(12) PATENT ABRIDGMENT **(11)** Document No. **AU-B-37727/89**
(19) AUSTRALIAN PATENT OFFICE **(10)** Acceptance No. **620888**

(54) Title
RECOVERY OF HIGH PURITY SELENIUM FROM ORES, SCRUBBER SLUDGES, ANODE SLIME DEPOSITS AND SCRAP

International Patent Classification(s)
$(51)^4$ **C22B 061/00** **C01B 019/02**
$(51)^5$ **C22B 003/12** **C22B 003/14**

(21) Application No. : **37727/89** (22) Application Date **16.06.89**

(87) PCT Publication Number : **WO89/12700**

(30) Priority Data

(31) Number **PI8852** (32) Date **17.06.88** (33) Country **AU AUSTRALIA**

(43) Publication Date : **12.01.90**

(44) Publication Date of Accepted Application **27.02.92**

(71) Applicant(s)
FMC TECHNOLOGIES LIMITED

(72) Inventor(s)
EDWARD DAVIS; LAKSHMAN JAYAWEERA

(74) Attorney or Agent
DAVIES COLLISON CAVE , GPO Box 3876, SYDNEY NSW 2001

(56) Prior Art Documents
SU 1348702
JP 57/179004
US 3848069

(57) Claim

1. A process of treating selenium bearing materials, containing any of the elements taken from the group of mercury, lead, artimony, and copper, to recover the selenium comprising the steps of:

a) reacting the selenium bearing materials with a reaction solution of alkaline metals/ammonium sulphide or sulphite or combination thereof with thiourea, as a catalyst, above atmospheric pressure and at a temperature at or above 100°C;

b) continuing the reaction at a pH from 9-10 to reduce dissolution of other impurities to a minimum;

c) separating the undissolved residuals from the leach solution; and

d) recovering the selenium from the leach solution by reducing the temperature to ambient temperature.

5. A process according to any one of claims 1 to 4 wherein after the recovery of the selenium from the leach solution the pH is adjusted lower and the leach solution is subjected to a solvent extraction stage wherein impurities such as mercury, artimony, arsenic and lead are substantially

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extracted in the organic phase, leaving the selenium in the aqueous phase.

6. A process according to claim 5 wherein the organic solvent is diethyl 2 phosphoric acid and diluted in kerosine.

7. A process according to claim 5 wherein the organic solvent is diethyl 2 phosphoric acid diluted in shellsol.

OPI DATE 12/01/90 APPLN. ID 37727 / 89

AOJP DATE 15/02/90 PCT NUMBER PCT/AU89/00264

PCT

620888

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 **:** **C22B 61/00, C01B 19/02** **// C22B 3/00, 5/00, 7/00** **C22B 7/02, 9/10, B01D 11/04** **B01J 31/02**	**A1**	**(11) International Publication Number:** **WO 89/12700** **(43) International Publication Date:** 28 December 1989 (28.12.89)

(21) International Application Number: PCT/AU89/00264

(22) International Filing Date: 16 June 1989 (16.06.89)

(30) Priority data:
PI 8852 17 June 1988 (17.06.88) AU

(71) Applicant *(for all designated States except US)*: FMC TECHNOLOGIES LIMITED [AU/AU]; 31-33 Smith Street, Marrickville, NSW 2204 (AU).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : DAVIS, Edward [AU/AU]; 3 Mannerim Place, Castle Cove, NSW 2069 (AU). JAYAWEERA, Lakshman [AU/AU]; 15 Grafton Street, East Lakes, NSW 2018 (AU).

(74) Agent: TAYLOR, Paul, Robert; Arthur S. Cave & Company, Level 10, 10 Barrack Street, Sydney, NSW 2000 (AU).

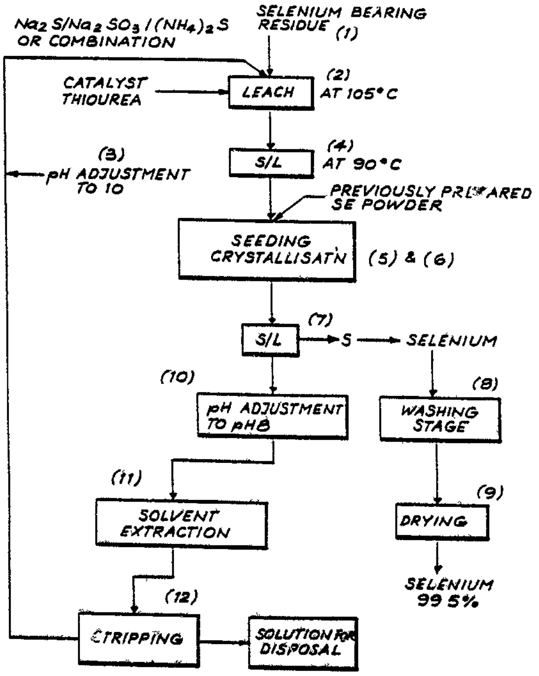
(81) Designated States: AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CM (OAPI patent), DE, DE (European patent), DK, FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NL (European patent), NO, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US.

