

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
10 February 2005 (10.02.2005)

PCT

(10) International Publication Number
WO 2005/012582 A1

(51) International Patent Classification⁷: C22B 3/06, 47/00

(21) International Application Number:

PCT/AU2004/000854

(22) International Filing Date: 28 June 2004 (28.06.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

2003903992

30 July 2003 (30.07.2003)

AU

(71) Applicant (for all designated States except US): **HITEC ENERGY LIMITED** [AU/AU]; 1/1 Walker Avenue, West Perth, Western Australia 6005 (AU).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **WARD, Christopher Brett** [AU/AU]; 19 Palmer Street, Attadale, Western Australia 6156 (AU).

(74) Agent: **WRAY & ASSOCIATES**; Level 4, The Quadrant, 1 William Street, Perth, Western Australia 6000 (AU).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, 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, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

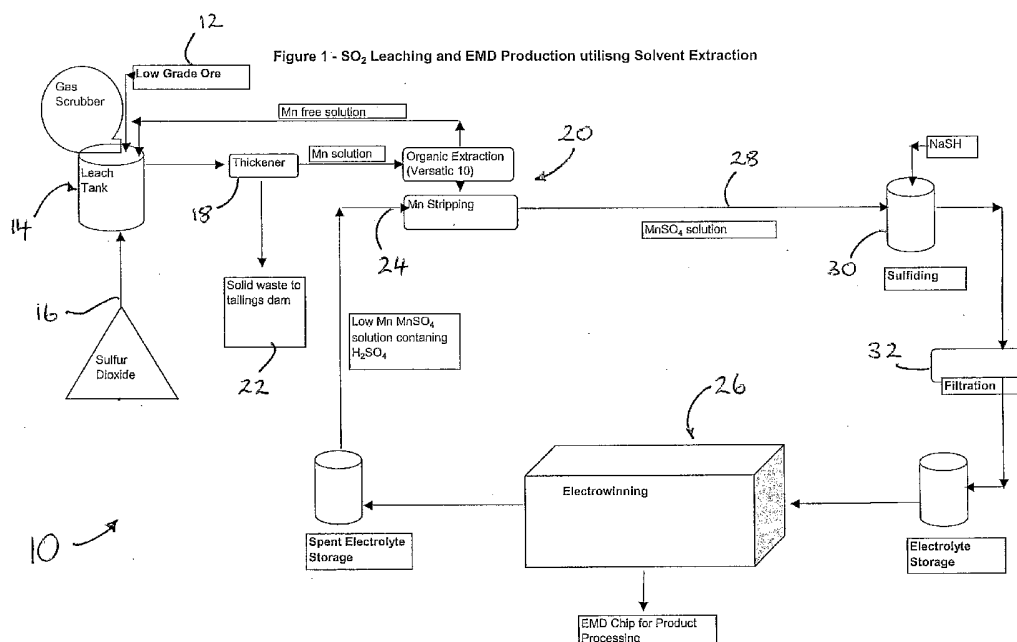
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: IMPROVED HYDROMETALLURGICAL PROCESSING OF MANGANESE CONTAINING MATERIALS



(57) Abstract: A process for the improved hydrometallurgical processing of manganese containing materials, the process characterised by the formation of a leach solution or slurry of manganese dioxide containing feedstock and acidic solution, passing a volume of sulphur dioxide gas through the leach solution whereby the levels of dithionite ion generated in the pregnant leach solution are less than about 5g/l, and subsequently passing the pregnant leach solution to a solvent extraction step.

"Improved Hydrometallurgical Processing of Manganese Containing Materials"

Field of the Invention

The present invention relates to the improved hydrometallurgical processing of manganese containing materials. More particularly, the process of the present invention is intended to allow efficient hydrometallurgical processing of low-grade manganese dioxide feedstock to produce manganese chemicals, including electrolytic manganese dioxide, utilising a solvent extraction process route.

Background Art

It is generally known that manganese may be leached from manganese dioxide containing ores using sulphur dioxide. However, the sulphur dioxide leaching of manganese dioxide containing materials is also known to produce by-product dithionate ion levels of >5g/l. These levels may be far higher depending upon the amount of manganese being leached. For example, levels of about 20g/l are not uncommon. Interestingly, it is reported in Cotton and Wilkinson, Advanced Inorganic Chemistry, 3rd Edition at page 452, that "the method for production of dithionate or dithionic acid is the reaction between sulphur dioxide or sulphite with manganese dioxide in the presence of acid".

