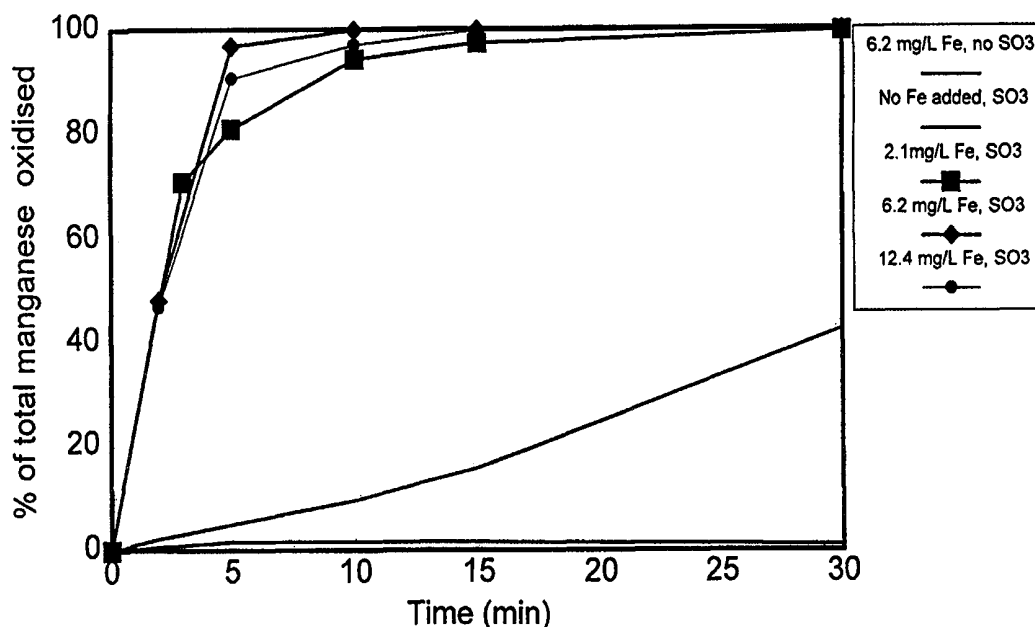




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/AU99/00620 (22) International Filing Date: 30 July 1999 (30.07.99) (30) Priority Data: PP 5008 31 July 1998 (31.07.98) AU (71) Applicants (for all designated States except US): AUSTRALIAN NUCLEAR SCIENCE & TECHNOLOGY ORGANISATION [AU/AU]; New Illawarra Road, Lucas Heights, NSW 2234 (AU). CRC FOR WASTE MANAGEMENT & POLLUTION CONTROL LTD. [AU/AU]; The University of NSW, Gate 11, Botany Street, Kensington, NSW 2033 (AU). (72) Inventors; and (75) Inventors/Applicants (for US only): GING, Hauw, Khoe [AU/AU]; 125 Nicholson Parade, Cronulla, NSW 2230 (AU). MYINT, Zaw [AU/AU]; 41 Delhi Street, Lidcombe, NSW 2141 (AU). (74) Agent: GRIFFITH HACK; GPO Box 4164, Sydney, NSW 2001 (AU).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>

(54) Title: IRON-CATALYSED OXIDATION OF MANGANESE AND OTHER INORGANIC SPECIES IN AQUEOUS SOLUTIONS



(57) Abstract

A method for oxidising an inorganic species in an aqueous solution of pH 5 or greater, comprises the steps of (i) supplying an oxidisable form of a sulfur compound, and oxygen to the solution; and (ii) adding a source of iron to the solution and allowing oxidation to take place. The method finds particular application in the treatment of manganese and other species in potable water, industrial waste waters and process liquors.

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IRON-CATALYSED OXIDATION OF MANGANESE AND OTHER INORGANIC SPECIES IN AQUEOUS SOLUTIONS

Field of the Invention

The present invention relates to a method for
5 oxidising (and optionally removing) manganese and other
inorganic species in aqueous solutions. For example, the
invention relates to the treatment of manganese and other
inorganic species in potable water, industrial waste waters
and process liquors.

10 Background to the Invention

Many drinking water supplies across the world are
contaminated by trace contaminants such as manganese,
arsenic and heavy metals. Manganese is also present in
mining and mineral processing effluents.
15 The removal of trace contaminants to very low
concentrations is often required for aesthetic reasons
(e.g. the presence of manganese gives rise to "dirty or
black water" problems and can result in soiling of clothes
and staining of household fixtures when present in
20 concentrations in excess of 0.020 mg/L in drinking water)
or for health reasons (the WHO drinking water guideline for
arsenic is 0.010 mg/L).

