in pH at $2.0 \leq \text{pH}_{\text{initial}} \leq 4.0$, which is due to the consumption of H^+ ions (see Reactions 12 and 13 in the next section). At $\text{pH}_{\text{initial}} > 4$ a downwards drift in pH was observed. The amount of pH drift also becomes significantly larger as the initial pH increase from 4 to 7. A feasible explanation for this depression in pH at higher initial pH values is the release of H^+ ions due to hydrolysis of the Cr(III) ions produced by the reaction, which dominates the consumption of H^+ ions by reactions 12 and 13. Above $\text{pH} = 5$, hydrolysis of the Cr(III) ions become significant (Richard and Bourg, 1991). The effect of pH drift on the reaction is also reflected by the shapes of the kinetic traces at different pH values. At $\text{pH}_{\text{initial}} = 5.0$, where the pH drift was relatively small, typical first-order-like time traces were observed (see Fig. 5a). The time traces observed at $\text{pH}_{\text{initial}} = 7.0$ exhibited a shape generally associated with autocatalytic processes (see Fig. 5b) - at first the reaction rate is slow, it then accelerates either by the formation of a species which accelerates the reaction rate or by the consumption of species which retards the reaction and eventually the reaction rate slows down again due to the depletion of one or more of the reagents. Indeed, the unbuffered reduction of aqueous Cr(VI) by S(IV), at $\text{pH}_{\text{initial}} > 4$, can be seen as an autocatalytic process. The kinetic trace in Fig. 5b can be explained as follows: initially the reaction rate is slow, then as reduction starts taking place the pH starts drifting down which accelerates the reduction rate and eventually the reduction rate slows down due to the depletion of Cr(VI). In the previous paragraph it was shown that $\log(t_{0.95}) \propto \text{pH}$, if the pH remains constant. The fact that a significant downwards drift in pH was observed at $\text{pH}_{\text{initial}} > 4$, means that the direct relationship between $\log(t_{0.95})$ and pH is no longer valid, explaining the discontinuity at $\text{pH} > 4$ in Fig. 2.

Initial pH	Final pH
2.0 ± 0.1	2.1 ± 0.1
3.0 ± 0.1	3.6 ± 0.2
4.0 ± 0.1	4.0 ± 0.1
5.0 ± 0.1	4.4 ± 0.3
6.0 ± 0.1	4.5 ± 0.3
7.0 ± 0.1	4.3 ± 0.3