Low grade manganese dioxide feedstock (<40% Mn) are presently uneconomic to process using conventional roast-reduction and sulphuric acid leaching to produce manganese sulphate. High grade ores (>40% Mn) are needed to justify the economics of the roast reduction process. Presently, all leaching of manganese dioxide containing materials using sulphur dioxide leads to the formation of >5g/l levels of dithionate ions in solution. With dithionate ion levels of this magnitude it is generally necessary to incorporate into any flow sheet a high capital cost stage, being "oxidation" or "aging". The long residence times required to "oxidise" the dithionate ion from the >5g/l levels down to lower than 1g/l are highly capital intensive.

- 2 -

Failure to control dithionate levels in the production of a manganese sulphate crystal product has previously led to the manganese dithionate contaminant in that product slowly reacting to release sulphur dioxide gas.

5 It would prove advantageous to provide a process whereby low-grade manganese dioxide containing materials or feedstock could provide manganese sulphate leach solutions with a level of dithionate ion less than about 5g/l, and preferably less than 1g/l.

10 The ability to recover manganese dioxide from low-grade feedstocks will avoid or at least reduce the need for further manganese ore mining and land disturbance, bringing various environmental benefits. For example, the utilisation of manganese tailings allows for conservation of existing resources.

15 Further, the use of a hydrometallurgical route for the reduction of Mn(IV) negates the need for the use of gas fired kilns or fluid bed reactors, feed stocks no longer need to be heated to about 1000°C and then cooled prior to leaching, and there is lesser need for carbon input, which in turn results in lower greenhouse gas emissions.

20 Still further, the use of the relatively easily controlled hydrometallurgical route allows monitoring of the solution potential of the leach solution or slurry thereby indicating complete dissolution of Mn(IV). The use of the sulphur dioxide leach provides complete conversion of Mn(IV) to Mn(II), thereby avoiding the production of leachable manganese species in solid residues.

25 In particular, if it is desired to produce electrolytic manganese dioxide ("EMD"), solutions containing elevated dithionate ion levels result in chemical reactions occurring that effect the quality and purity of the EMD produced in the electrowinning cells. Also, hydrogen sulphide is evolved, bringing with it certain occupational health and environmental issues.

The present applicant has previously proposed a hydrometallurgical processing route for manganese containing materials utilising a sulphur dioxide leach over 10

to 15 hours, during which a stoichiometric amount of sulphur dioxide is added to the leach solution to achieve a 95% dissolution of the manganese dioxide present, after which the reaction is halted, the dithionate ion levels are preferably maintained at less than about 5g/l, and preferably less than 1g/L, and the resulting
5 leach solution is then processed by way of a jarositing step to reduce potassium and sodium levels as desired, and a goethiting step to reduce iron levels to sub-ppm levels, to provide an electrolyte that is passed to an electrowinning stage during which electrolytic manganese dioxide is deposited. In effect, the leach conditions are controlled to control or minimise the formation of dithionate ion,
10 which of course requires careful monitoring of the leach conditions. This process is described in the Applicant's International Patent Application PCT/AU03/01295 (WO 04/033738).

US Patent 4423012 describes a process whereby the concentration of a desired metal, such as manganese or zinc, with respect to certain impurities in an
15 electrowinning feed stream, may be increased. This is said to be achieved by mixing an aqueous bleed stream from the feed stream with a solvent extraction agent (DEHPA), after which that bleed stream is subjected to solvent extraction over several counter-current stages, the resulting loaded organic then being stripped with spent electrolyte from the electrowinning circuit. That loaded strip
20 solution is then recycled to the electrowinning circuit for recovery of manganese and zinc metal. Importantly, this process is applied to only a small bleed stream from a conventional roast reduction/acid leach EMD process, is not appropriate for saline leach solutions and the extractant utilised is a phosphoric acid.

The preceding discussion of the background art is intended to facilitate an
25 understanding of the present invention only. It should be appreciated that the discussion is not an acknowledgement or admission that any of the material referred to was part of the common general knowledge in Australia as at the priority date of the application.

Throughout the specification, unless the context requires otherwise, the word
30 "comprise" or variations such as "comprises" or "comprising", will be understood to

imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

Disclosure of the Invention

In accordance with the present invention there is provided a process for the improved hydrometallurgical processing of manganese containing materials, the process characterised by the formation of a leach solution of manganese dioxide containing feedstock and acidic solution, passing a volume of sulphur dioxide gas through the leach solution whereby the levels of dithionate ion generated in the pregnant leach solution are less than about 5g/l, and subsequently passing the pregnant leach solution to a solvent extraction step.