Published
With international search report.

(54) Title: RECOVERY OF HIGH PURITY SELENIUM FROM ORES, SCRUBBER SLUDGES, ANODE SLIME DEPOSITS AND SCRAP

(57) Abstract

Selenium is derived naturally from various sulphide ores in association with its sulphur analogue. In addition, it is present in higher concentrations in sludges extracted from scrubbers in flues, anode slime deposits and scrap. The selenium bearing material is crushed to a suitable size and then leached (2) in a solution of alkali metal (e.g. Na)/ammonium sulphide or sulphite or combinations of these on the basis of 2-6 moles of sulphide/sulphite per mole of Se, at elevated temperatures > = 100°C and elevated pressures in an autoclave, preferably in the presence of an activator/catalyst such as thiourea. The preferred temperature is 100-150°C and the pressure 1-10 atmospheres. Leaching is continued at a controlled pH (9-10), to keep dissolution of impurities to a minimum. Undissolved residuals are then separated (4) and the solution is cooled to ambient temperature for seeding with previously prepared Se (5, 6). Se powder recovered at this stage is separated from the liquor (7) and then subjected to washing in boiling water (8) and drying (9), giving a finished product which is 99.5 % pure. The liquor at (7) still contains some Se, and this is adjusted to pH 8 (10) and subjected to a liquid-liquid extraction, utilising, for example, 5 % diethyl 2 phosphoric acid in kerosine as the organic phase. As, Sb, Hg, Pb are extracted into the organic phase and stripped therefrom with HCl (12). Se remains in the aqueous phase, which is readjusted to pH 10 (3) and recycled through the process, commencing at the leaching stage.



RECOVERY OF HIGH PURITY SELENIUM FROM ORES, SCRUBBER SLUDGES, ANODE SLIME DEPOSITS AND SCRAP

This invention relates to an improved process for extraction of high purity selenium from various smelter sludges and selenium ore using a hydrometallurgical process.

Selenium bearing residues such as smelter sludges and slime frequently contain many other undesirable impurities such as arsenic, antimony, bismuth, lead, mercury, cadmium and copper.

The conventional processes for extraction of selenium from various feed material varies according to the nature of the feed. In the present day industry, the main raw materials for selenium recovery are the anode slimes of electrolytic copper and nickel refineries and sludges collected from the dust generating from the lead zinc smelters.

In the conventional processes, the feed is roasted and the selenium is volatalized and scrubbed into either water or solutions of sodium hydroxide or soda ash. Once the selenium is dissolved in the water it is reduced to selenium by passing sulpher dioxide.

Roasting of the sludge is carried out under various conditions and it would vary according to the nature of the feed including the impurities. Roasting is carried out either under neutral, acidic or alkaline conditions. The major disadvantages of such a prometallurgical process are the control of pollution, longer residence time and contamination of the waste gases with other impurities such as mercury, arsenic, antimony and lead.

Over the years a variety of hydrometallurgical systems have been studied for dissolving selenium. These include nitric acid, alkaline pressure leaching and wet chlorination.

The major problems in the above processes have been the selective dissolution of the selenium and subsequent control of impurities. In the case of alkaline pressure leaching, the capital cost and the economics of this process are prohibitive.

Leaching with sodium sulphide has also been studied. However, the process has been studies with sodium sulphide alone and, as a result the kinetics of dissolution was not high.

The present invention seeks to ameliorate these disadvantages by providing a process of treating selenium bearing materials containing mercury, lead, antimony, and copper, to recover the selenium comprising the steps of:

reacting the selenium bearing materials with a solution of alkaline metals/ammonium sulphide or sulphite or combination thereof with thiourea a catalyst above atmospheric pressure and at a temperature at or above 100°C;

continuing the reaction at a pH from 9 - 10 to reduce dissolution of other impurities to a minimum;

separating the undissolved residuals from the lead solution; and

recovering the selenium from the leach solution by reducing the temperature to ambient temperature.