Manganese removal is often difficult because
dissolved divalent manganese (Mn(II)) is poorly adsorbed by
25 coagulants commonly used for water treatment such as iron
and aluminium compounds. Consequently, the removal of trace
manganese requires a pre-oxidation step in which dissolved
manganese(II) is converted to the insoluble manganese(III)
and/or (IV) oxides (or oxyhydroxides). Thereafter, a
30 coagulation step using iron or aluminium salt can be used
to remove the manganese oxide particles.

The oxidative precipitation of manganese in
ambient conditions, however, requires powerful oxidants
such as permanganate (the oxidation rate using chlorine is
35 usually too slow) which can be expensive and difficult to
handle.

The removal of arsenic from process liquors by
the oxidation of iron(II), arsenic(III) and sulfur(IV) with

oxygen has been studied (T. Nishimura et al., "Removal of Arsenic from Process Liquors by Oxidation of Iron(II), Arsenic(III) and Sulfur(IV) with Oxygen", Proceedings of the second International Symposium on Iron Control in Hydrometallurgy, CIM, Montreal, Ottawa, Canada, 1996, 535-547). However, it was disclosed in this paper that in the presence of dissolved iron, the oxidation reactions (As(III) to As(V), and Fe(II) to Fe(III)) were only effective at $2 < \text{pH} < 5$.

Summary of the Invention

Surprisingly, the present inventors have discovered that the addition of iron(III) compounds in neutral or alkaline aqueous solutions can accelerate the rate of oxidation of manganese and other inorganic species in the presence of oxygen and sulfur(IV). This is despite the fact that iron exists in a solid (precipitated) form in these solutions.

Accordingly, the present invention provides a method for oxidising an inorganic species in an aqueous solution of pH 5 or greater, comprising the steps of:

- (i) supplying an oxidisable form of a sulfur compound, and oxygen to the solution; and
- (ii) adding a source of iron to the solution and allowing oxidation to take place.

25 Typically the source of iron is a soluble
iron(III) compound such as ferric-chloride or sulfate.

Alternatively, iron(II) can be supplied to the solution in a form which can be readily oxidised to iron(III) (eg. as ferrous sulfate), which then accelerates the oxidation reaction.

Typically the species oxidised is manganese and preferably oxidation is effected by the addition of sodium sulfite and oxygen (air) in the presence of an iron compound (eg. as precipitated iron compounds).

35 Furthermore, the product resulting from the added iron can subsequently (and advantageously) serve as a coagulant to remove the oxidised species from the solution.

Oxygen is advantageously used as the oxidising

agent because it has no residual contaminating after-effects. Sulfur sources can be selected, (e.g. sulfite or SO_2 gas) such that in the oxidising procedure, a relatively benign product is produced (e.g. sulfate). Whilst the final
5 product of using sulfite is a relatively benign dissolved sulfate, it is still preferable to use it sparingly, especially if an ion-exchange process is subsequently used to remove the contaminant (e.g. arsenic). In this latter case residual dissolved sulfate of no more than 25 mg/L is
10 preferred, as this then enables effective arsenic(V) removal (ie. sulfate and arsenate may otherwise compete for sites on the ion-exchange material).

The oxidisable sources of sulfur can be SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_4\text{O}_6^{2-}$, $\text{SO}_2(\text{g})$, aqueous SO_2 , or HSO_3^- . However, sulfur
15 dioxide and sulfite are the most preferred sources. Also, waste sulfur dioxide gas may be available for use in industrial applications.

Typically the process is applied in the treatment of trace quantities of inorganic species but the process
20 can also find application with more concentrated quantities of contaminants (e.g. in geothermal waters, leachates obtained from smelter wastes, industrial process liquors etc).

In addition to manganese, the species oxidised
25 can include one or more of arsenic, sulfide, selenium and may also include uranium, cobalt, antimony, bismuth and other inorganic species.

Typically the oxygen is sparged into the aqueous solution as air but other methods of addition are possible.
30 As indicated above, the solution is typically a drinking water solution, an industrial waste water or process liquor etc.

Typically the pH of the solution is, if necessary, made to be near neutral or basic.

35 **Brief Description of the Drawings**

Notwithstanding any other forms which may fall within the scope of the present invention, preferred forms of the invention will now be described, by way of example

only, with reference to the accompanying drawings and the following non-limiting examples. In the drawings:

Figure 1 graphs the oxidation of manganese(II) as a function of added iron(III) concentrations. In this graph
5 the initial manganese(II) concentration was 5 mg/L, sodium sulfite solution was added to 1.7 litres of a reaction mixture at a dose rate of 8 mg S/L/min, air was sparged at a rate of 2.5 L/min and pH was maintained at 6.5. Dissolved manganese(II) concentrations were determined
10 using electron paramagnetic resonance (EPR) spectroscopy.

Figure 2 graphs the oxidation of dissolved manganese(II) using sulfite and oxygen at pH 8 (adjusted using sodium bicarbonate) in the presence/absence of iron(III). Sodium sulfite solution was added at a dose rate
15 of 8 mg S/L/min and air was sparged at a rate of 2.5 L/min. The initial conditions were: solution volume 1.7 L manganese(II) concentration 5 mg/L. Dissolved manganese(II) concentrations were determined using EPR spectroscopy.