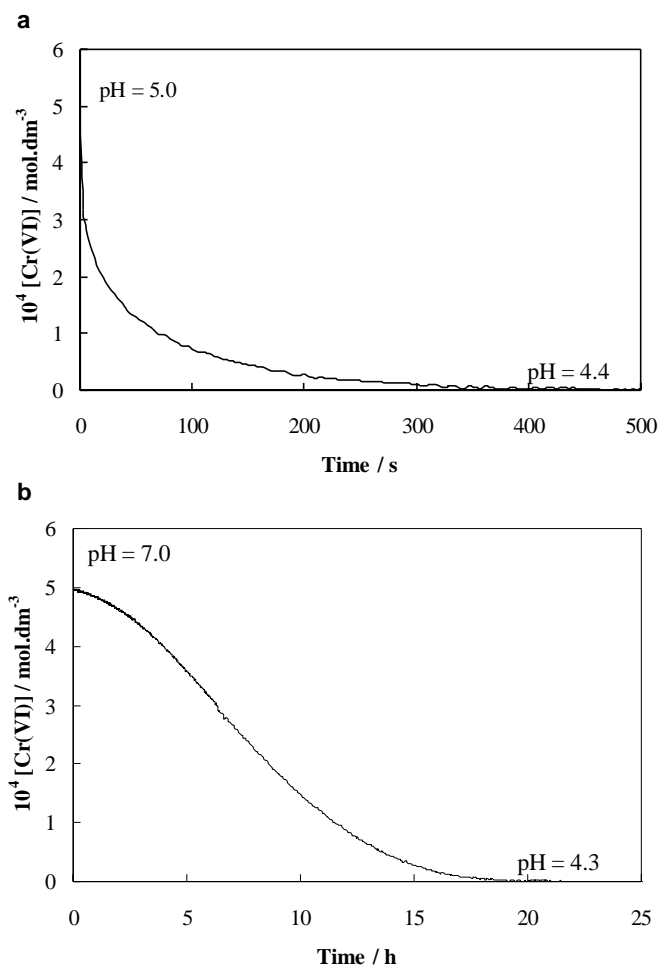


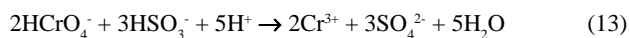
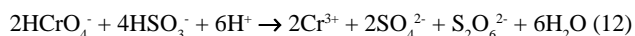
Figure 5
Kinetic traces for the reduction of Cr(VI) by S(IV)
[Cr(VI)]_{initial} = 5.0 x 10⁻⁴ mol·dm⁻³; [S(IV)] = 15 x [Cr(VI)]_{initial}; I = 0.1 mol·dm⁻³; T = 25.0 ± 0.5°C
a: pH_{initial} = 5.0 ± 0.1
b: pH_{initial} = 7.0 ± 0.1

Required dosage of [S(IV)]

As was shown in the previous section, initial pH of the reaction mixture is of great importance for effective reduction of aqueous Cr(VI) by S(IV). For the sake of practicality, the required dosage of S(IV) to ensure complete reduction of [Cr(VI)]_{initial} was firstly investigated at the optimum pH_{initial}.

The optimum pH for Cr(VI) reduction, by S(IV), seems to be at low pH values - in fact the lower the pH_{initial}, the faster the reduction process (see Figs. 1 and 2). But to assume that pH_{initial} = 2 (or even lower pH values) would be the optimum pH for industrial application might be wrong. From the distribution curve of the different S(IV) species (Fig. 4) it is clear that the largest changes in speciation occur between pH 0 and 4, where SO₂.H₂O(aq) decreases from approximately 99% to less than 1% of the total S(IV) concentration. Between pH 1 and 3, SO₂.H₂O(aq) concentration changes from approximately 87% to 7% of the total S(IV) concentration. Taking into account that SO₂.H₂O(aq) is in equilibrium with SO₂(g), it might be contra-productive to perform reduction of Cr(VI) by S(IV) at very low pH values, since S(IV) would be lost to the atmosphere in the form of SO₂(g). At pH = 3.0, the SO₂.H₂O(aq) component is only 7% of the total S(IV) concentration and was therefore chosen as an appropriate pH to investigate the required dosage of S(IV).

Haight et al. (1965) as well as Wawrzenczyk and Cyfert (1994) explained the stoichiometry of the reaction of Cr(VI) with S(IV) in terms of the competition between two over-all reactions:



An excess of S(IV) favours reaction (12), while an excess of Cr(VI) favours reaction (13). According to reactions (12) and (13), a S(IV) concentration of 1.5 to 2 times the [Cr(VI)]_{initial} would be sufficient to ensure complete reduction of Cr(VI). The practicality of this assumption is, however, poor. Table 2 gives an indication of [S(IV)] required for effective reduction of aqueous Cr(VI). When [S(IV)] was 3 or 4 x [Cr(VI)]_{initial} a 95% reduction of Cr(VI) was not obtained. A [S(IV)] of at least 5 x [Cr(VI)]_{initial} was required to reduce the aqueous Cr(VI) beyond a level of 95%. It furthermore follows from Fig. 2 that this S(IV) dosage would also be effective at 2.0 ≤ pH_{initial} ≤ 5.0.

Industrial relevance of results

All the results presented thus far were obtained using Na₂Cr₂O₇.2H₂O as the aqueous source of Cr(VI). To investigate the industrial relevance of these results, baghouse dust from a ferrochromium plant was leached to serve as a model source of industrial wastewater containing aqueous Cr(VI). This leached solutions was diluted, as required and treated with S(IV) under identical experimental conditions to make comparison of results possible.