Preferably the reaction temperature is 100-150°C, with the reaction pressure between 1 atmospheres to 10 atmospheres.

A flow diagram of one embodiment of the present invention is shown in figure 1.

In the leaching or solubilization step in the hydrometallurgy of selenium sludges according to one embodiment of the present invention, the metal is transferred from the solid phase to a liquid phase by a complex reaction with sodium sulphide or sulphite in the presence of a catalyst. The typical complexing agent used in the process is sodium sulphide, ammonium sulphide or sodium sulphite, and the activator or the catalyst is Thiourea. Other conditions which usually favour the leaching kinetics are elevated temperature, preferably over 100°C under pressure. The process of this invention can be used to leach selenium from either metal sulphide containing selenide or selenium in elemental form present in anode slimes, smelter sludge or scrap.

The reaction will take place without oxidation, and sulphide or sulphite of sodium or ammonium salts complexes with selenium according to the following equation:

$$Na_2S + Se \qquad Na_2SeS$$

The equilibrium constant of this reaction is significantly influenced by temperature with $K = 4.35$ at 20°C and $K = 0.80$ at 97.5°C. Furthermore it is also influenced by a catalyst. The recovery of selenium is carried out by decreasing the temperature aided with seeding. Previously prepared fine powder of selenium improves the kinetics of precipitation by reducing the induction period and also controls the desired particle size of the product. The selenium so produced is washed in hot water to achieve the purity over 99%. In order to achieve the purity of 99.9% the product is redissolved in the same leaching system and reprecipitated as selenium.

The steps of recovery of selenium as shown in figure 1 are as follows:

1. The process of crushing to a suitable size selenium bearing materials containing mercury, lead, antimony, arsenic and copper for the separate recovery of selenium.
2. Leaching the said residues with a solution of sodium sulphide or ammonium sulphide or sodium sulphite or combination which contains from about 2 moles to about 6 moles of the sulphide or sulphite per mole of selenium at an elevated temperature of at or above 100°C for example 105°C in the presence of thiourea as a catalyst.
3. Continuing the leaching step to obtain extraction of selenium, controlling the pH level around 9-10 to sustain the dissolution of other impurities to a minimum.
4. Separating the undissolved residue from the leach solution.
5. Recovering the selenium from the leach solution by reducing the temperature to ambient temperature.
6. By controlling the desired particle size and reducing the induction period by adding previously prepared selenium.

7. Separating the precipitated selenium from the solution; if required steps 1 to 5 can be reputed to further purify the selenium.
8. Washing the precipitated selenium in a boiling fresh water to wash all the contaminated soluble materials.
9. Drying the selenium (99.5% purity in the finished product of selenium). Further to reduce any pollution:
10. Adjusting the pH of the plant end solution to pH 8.
11. Subjecting the end solution to a solvent extraction stage with D2 EHPA to extract any build up impurities such as mercury, antimony, arsenic and lead.
12. Stripping the loaded organic with hydrochloric acid to dispose of the harmful residuals.

The process according to steps 10-12 allow the plant end solution to be recycled back to the leach tank after making up for some of the decomposed reagents, and after a purification stage.

The purification stage comprises of an adjustment of slightly acidic conditions close to 8 and then subjecting the solution to a solvent extraction stage with diethyl 2 phosphoric acid (D2 EHPA) diluted to 5% in kerosine. At this pH most of the build up impurities such as arsenic, antimony, mercury and lead is extracted into the organic phase leaving the selenium in the aqueous phase. Using this technique the process has been developed almost into a closed system of the reagent whereby practically almost all the reagent is recycled.

Examples of tests carried out using the present invention are as follows:

EXAMPLE 1

This example illustrates the results obtained in leaching a selenium bearing residue under varying conditions of temperature, sulphide, sulphite and Thiourea concentrations.

Selenium bearing residue contained by weight approximately 50% selenium, 10% lead, 5% arsenic, 3%

mercury, 2% antimony, 20% moisture and 2% sulphuric acid.

The residue was charged into an autoclave and leached in various concentrations of sodium sulphide, ammonium sulphide and sodium sulphite. the effect of Thiourea as a catalyst was also studied. The results obtained from the leaching step are set out in the table 1. These results demonstrate that the carefully controlled pH level has minimised the dissolution of impurities and furthermore, the temperature and the presence of thiourea increased the kinetics of extraction.