Figures 3 (a) and (b) graph the oxidation of
20 manganese(II) as a function of pH using Nepean dam water which had been spiked to (a) 0.55 mg/L or (b) 5.15 mg/L manganese(II) concentration. Iron(III) was added to 1.7 litre of dam water at a concentration of 15 mg Fe/L; sodium sulfite solution at a dose rate of 8 mg S/L/min, air at a
25 rate of 2.5 L/min and pH was maintained at 6.5, 8 or 8.5. Dissolved manganese(II) concentrations were determined using EPR spectroscopy.

Figure 4 graphs residual manganese concentrations in 1.7 litre of Nepean dam water as a function of time. The
30 solution pH was maintained at pH 8.5, sodium sulfite was added at 3.2 mg S/L/min, iron at 10 mg/L and air was sparged at a flow rate 2.5 L/min. Dissolved manganese concentrations were determined using ICP-AES after samples had been filtered through 0.45 micron membrane.

35 Figures 5 (a) and (b) graph the oxidation of 0.5 mg/L arsenic(III) at pH 6.5 using in (a) sodium sulfite solution

added at 0.8 mg S/L/min in the absence and presence of 6 mg Fe/L. In Figure 5(b) sulfur dioxide gas at 0.02 L/min was used instead of sodium sulfite solution. Iron was added at 4 mg/L and air was sparged at 2.5 L/min.

5 **Modes For Carrying Out The Invention**

Referring firstly to the drawings, Figure 1 shows the rates of oxidation of manganese(II) as a function of added iron(III) concentrations. The percentage of total manganese oxidised was calculated from the initial
10 dissolved manganese(II) concentration (5 mg/L) and the dissolved manganese(II) concentrations in the solution as a function of time (determined using electron paramagnetic resonance (EPR) spectroscopy). Sodium sulfite solution was added to the synthetic reaction mixture of 1.7 litre at a
15 dose rate of 8 mg S/L/min, air was sparged at a rate of 2.5 L/min and the pH of the reaction mixture was maintained at 6.5 by the addition of sodium hydroxide solution. Experimental data with iron added but without sulfite dosing are also shown.

20 Figure 1 clearly indicates that the added iron significantly catalyses the oxidation of dissolved manganese(II). After the oxidation reaction was completed, a mixture of brown and black particles settled at the base of the reaction vessel indicating that iron-hydroxide and
25 manganese-oxide or -oxyhydroxide solids had been formed (manganese(III)- or manganese(IV)-oxide or -oxyhydroxide precipitate is black).

The curve pertaining to the experimental data with 6.2 mg/L of iron added but without sulfite dosing
30 (Figure 1) shows that the manganese(II) concentration in the solution remained unchanged throughout the experiment (the same results were obtained irrespective of whether the iron precipitates were removed by membrane filtration (0.45 μ m) before EPR spectroscopy analyses for manganese(II)).
35 This indicates negligible adsorption of un-oxidised manganese(II) on the iron(III)-hydroxide precipitate.

Figure 2 depicts the oxidation of dissolved manganese(II) using sulfite and oxygen at pH 8 (adjusted

using sodium bicarbonate). Residual manganese(II) concentrations as a function time are shown in the presence/absence of iron(III). Clearly, the presence of bicarbonate at higher pH does not affect the rate of oxidation of manganese(II). In fact, as shown in Figure 2 when compared to the results given in Figure 1, the rate of manganese oxidation increased with the addition of sodium bicarbonate.

Sodium sulfite solution was added at a dose rate of 8 mg S/L/min and air was sparged at a rate of 2.5 L/min. The initial conditions were: solution volume 1.7 L manganese(II) concentration 5 mg/L. Dissolved manganese(II) concentrations were determined using EPR spectroscopy.

Figures 3(a) and 3(b) show the results of tests as in Figures 1 and 2 but using water taken from Nepean dam, one of the several reservoirs for water supply in Sydney, Australia (the compositions are given in Table 1 below). The initial dissolved manganese(II) concentration in the dam water was increased from 0.15 mg/L to 0.55 (Figure 3(a)) and 5.15 mg/L (Figure 3(b)) by spiking in order to facilitate EPR spectroscopy measurements.

Figures 3(a) and 3(b) show that increasing the water pH to 8.5 resulted in the oxidation reaction being completed in less than 5 and 10 minutes for the initial concentrations of 0.55 and 5.15 mg/L respectively. It should be noted that the concentration of dissolved organic carbon in the water was not low (7 mg/L).