Preferably, the levels of dithionate ion generated in the leach solution are less than about 1g/l.

Still preferably, the pH of the leach solution is maintained at less than about 5. Still further preferably, the pH of the leach solution is maintained at less than about 3.

In one form of the present invention the leach is conducted at a temperature of less than about 60°C.

Preferably, sufficient sulphur dioxide is passed through the leach solution to ensure that 95% of the manganese present is leached over a period of less than about 2 hours.

In another form of the invention the manganese dioxide containing feedstock contains less than 40% manganese.

The ratio of ferric to ferrous may be monitored throughout the leach to ensure an oxidation reduction potential (ORP) of about 550mV, or above (vs Ag/AgCl reference electrode).

The solvent extraction step is preferably followed by a stripping step, in which a loaded organic phase is contacted with a spent sulphuric acid electrolyte from an electrowinning step, providing a manganese sulphate solution that is in turn passed to the electrowinning step. The dithionate ions present in the leach
5 solution remain in the aqueous phase during solvent extraction.

Brief Description of the Drawings

The present invention will now be described, by way of example only, with reference to one embodiment thereof and the accompanying drawing, in which:-

Figure 1 is a schematic flow chart of a process for the production of an
10 electrolytic manganese dioxide product from a low grade manganese feedstock in accordance with the present invention.

Best Mode(s) for Carrying Out the Invention

In Figure 1 there is shown a process 10 for the production of electrolytic manganese dioxide product in accordance with the present invention. A
15 manganese dioxide ore feedstock 12, containing less than about 40% manganese, is ground and the resulting slurry passed to a leach 14 conducted in at least one agitated reactor, forming a 10% w/w leach solution.

Sufficient sulphur dioxide 16 (as a gas or a liquid) is passed through the leach solution at a pH of less than about 5, preferably less than about 3, at a
20 temperature of less than about 60°C, preferably less than about 50°C. The sulphur dioxide is passed through the leach solution at a rate to ensure that 95% of the manganese is leached in less than about 2 hours.

The ratio of ferric ion to ferrous ion in the leach 14 is monitored by the use of an ORP (Oxidation Reduction Potential) probe with a minimum value of 550mV
25 required (vs Ag/AgCl reference electrode). If the ORP value falls it can be increased by the addition of more manganese dioxide ore feedstock 12. The

- 6 -

ORP is required to be above this level at completion of the leach to ensure that all the iron is in the ferric state.

The leaching reaction is as below:

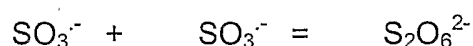


- 5 Once the stoichiometric quantity of sulphur dioxide has been added to the leach to achieve 95% extraction of the manganese dioxide, the reaction is halted by stopping the addition of further sulphur dioxide. The pH of the solution is then increased to between pH 5 and 7 by the use of lime or limestone and the solid liquid separation step performed by the use of a thickener 18 and a filter (not shown).

It is envisaged that the sulphur dioxide 16 may be provided as a waste gas from a smelting or an industrial process. Further, the sulphur dioxide may be added to the leach solution as a sulphite solution (SO_3^{2-}).

- 15 The soluble manganese content is expected to be less than about 20 g/L at this stage but the concentration will be dependent upon the throughput used from the leach 14. It should also be noted that any manganese species in an aqueous solution can also be added to this stream at this stage and the manganese will be recovered and utilised to make extra EMD. Such streams can come from neighbouring mines and processing plants, or spillages from the manganese processing facility.

- 20 While the predominant reaction occurring during the sulphur dioxide leaching of manganese dioxide in acid solutions produces MnSO_4 , an amount of dithionate ion production will also still occur. The formation of dithionate is favoured with higher pH values and is believed to occur via the following free radical combination mechanism:



- 7 -

Following the removal of solids the solution is fed to a solvent extraction step 20 in which an aqueous solution (raffinate) is contacted with a carboxylic acid extractant, for example Versatic 10™, at a concentration of about 0.5M in an aliphatic diluent, for example Shellsol D70™, in up to 5 extraction stages with an aqueous to organic ratio of approximately 2 to 1. The pH is controlled by way of a suitable base, such as Na OH, NH₄ OH or Na₂ CO₃, to between 4.5 and 7, preferably 5.5 and 6.5.