TABLE 1

SERIES	LEACH CONDITIONS							EXTRACTION AFTER 30 MINS.				
	Feed g/l	Temp °C	Na_2S g/l	$(NH_4)_2S$ g/l	Na_2SO_3 g/l	Thiourea g/l	pH	Se g/l	Pb mg/l	As mg/l	Sb mg/l	Hg mg/l
1	65	105	80	-	-	2	9	30.5	5	10	12	1
2	65	105	-	90	-	2	9	31.5	10	30	5	0.5
3	65	105	-	-	90	2	9	29.5	18	15	4	1
4	65	100	80	-	-	-	9	18	5	200	400	10
5	65	100	-	90	-	-	9	20	20	300	200	20
6	65	100	-	-	90	-	9	18	15	300	300	20
7	65	105	40	-	40	2	10	30	10	8	5	1

EXAMPLE 2

The example illustrates the operation of the precipitation step. The leach solution contained 30g/l of selenium and 120g/l of sodium sulphite solution. The precipitation was carried out by lowering the temperature of the solution from 100°C TO 30°C BY COOLING. At the same time, previously prepared fine selenium powder less than 20m particle size was added to the leach at a rate of 5g/l.

This example illustrates that the lowering of the temperature reduced the solubility of selenium in the sodium sulphite solution and furthermore, the addition of previously prepared fine powder of selenium has reduced the induction period of precipitation.

Furthermore, the analysis of the product selenium after washing and drying demonstrates the purity and the particle size.

TABLE 2

SERIES	SEED ADDITION g/l	TEMP °C	PREG. SOL. Se g/l	AFTER PRECIPITATION Se g/l Time h			
				¼	½	3/4	1 hr
1	-	40	30	28	29	15	10
2	5	30	29.5	10	6	6	7
3	5	40	30	15	12	10	8

TABLE 2A

QUALITY OF SELENIUM

SERIES	Se%	Pb	Sb	Hg	Fc	As
1.	99.6	0.01	0.01	0.001	0.01	0.001
2.	99.8	0.001	0.01	0.001	0.01	0.05
3.	99.7	0.00	0.02	0.001	0.01	0.01

PARTICLE DISTRIBUTION

SERIES	<100 μm %	<75 μ %	<35 μ %	<10 μ %
1	99	90	10	2
2	99	98	15	1
3	99.5	98	10	0.5

EXAMPLE 3

The following example illustrates the results of the purification step developed for the plant end liquor enabling it to be recycled back to the leaching system.

The plant end liquor was mixed with a solution of Diethyl 2 phosphoric acid (D2EHPA) diluted to 5% shellsol. Aqueous and organic ratio was 1:1 allowing a mixing time and the phase settlement time of 3 and 10 minutes respectively. Table 3 shows the selective separation of most of the impurities while selenium being un extracted.

TABLE 3

SOLVENT	O/A	LOADED AQUEOUS					STRIPPED AQUEOUS				
		Se	Pb	As	Sb	Hg	Se	Pb	As	Sb	Hg
		g/l		PPM			g/l		PPM		
5% DZEHPA	1:1	10	100	80	20	20	9.9	2	3	14	1
6% DZEHPA	1:1	9.9	60	40	40	38	9.8	1	4	2	0.5

As can be seen the present invention provides an efficient process for the recovery of selenium with a large reduction in pollution and a large recycling of reactants. It should be obvious to people skilled in the art that variations and modifications can be made to the above description without departing from the scope or spirit of the present invention.

The claims defining the invention are as follows:

1. A process of treating selenium bearing materials, containing any of the elements taken from the group of mercury, lead, artimony, and copper, to recover the selenium comprising the steps of:

a) reacting the selenium bearing materials with a reaction solution of alkaline metals/ammonium sulphide or sulphite or combination thereof with thiourea, as a catalyst, above atmospheric pressure and at a temperature at or above 100°C;

b) continuing the reaction at a pH from 9-10 to reduce dissolution of other impurities to a minimum;

c) separating the undissolved residuals from the leach solution; and

d) recovering the selenium from the leach solution by reducing the temperature to ambient temperature.

2. A process according to claim 1 wherein the reaction solution contains from 2 to 6 moles of sulphide or sulphite per mole of selenium.

3. A process according to claims 1 or 2 wherein after the undissolved residuals are removed from the leach solution the solution is seeded with fine selenium powder.