In order to draw any conclusions from the results, it was important to characterise the baghouse dust used to prepare the Cr(VI) solutions, so that possible differences in the kinetic behaviour could be explained. A scan electron microscope (SEM) photograph of 11 177 times magnification (Fig. 6) showed that the baghouse dust consisted of small rounded particles, indicating that

TABLE 2
INFLUENCE OF [S(IV)] ON THE TIME REQUIRED TO REACH 50% AND 95% REDUCTION OF [Cr(VI)]_{INITIAL}
[Cr(VI)]_{INITIAL} = 5.0 x 10⁻⁴ mol·dm⁻³; [S(IV)] = 3, 4, 5, 10 OR 15 x [Cr(VI)]_{INITIAL};
pH_{INITIAL} = 3.0 ± 0.1; I = 0.1 mol·dm⁻³; T = 25.0 ± 0.5°C

[S(IV)] /mol·dm ⁻³ x 10 ⁻³	Excess S(IV)	Time to reach 50% reduction/s	Time to reach 95% reduction/s
1.5	3	25.0 ± 2.5	-
2.0	4	18.0 ± 2.0	-
2.5	5	3.0 ± 0.3	112.0 ± 10.0
5.0	10	0.6 ± 0.04	11.0 ± 0.9
7.5	15	0.3 ± 0.02	2.8 ± 0.2

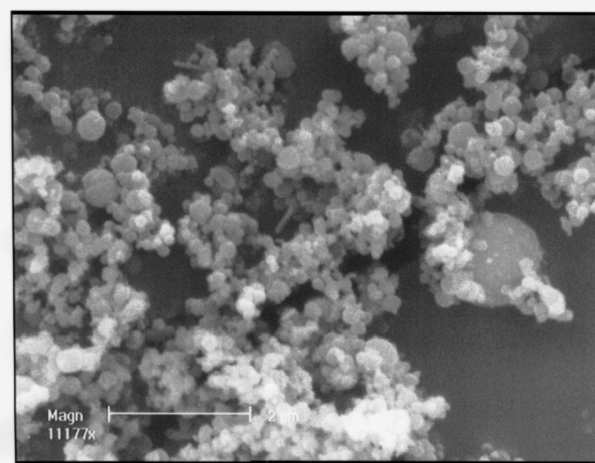


Figure 6
SEM photograph of baghouse dust from a ferrochromium plant at 11 177 time magnification

melting had taken place. No unreacted chromite was observed (as would have been indicated by uneven-shaped particles). SEM-EDAX elemental analyses of the baghouse dust (the presence of oxygen and carbon were ignored) showed a relatively high percentage (i.e. 3.12%) of chromium. The numerical values of the SEM-EDAX elemental analyses are given in Table 3. Of particular interest in this table are the presence of significant amounts of iron, since it is well known that Fe(III) will catalyse the oxidation of S(IV) by oxygen (Brandt and Van Eldik, 1995). If Fe(III) is present in the leached solutions, it will compete with Cr(VI) for the oxidation of S(IV), which will impact negatively on the reduction of Cr(VI).

Since the direct photometric absorption method was chosen as the standard procedure with which the aqueous concentration of Cr(VI) was monitored, the validity of this method for the accurate determination of the Cr(VI) concentrations in the leached solutions needed to be evaluated. To determine if there were any interfering absorption peaks in the UV/visible spectra, the pH of both a leached solution, as well as a 5.0 x 10⁻⁴ mol·dm⁻³ Cr(VI) solution (Na₂Cr₂O₇.2H₂O dissolved in milli-Q deionised water) were adjusted to pH 6.0 and the UV/visible spectra recorded separately. The molar absorption coefficients of the 5.0 x 10⁻⁴ mol·dm⁻³ Cr(VI) solution was calculated at intervals of 0.5 nm for λ = 330 to 480 nm. By using this data, a calculated Cr(VI) spectrum of any concentra-

TABLE 3
SEM-EDAX ELEMENTAL ANALYSES OF THE BAGHOUSE DUST USED IN THIS STUDY. NUMERICAL VALUES ARE GIVEN IN TERMS OF THE PERCENTAGE WEIGHT, AS WELL AS THE PERCENTAGE ATOMIC WEIGHT FOR EACH ELEMENT, AS A FUNCTION OF ALL THE ELEMENTS DETECTED (NOTE THAT THE PRESENCE OF CARBON AND OXYGEN WERE IGNORED DURING THESE DETERMINATIONS)

Element	Wt%	At%
Na	13.58	18.28
Mg	12.90	16.42
Al	6.74	7.73
Si	32.12	35.39
P	1.08	1.08
S	4.17	4.02
Cl	1.21	1.06
K	6.26	4.96
Cr	3.12	1.86
Fe	3.41	1.89
Cu	1.11	0.54
Zn	14.30	6.77
Total	100.00	100.00