At this stage all the dithionate ions, any chloride ions and the majority of the magnesium, calcium, potassium and iron remain in the aqueous phase and are not loaded onto the organic extractant. The aqueous phase can then be either recycled back to the leach 14 for further manganese leaching or is rejected to a tailings dam 22 together with solids removed in the thickener 18. A synergistic extractant, such as the oxime LIX63, may also be added to the Versatic 10™ extractant to assist in the separation of any calcium.

The extractant and diluent described above have been found to be effective in the process of the present invention and are relatively inexpensive.

Following a scrubbing step the loaded organic phase is stripped of the manganese by contacting it with sulfuric acid containing spent electrolyte 24 returning from a electrowinning step 26. The stripping solution 24 is expected to be between about 40 and 70 g/L manganese and about 25 to 50 g/l sulphuric acid along with some other minor impurities. The hydrogen ions generated in the electrowinning step 26 are replaced by the manganese ions from the organic phase and the pH rises towards a neutral pH. The resulting solution is called the pregnant leach solution 28 and is passed through a range of filtration steps (not shown) to remove any residual organic components. The solution 28 is then fed to a sulfiding step 30 for further purification by the addition of a sulfiding reagent to remove heavy metals, before a further filtration step 32. The solution 28 is then ready for feeding to electrowinning cells of the electrowinning step 26, during which the manganese is plated for high quality electrolytic manganese dioxide (EMD), suitable for use by alkaline battery manufacturers.

The electrowinning step 26 proceeds utilising submerged titanium anodes, tubular copper cathodes and a totally wax free environment. Fully laden anodes are harvested on a two-weekly cycle with resulting EMD chip being passed to produce processing and packaging operations.

- 5 It is envisaged that a small side or bleed stream may also be included, of the order of 5% of the flow from the electrowinning step, returning to the leach 14 to recover manganese and reject unwanted contaminants, such as sodium, and to further lower the recirculating calcium load so that the chance of gypsum precipitation is further reduced. The loss of pregnant leach solution volume may
10 be made up by the addition of demineralised water to the electrolyte circuit.

- It is further envisaged that the process of the present invention, specifically as it resides in the leaching of manganese containing feedstocks to produce leach solutions with dithionate ion levels of less than 5g/l, and preferably less than 1g/l, may be applied to the processing of all types of manganese dioxide containing
15 ores (including both high and low grade), mine tailings, fines, fumes and tailings of manganese ferro-alloy production facilities, ocean floor manganese nodules, ferromanganese nodules, wastes from zinc refinery cells and manganese dioxide contained in used or partially used alkaline or carbon zinc batteries. The leach solutions generated by reprocessing such materials in accordance with the
20 present invention can then be purified and used in the production of EMD, EMM and other manganese chemical products.

- The improved hydrometallurgical processing of manganese containing materials described herein has a significantly reduced requirement for capital expenditure when compared with equivalent processes of the prior art, including the
25 Applicant's prior art process described in International Patent Application PCT/AU03/01295 (WO 04/033738) and referred to hereinabove. For example, the relatively low temperature leach requires less steam and is able to utilise standard fibreglass (FRP) as the leach vessels. Still further, the less aggressive pH utilised in the process of the present invention has less impact on the
30 equipment and requires significantly less acid than prior art processes.

As a result of the chloride and magnesium being rejected in the leach step 14, the leach of the present invention is able to be performed in raw water, for example from the Kalgoorlie region of Western Australia, which consequently lowers any requirement for demineralised water in the process.

- 5 When compared with the process described in International Patent Application PCT/AU03/01295 (WO 04/033738) the process of the present invention does not require Jarositing and Goethiting steps. The specific solvent extraction process utilised in the present invention, including use of Versatic acid, rejects potassium. Further, no iron leach, nor any iron source is required. This provides further
10 relative savings in relation to both capital and operating costs.

The conduct of the leach at the relatively mild pH 3, and the use of electrowinning cell-generated acid for regeneration of the extractant, there is a relative reduction in the amount of limestone and lime required in the process of the present invention when compared with prior art processes.

- 15 As a result of relatively fewer and smaller tanks, as the circuit is less complex with less stringent temperature and pH conditions, an associated reduction in maintenance costs and operating labour (1 to 2 people per shift) is expected.

- Due to the ability to extract manganese from saline water and leave the water behind, all liquid spillages may now be directed to the leach step and the
20 manganese recovered extra space. Previously there was concern for increased chloride levels and expansion of the total solution inventory that could end up exceeding the available tankage volume.