4. A process according to claim 3 wherein the fine selenium powder is less than 20 particle size, is added to the leaching solution at a rate of 5g/l of leach solution.

5. A process according to any one of claims 1 to 4 wherein after the recovery of the selenium from the leach solution the pH is adjusted lower and the leach solution is subjected to a solvent extraction stage wherein impurities such as mercury, artimony, arsenic and lead are substantially extracted in the organic phase, leaving the selenium in the aqueous phase.

6. A process according to claim 5 wherein the organic solvent is diethyl 2 phosphoric acid and diluted in kerosine.

7. A process according to claim 5 wherein the organic solvent is diethyl 2 phosphoric acid diluted in shellsol.

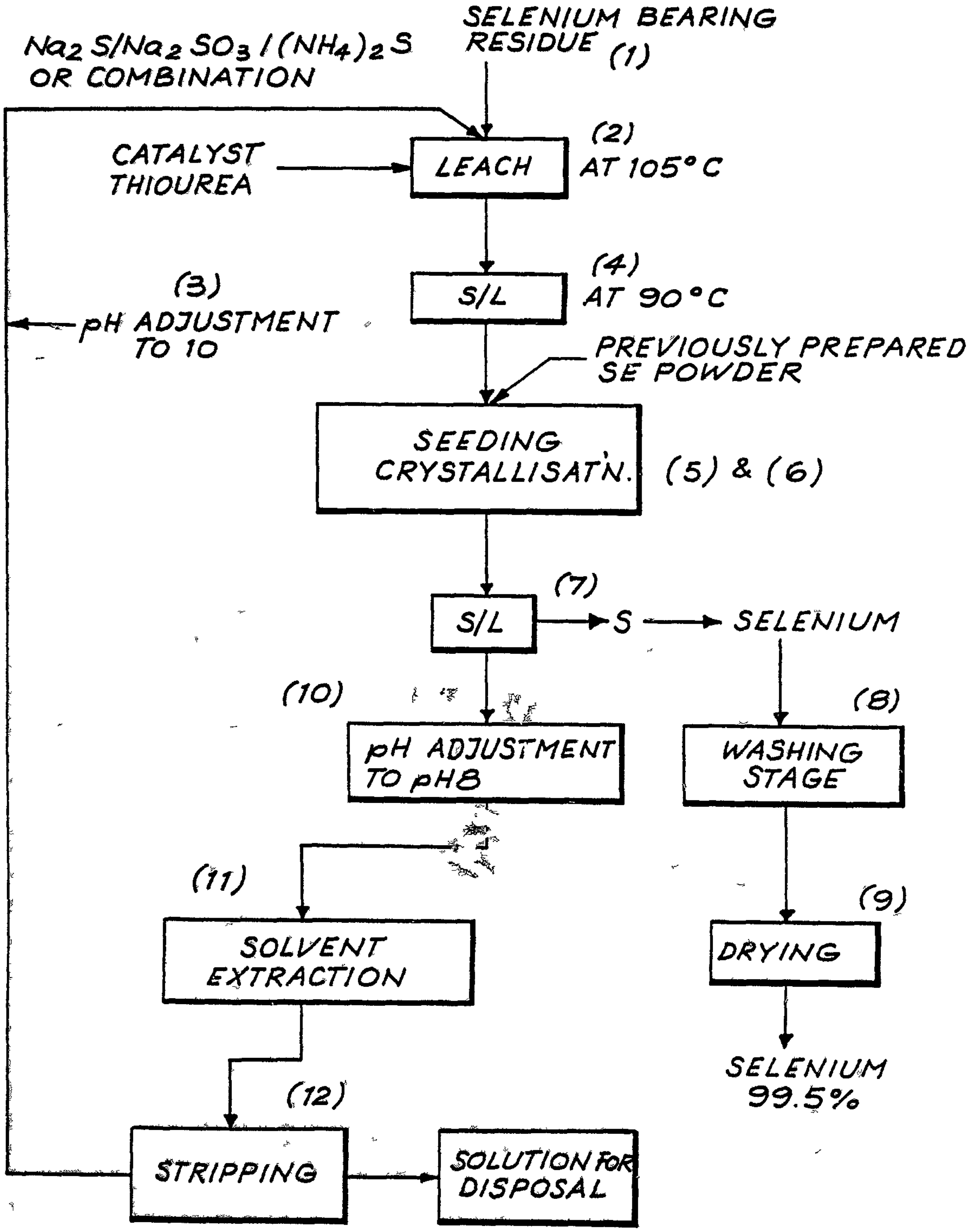
8. A process according to claim 4 or any one of claims 5 to 7 when appended to claim 4 wherein the recovered selenium undergoes the steps a) to d) of claim 1 to purify the selenium.