In contrast to the results shown in Figures 1 to 3 in which specific measurements of the aquated (dissolved) manganese(II) concentrations were determined using EPR spectroscopy, residual concentrations of total manganese in the Nepean dam water are shown in Figure 4. They were determined by ICP-AES method after filtration using a 0.45 μ m membrane filter. Figure 4 shows that the initial dissolved manganese(II) concentration of 0.15 mg/L in the Nepean dam water (no spiking) was reduced to 0.003 mg/L in $\frac{1}{2}$ minute. 1.7L of the dam water was treated with sodium sulfite solution added at a dose rate of 3.2 mg S/L/min.

Air was sparged at a rate of 2.5 L/min, ferric chloride was added at 6.2 mg Fe/L and the pH was adjusted using sodium hydroxide solution at pH 8.5. Thus, during the treatment of Nepean water, less than 10 mg/L of sulfate was generated from the oxidation of added sulfite into the water.

Table 1

Composition of the Nepean dam water on 6 May 1999

Analyte	Concentration in mg/L unless otherwise stated
Manganese	0.15
Iron	0.64
Aluminium	0.05
Sodium	6.01
Potassium	0.72
Calcium	1.45
Magnesium	1.64
Chloride	10.65
Sulfate	2.17
Nitrate	0.92
Dissolved organic carbon	7
Alkalinity	8
PH	6.58
Colour, Hazen unit	48
Turbidity, NTU	1.2

10

Arsenic(III) oxidation

Figure 5(a) shows the oxidation of 0.5 mg/L As(III) when sodium sulfite solution was added at 0.8 mg S/L and air was sparged at 2.5 L/min in the absence and presence of iron which was added at 6 mg Fe/L (at pH 6.5). The presence of iron accelerated the oxidation of arsenic(III). In the absence of sulfite, arsenic oxidation did not occur.

In Figure 5(b), the oxidation experiment at pH 6.5 was repeated using sulfur dioxide gas (0.02 L/min) instead of sodium sulfite solution. Experimental results

20

very similar to those shown in Figure 5(a) were obtained. Iron was added at 4 mg Fe/L and air was sparged at 2.5 L/min.

Removal of dissolved manganese(II) by oxidative

5 precipitation

A reaction mixture (1700 mL) containing 5 or 0.5 mg/L Mn(II) (typical concentrations in lakes, reservoirs and ground water for drinking water supply are less than 1 mg/L), was prepared by dissolving $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ in
10 demineralised water. Iron was added as ferric chloride to give the required iron concentration value. The solution pH was controlled at the selected value using an automatic titrator which added sodium hydroxide solution when required. Sodium sulfite was added by the continuous
15 injection of a stock solution (1.7 g/L of sulfite or 0.68 g S/L) at a precisely controlled flow rate using a titrator in order to give the required dose rate. For example, for a dose rate of 2 mg/L/min (for an initial Mn(II) concentration of 0.5 mg/L), 2 mL/min of the sodium sulfite
20 stock solution was injected into the 1.7 L of reaction mixture. This method of sulfite dosing was observed to be more efficient than a procedure whereby the sodium sulfite was added in a single dose. It also simulated the procedure where SO_2 gas was used. Air was sparged at a
25 rate of 2.5 L/min.

Alternatively, SO_2 gas was used instead of sulfite solution by mixing SO_2 gas and air in various proportions and in different flow rates.

Samples of the reaction mixture were taken at
30 specified time intervals. For manganese removal experiments, the collected samples were filtered using a 0.45 μm membrane. The residual manganese concentrations in the filtrate were analysed using ICP-MS, ICP-AES or atomic absorption spectroscopy with a graphite furnace (after
35 acidification to pH < 1.5).

Total As and As(III) concentrations were determined using atomic absorption spectroscopy with hydride generation. Concentrations of As(V) in the reaction mixture were determined using the molybdenum blue spectrophotometric method (Johnson D. and Pilson M., Analytical Chimica Acta, 58, 289-299 (1972)). Sulphite concentrations were also determined spectrophotometrically (Humphrey R.E., Ward M.H. and Hinze W., Analytical Chemistry, 42, 698-702 (1970)).

Electron paramagnetic resonance spectroscopy

For experiments where concentrations of dissolved divalent manganese (aquated manganese(II)) in the solution were specifically analysed using electron paramagnetic resonance spectroscopy (EPR), the procedure was as follows. Approximately 1 mL of the sample of reaction mixture was placed in a fused-silica tube (Wilmad Glass Co., USA). EPR spectroscopy analysis was performed for aquated manganese(II) using a Bruker ER200D spectrometer with a microwave frequency of 9.26 ± 0.02 GHz. Calibration curves were prepared from standard solutions, where the normalised peak height of the fourth peak from the low field side was plotted as the dependent variable. All EPR spectroscopy spectra were run at a controlled room temperature of 20 ± 2 °C.

Source of Oxidant

Oxygen was the oxidant for the process. It was typically supplied as air at about 0.2 atmospheres partial pressure by aerating the reaction mixture. Alternatively, oxygen was supplied by sparging a gas mixture of sulfur dioxide with air, or an oxygen/nitrogen mixture into the solution (or any other compatible gas source). Oxygen partial pressures greater than or less than 0.2 atm were also used as appropriate.