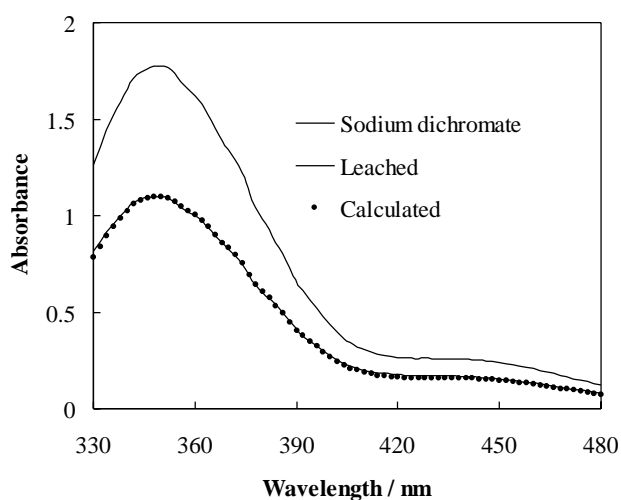


Figure 7

Comparison of the UV/visible spectra of Cr(VI) obtained by using $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot \text{H}_2\text{O}$ and baghouse dust from a ferrochromium plant

tion could be constructed. Figure 7 shows that a Cr(VI) spectra could be calculated which corresponded almost perfectly with the spectrum of the leached solution. The residual spectrum (spectrum of leached solution minus calculated spectrum) was almost negligible, indicating that no absorption peaks of other species occurred. The same direct photometric absorption method used previously could therefore also be used for experiments with the leached solutions.

A number of comparative experiments were conducted. Firstly, a leached solution was diluted so that a Cr(VI) solution with a concentration of $5.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ was obtained. This solution was treated with the minimum required S(IV) concentration ($5 \times [\text{Cr(VI)}]_{\text{initial}}$) and within the effective pH range ($2.0 \leq \text{pH}_{\text{initial}} \leq 5.0$) as determined in previous experiments. A comparison of reduction times observed when $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ and the leached solutions were respectively used as the aqueous sources of Cr(VI) is shown in Table 4. The results correlated almost perfectly. Surprisingly no interference by other species present in the leached solutions was observed. If for instance any Fe(III) was present, it would have influenced the reduction process by catalysing the oxidation of S(IV). Atomic absorption (AA) measurements also confirmed that iron concentrations in the leached solutions were negligible.

To further facilitate the evaluation of S(IV) as reducing agent for Cr(VI), a comparison with other reducing agents is necessary. A large number of chemical reducing agents exist for Cr(VI). Of those, Fe(II) is probably the most important since it is used extensively for Cr(VI) reduction in wastewater of baghouse and/or scrubber dust by the ferrochromium industry (Gericke, 1995). Although Buerge and Hug (1997), as well as Sedlak and Chan (1997), conducted very detailed investigations on the reduction of Cr(VI) by Fe(II), their results were made less comparable to the experimental results due to the fact that buffers were used. Fendorf and Li (1996), on the other hand, only investigated the reduction process over a narrow pH range of 6.0 to 8.0. Table 5 shows a comparison between optimum parameters found experimentally for the Cr(VI)-S(IV) system and those reported for the Cr(VI)-Fe(II) system (Eary and Rai, 1988; Lin and Vesilind, 1995 and Gericke, 1995). From these data it is clear that Fe(II) can be used to reduce Cr(VI) from pH 2.0 up to at least pH 8.0. S(IV) on the other hand is only effective from pH 2.0 to 5.0. The effective dosage required for S(IV) is $[\text{S(IV)}] = 5.0 \times [\text{Cr(VI)}]_{\text{initial}}$ dosage, while that of Fe(II) is in the order of $[\text{Fe(II)}] = 3.5 \text{ to } 4 \times [\text{Cr(VI)}]_{\text{initial}}$. Direct comparison of the contact time required to reach a certain percentage Cr(VI) reduction by the two different reducing agents is, however, difficult due to the fundamental differences in the monitoring techniques employed. The DPC (diphenylcarbazide) colorimetric method used to measure Cr(VI) concentration for the Fe(II)-Cr(VI) system is a batch method, which does not allow