9. A process according to any one of the preceeding claims wherein the reaction of step a) is carried out at a pressure up to 10 atmospheres.

10. A process according to any one of the preceeding claims wherein the reaction of step a) is carried out at a temperature up to 150°C.

DATED this 10th day of December, 1991.

FMC TECHNOLOGIES LIMITED
By Its Patent Attorneys
DAVIES COLLISON CAVE



SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No PCT/AU89/00264

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl.^{4}:- C22B 61/00, C01B 19/02 // C22B 3/00, 5/00,7/00,7/02,9/10, B01D 11/04,B01J 31/02.

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	C22B 3/00, C22B 61/00, C01B 19/02.

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [*]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	AU B1 484610 (76938/74), (AMAX INC.), 27 June 1977 (27.06.77), (see Claim 1 and Examples 1, 2).	1,4,11,12.
A	AU B2 536775 (75614/81), (INCO LIMITED), 24 May 1984 (24.05.84), (see Claims 1-19 & 26, page 8 lines 27-35 and page 9 lines 1-7).	1, 3, 4, 10-12.
A	EP A1 102754 (XEROX CORPORATION), 14 March 1984 (14.03.84), (see the Examples).	1, 4.
A	EP A1 103383 (XEROX CORPORATION), 21 March 1984 (21.03.84), (see the Claims, Examples and Drawings).	1, 2, 4, 11,12.
A	EP A2 157514 (XEROX CORPORATION), 9 October 1985 (09.10.85), (see the Claims, Examples and Drawing).	1,4,11,12.

[*] Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"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.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 27 September 1989 (27.09.89)	Date of Mailing of this International Search Report 30 October 1989
International Searching Authority Australian Patent Office.	Signature of Authorized Officer (Swapan Ghosh)

International Application No. PCT/AU89/00264

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
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X	PATENT ABSTRACTS OF JAPAN, Volume 7, Number 22, issued 28 January 1983, (THE PATENT OFFICE, JAPANESE GOVERNMENT). Asahi Glass K. K., ' JP A2 57/179004 ', 4 November 1982 (04.11.82), page 56 C 148, (see the whole abstract).	1, 3, 4, 5, 10-12.
X	RO B 79099 (INSTITUTUL DE CERCETARI SI PROIECTARI PENTRU MINEREURI SI METALURGIE NEFEROASA), 30 June 1982 (30.06.82) (see page 2 lines 5-31 and page 3 lines 1-8).	1, 4, 10-12.
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X	SOVIET INVENTIONS ILLUSTRATED, Week 8341, issued 23 November 1983, (DERWENT PUBLICATIONS LTD., London, ENGLAND), Leningrad Plekhanov Mine, ' SU 979517 A1 ' 7 December 1982 (07.12.82), METALLURGY, page 4, (see the whole abstract).	1,3,4,10-12.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
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X (A)	US A 3848069, (C.D.CAREY,R.N.PLATZKE), 12 November 1974 (12.11.74), {see Claims 1-5(6), page 2 lines 33-72, page 3 lines 1-40 and Example III (and the Drawing)}.	1,3,4,10-12.
A	US A 4163046, (K.N.SUBRAMANIAN, A.ILLIS, N.C.NISSEN), 31 July 1979 (31.07.79), (see the Claims, Examples and the Drawing).	1,3,4,10-12.
X	Kirk-Othmer, 'Encyclopaedia of Chemical Technology ', Volume 20, Third Edition, published 1982 by John Wiley & Sons, New York, New York, (USA), (see page 582 lines 21-26).	1,3,4,10-12.

ANNEX TO THE INTERNATIONAL SEARCH REPORT OF INTERNATIONAL PATENT APPLICATION NO. PCT/AU89/00264.

This annex lists the 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 provided merely for the purpose of information.

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AU B2 536775 ------------ AU A1 75614/81 BR A 8106260 CA A1 1154599 EP A2 49169 FI A 813039 JP A2 57/092147 NO A 813299 US A 4615731 ZA A 816193	EP A1 103383 ------------ CA A1 1178027 JP A2 59/035007 US A 4548800	
	EP A2 157514 ------------ BR A 8501378 CA A1 1230734 JP A2 60/215508 US A 4530718	
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