Whilst the invention has been described with reference to a number of preferred embodiments, it should be appreciated that the invention can be embodied in many other forms.

CLAIMS

1. A method for oxidising an inorganic species in an aqueous solution of pH 5 or greater, comprising the steps of:
 - 5 (i) supplying an oxidisable form of a sulfur compound, and oxygen to the solution; and
 - (ii) adding a source of iron to the solution and allowing oxidation to take place.
2. A method as claimed in claim 1 wherein the source
10 of iron is an iron(III) containing water soluble compound.
3. A method as claimed in claim 1 wherein iron(II) is supplied to the solution in a form which can be readily oxidised to iron(III), which then participates in the oxidation reaction.
- 15 4. A method as claimed in any one of the preceding claims wherein, subsequent to oxidation of the species, the iron product resulting from the added iron acts as a coagulant for the oxidised species.
5. A method as claimed in any one of the preceding
20 claims wherein air is used as the oxidising agent.
6. A method as claimed in any one of the preceding claims wherein the oxidisable form of a sulfur compound is SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_4\text{O}_6^{2-}$, $\text{SO}_2(\text{g})$, aqueous SO_2 , or HSO_3 .
7. A method as claimed in claim 6 wherein the
25 oxidisable source of sulfur is sulfur dioxide and/or sulfite.
8. A method as claimed in any one of the preceding claims that is applied in the treatment of trace quantities of inorganic species.
- 30 9. A method as claimed in any one of the preceding claims wherein the species oxidised is manganese.
10. A method as claimed in any one of the preceding claims wherein the species oxidised is arsenic.
11. A method as claimed in any one of the preceding
35 claims wherein the species oxidised is one or more of sulfide, selenium, uranium, cobalt, antimony, bismuth and other oxidisable inorganic species.
12. A method as claimed in any one of the preceding

claims wherein the oxygen is sparged into the aqueous solution as air.

13. A method as claimed in any one of the preceding claims wherein the solution is a drinking water solution,
5 an industrial waste water or an aqueous process liquor.

14. A method as claimed in any one of the preceding claims wherein the pH of the solution is neutral or basic.

15. A method for oxidising an inorganic species in an aqueous solution substantially as herein described with
10 reference to the examples and/or the accompanying drawings.