- The leach tank utilised in the leach step will be a vessel suitable to accept a large range of manganese inputs (solid and liquid) irrespective of the anion attached to
25 the manganese, if they were proven to lower cost inputs.

In the prior art processes a control strategy and analytical capability was required to ensure that the dithionate levels to the cell house were maintained below 500

ppm. The process of the present invention avoids dithionate ions circulating throughout the process as it is rejected at the solvent extraction stage.

It is envisaged that a bleed stream may be introduced back to the leach tank, whereby it is conceivable that the frequency of cathode cleaning to remove
5 gypsum could be reduced dramatically, thereby providing a system to lower magnesium and sodium levels to even lower levels than previously considered. While magnesium is not a significant concern, the process of the present invention had no route to reduce Mg levels other than through solution losses and replacement with clean demineralised water. Lower gypsum deposition in pipe
10 work and tankage will have a significant maintenance cost benefit, once the plant has reached equilibrium conditions.

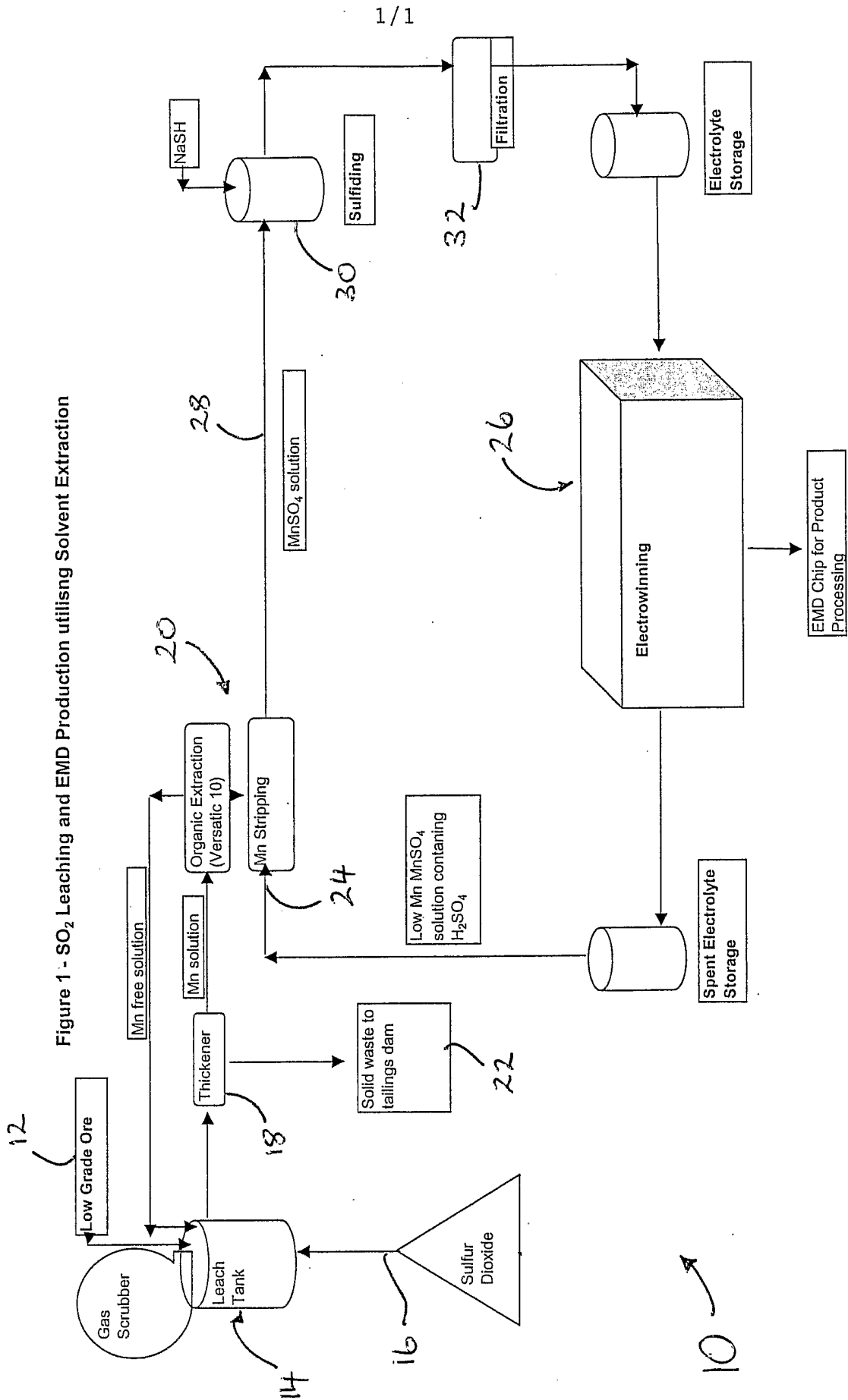
Modifications and variations such as would be apparent to the skilled addressee are considered to fall within the scope of the present invention.