TABLE 4
A COMPARISON OF REDUCTION TIMES USING $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot \text{H}_2\text{O}$ AND THE BAGHOUSE DUST FROM A FERROCHROMIUM PLANT, AS THE RESPECTIVE AQUEOUS SOURCES OF Cr(VI)
 $[\text{Cr(VI)}]_{\text{INITIAL}} = 5.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$; $[\text{S(IV)}] = 5 \times [\text{Cr(VI)}]_{\text{INITIAL}}$; $I = 0.1 \text{ mol} \cdot \text{dm}^{-3}$; $T = 25.0 \pm 0.5^\circ\text{C}$

pH	Sodium dichromate		Baghouse dust	
	Time required for 50% reduction/s	Time required for 95% reduction/s	Time required for 50% reduction/s	Time required for 95% reduction/s
2.0	0.88 ± 0.06	7.8 ± 0.8	0.80 ± 0.07	7.9 ± 0.8
3.0	3.0 ± 0.3	112 ± 9	3.2 ± 0.3	100 ± 8
4.0	31.6 ± 2.9	$1\ 258 \pm 80$	30.0 ± 2.8	$1\ 122 \pm 91$
5.0	220 ± 20	$2\ 040 \pm 110$	200 ± 18	$2\ 043 \pm 115$

TABLE 5
COMPARISON OF REDUCING CAPABILITY OF S(IV) (FOUND EXPERIMENTALLY) WITH THAT REPORTED FOR Fe(II)

Reference	Cr(VI) source	Fe(II) or S(IV) source	Effective pH range	Effective Fe(II) dosage
Experimental	Na ₂ Cr ₂ O ₇ or leached bahuouse dust K ₂ Cr ₂ O ₇ K ₂ Cr ₂ O ₇	Na ₂ SO ₃ at pH > 6 and Na ₂ S ₂ O ₅ at pH ≤ 6	2.0 – 5.0	5 x [Cr(VI)] _{initial}
Eary and Rai, 1988		Fe(NH ₄) ₂ (SO ₄) ₂	2.0 – 10.0	3 x [Cr(VI)] _{initial}
Lin and Vesilind, 1995		FeSO ₄	5.0 – 9.0	~3.5 – 4.0 x [Cr(VI)] _{initial}
Gericke, 1995	Leached baghouse dust	FeSO ₄	2.0 – 8.0	~4 x [Cr(VI)] _{initial}

continuous monitoring of the Cr(VI) concentration. This is in contrast to the direct photometric absorption method used during this investigation, which allowed continuous monitoring. However, comparison of $t_{0.5}$ calculated from the results reported by Buerge and Hug (1997) indicates that S(IV) reduces Cr(VI) faster than Fe(II) at $2 \leq \text{pH} \leq 5$, while Fe(II) is faster at $\text{pH} > 5$.

Conclusions

From the results presented the following conclusions can be drawn:

- The pH of the reaction mixture has a strong effect on the reduction rate of Cr(VI) by S(IV).
- During the unbuffered reduction of Cr(VI) by S(IV), pH drift takes place, which influences the reduction process.
- Fast and complete reduction of Cr(VI) is favoured by low $\text{pH}_{\text{initial}}$ ($2.0 \leq \text{pH}_{\text{initial}} \leq 5.0$).
- At $\text{pH}_{\text{initial}} > 6$ a very large excess of S(IV) is required for the effective reduction of Cr(VI).
- The concentration of S(IV) required for effective reduction of Cr(VI) seems to be in the order of $[\text{S(IV)}] = 5 \times [\text{Cr(VI)}]_{\text{initial}}$ for $2.0 \leq \text{pH}_{\text{initial}} \leq 5.0$.
- An excellent correlation between results obtained using Na₂Cr₂O₇·2H₂O as the aqueous source of Cr(VI) and baghouse dust from a ferrochromium plant leached with milli-Q water was found. This correlation showed that the results obtained indicate optimum conditions for industrial application.
- The required dosage for effective reduction of Cr(VI) by S(IV) compare favourably with the dosage required for Cr(VI) reduction by Fe(II). The Fe(II) system is however effective over a larger pH range (see Table 5).

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