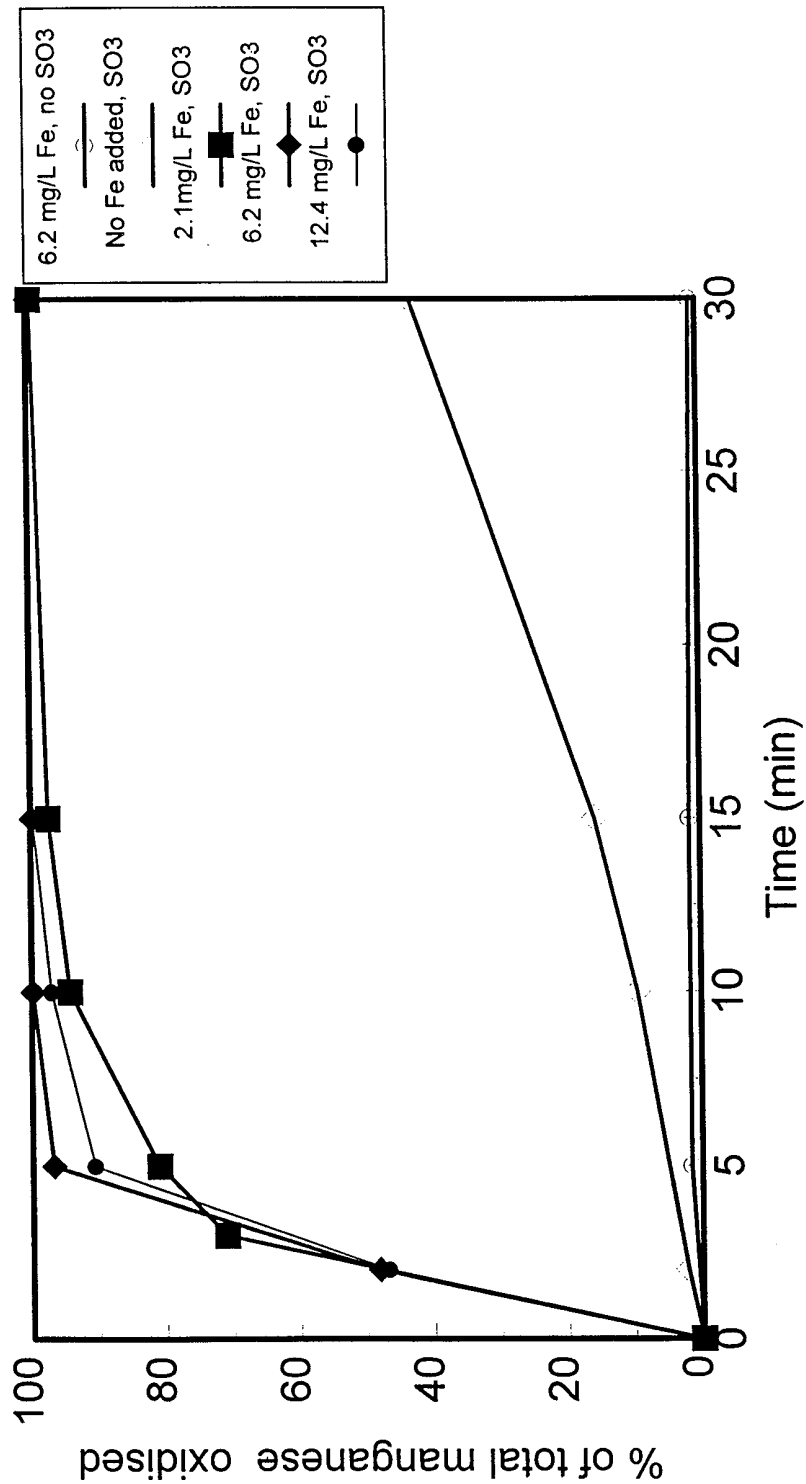


FIG. 1

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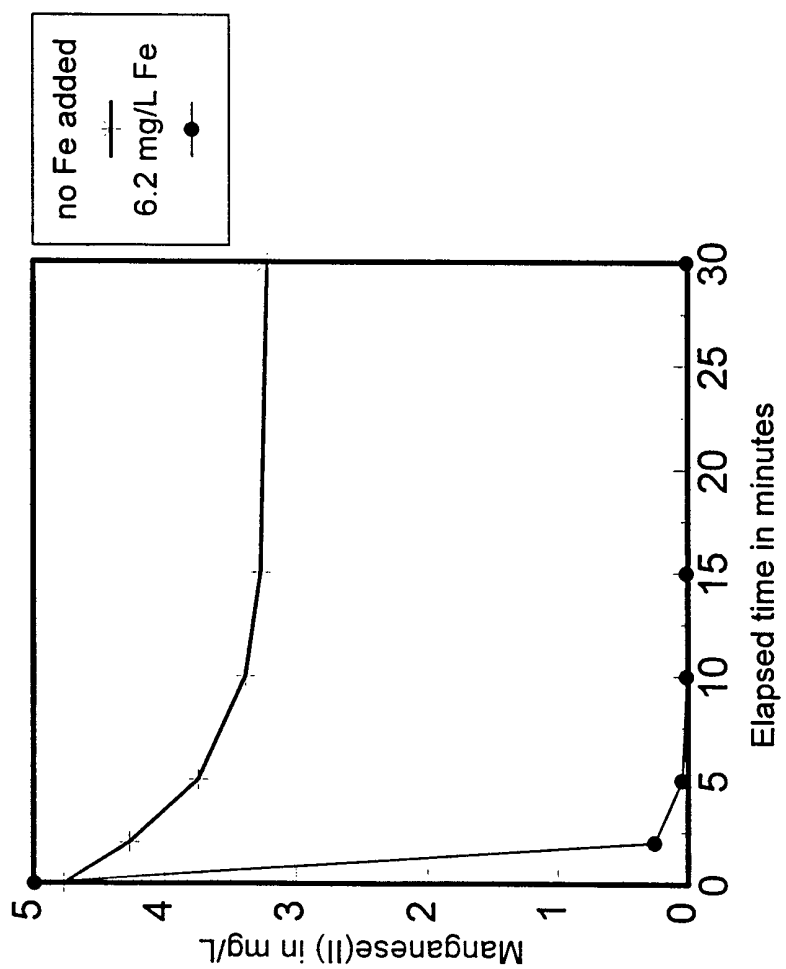