Claims

1. A process for the hydrometallurgical processing of manganese containing materials, the process characterised by the formation of a leach solution of manganese dioxide containing feedstock and acidic solution, passing a
5 volume of sulphur dioxide gas through the leach solution whereby the levels of dithionate ion generated in the pregnant leach solution are less than about 5g/l, and subsequently passing the pregnant leach solution to a solvent extraction step.
2. A process according to claim 1, wherein the levels of dithionate ion
10 generated in the leach solution are less than about 1g/l.
3. A process according to claim 2, wherein the pH of the leach solution is maintained at less than about 5.
4. A process according to claim 1 or 2, wherein the pH of the leach solution is maintained at less than about 3.
- 15 5. A process according to any one of the preceding claims, wherein the leach is conducted at a temperature of less than about 60°C.
6. A process according to any one of the preceding claims, wherein sufficient sulphur dioxide is passed through the leach solution to ensure that 95% of the manganese present is leached over a period of less than about 2
20 hours.
7. A process according to any one of the preceding claims, wherein the manganese dioxide containing feedstock contains less than 40% manganese.
8. A process according to any one of the preceding claims, wherein the ratio
25 of ferric ion to ferrous ion is monitored throughout the leach to ensure an

oxidation reduction potential (ORP) of about 550mV, or above (vs Ag/AgCl reference electrode).

- 5 9. A process according to any one of the preceding claims, wherein the solvent extraction step is followed by a stripping step, in which a loaded organic phase is contacted with a spent sulphuric acid electrolyte from an electrowinning step, providing a manganese sulphate solution that is passed in turn to the electrowinning step.
- 10 10. A process according to any one of the preceding claims, wherein the dithionate ions present in the leach solution remain in the aqueous phase during solvent extraction.
11. A process for hydrometallurgical processing of manganese containing materials, the process substantially as hereinbefore described with reference to Figure 1.



INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2004/000854

A. CLASSIFICATION OF SUBJECT MATTER												
Int. Cl. ⁷ : C22B 3/06, 3/26, 47/00												
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) C22B 3/06, 3/08, 3/26, 47/00 with key words below												
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched NIL												
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DWPI: IPC as above with key words manganese, dithio+												
C. DOCUMENTS CONSIDERED TO BE RELEVANT												
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.										
P, Y	WO 2004/033738 A1 (Hitec Energy Limited), 22 April 2004 Whole Document	1- 11										
Y	WO 1998/014623 A1 (International Curator Resources Limited), 9 April 1998 Page 1, lines 6- 15; page 5, lines 25- 32; page 6, lines 8- 33; page 15, lines 29- 34; Claims 21, 22	1- 11										
A	Derwent Abstract Accession No. 27328b/14, Class M25, SU 606888 (Baikov Metallurgy Inst.), 17 April 1978 Abstract	1- 11										
A	Derwent Abstract Accession No. 90-081457/11, Class M25, SU A 1479540 (Mekhanobrchermet), 15 May 1989 Abstract	1- 11										
☒ Further documents are listed in the continuation of Box C ☒ See patent family annex												
* Special categories of cited documents: <table border="0"> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>"E" earlier application or patent but published on or after the international filing date</td> <td>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td>"&" document member of the same patent family</td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family	"P" document published prior to the international filing date but later than the priority date claimed	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention											
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone											
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art											
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family											
"P" document published prior to the international filing date but later than the priority date claimed												
Date of the actual completion of the international search 27 July 2004		Date of mailing of the international search report - 4 AUG 2004										
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. (02) 6285 3929		Authorized officer  MR KIM WELLENS Telephone No : (02) 6283 2162										

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2004/000854

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Derwent Abstract Accession No. 84-151141/24, Class M25, SU A 1044651 (Mekhanobrchermet), 30 September 1983 Abstract WO 2004/033738 may be combined with WO 1998/014623 to disclose all of the features of the claims.	1- 11

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU2004/000854

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member
WO	2004033738	NIL
WO	9814623	NIL
SU	606888	NIL
SU	1479540	NIL
SU	1044651	NIL
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.		
END OF ANNEX		