FIG. 2

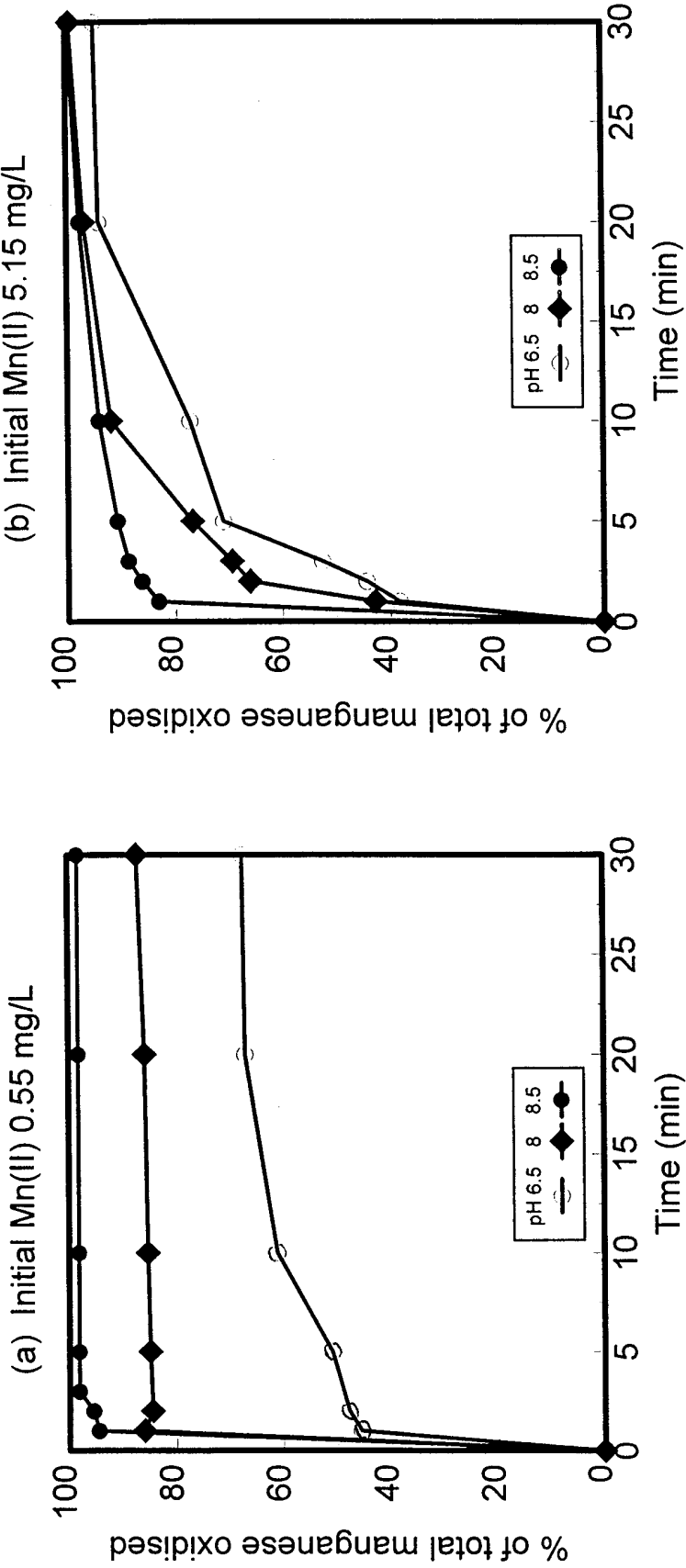


FIG. 3

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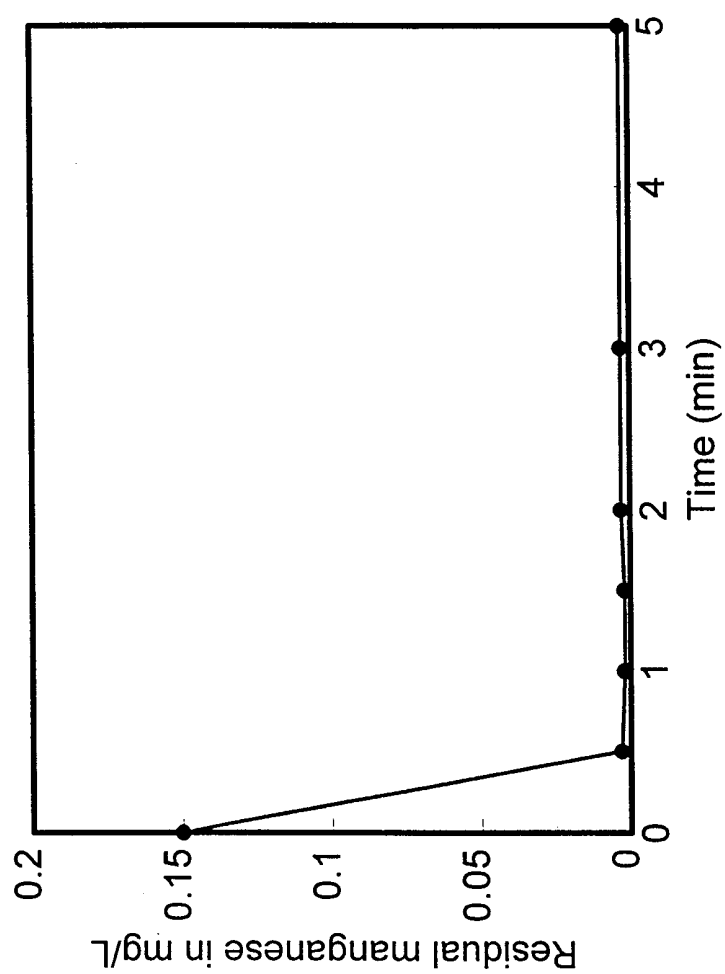


FIG. 4

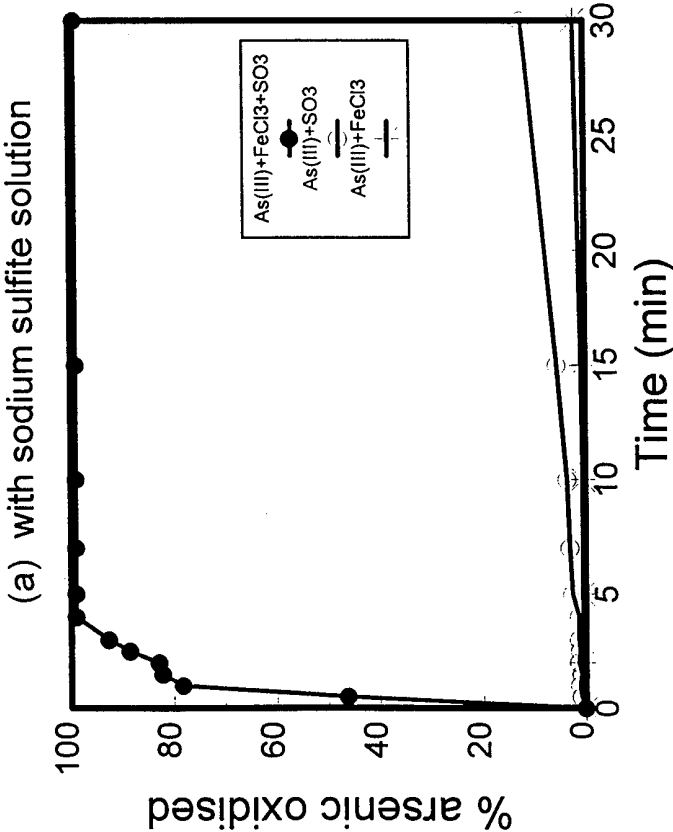
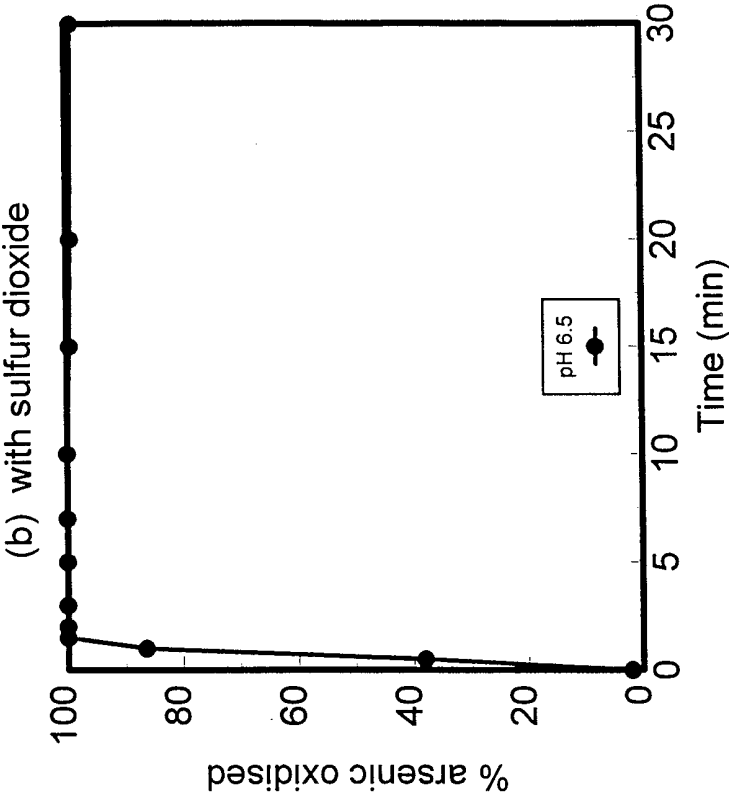


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 99/00620

A. CLASSIFICATION OF SUBJECT MATTER

Int Cl⁶: C02F 1/58, 1/62, 1/64, 1/68, 1/74

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C02F, C02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPAT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 480243 (WISER OY), 15 April 1992 Whole document	1-15
X	US 4622149 (DEVUYST et al.), 11 November 1986 Whole document	1-15

☐ Further documents are listed in the
continuation of Box C

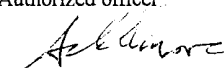
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Date of the actual completion of the international search
28 September 1999

Date of mailing of the international search report
- 8 OCT 1999

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU 99/00620

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Patent Document Cited in Search Report				Patent Family Member			
US	4622149	GB	2159141	AU	42537/85	BR	8502392
		CA	1241774	ZA	8503258		
EP	480243	FI	904979				

END OF ANNEX