



(51) International Patent Classification:
C22B 3/10 (2006.01) C22B 34/22 (2006.01)

(74) Agent: WRAYS; Ground Floor, 56 Ord Street, West Perth, Western Australia 6005 (AU).

(21) International Application Number:
PCT/AU20 11/0005 19

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(22) International Filing Date:
5 May 2011 (05.05.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2010902191 19 May 2010 (19.05.2010) AU

(71) Applicants (for all designated States except US): TNG LIMITED [AU/AU]; Level 1, 282 Rokeby Road, Subiaco, Western Australia 6008 (AU). MINERAL ENGINEERING TECHNICAL SERVICES PTY LTD [AU/AU]; Level 6, 524 Hay Street, Perth, Western Australia 6000 (AU).

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (for US only): CONNELLY, Damian Edward Gerard [AU/AU]; 9 Milson Street, South Perth, Western Australia 6151 (AU). YAN, Denis Stephen [AU/AU]; 15 Bottlebrush Drive, Morley, Western Australia 6062 (AU). LAM, Sai Wei [MY/AU]; 98/369 Hay Street, Perth, Western Australia 6000 (AU).

Published:

— with international search report (Art. 21(3))

(54) Title: METHOD FOR THE EXTRACTION AND RECOVERY OF VANADIUM

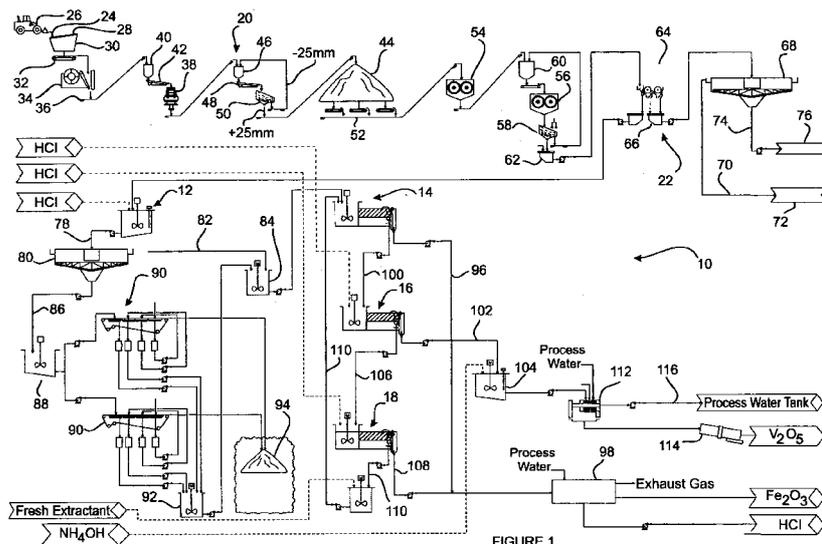


FIGURE 1

(57) Abstract: A method (10) for the extraction and recovery of vanadium from its ores, the method (10) characterised by the steps of: (i) Acid leaching (12) of an ore containing vanadium and iron to extract vanadium and iron into solution; (ii) Passing the product (78) of the leach step (i) to a solid/liquid separation step (80); (iii) Passing the liquid product (82) of separation step (ii) to a solvent extraction step (14) in which vanadium and iron are extracted into an organic extractant from that liquid product; (iv) Passing the loaded organic extractant produced in step (iii) to a stripping step (16, 18) in which acid is used to selectively and sequentially strip the vanadium and iron from the organic extractant; and (v) Passing the vanadium containing strip solution of step (iv) to a recovery step (104).

"Method for the Extraction and Recovery of Vanadium"

Field of the Invention

The present invention relates to a method for the extraction and recovery of vanadium. More particularly, the method of the present invention utilises a hydrometallurgical route for the extraction of vanadium from its ores.

Background Art

Traditionally, vanadium is extracted and recovered from its ores through a pyrometallurgical process that involves a salt roasting step followed by water leaching. Environmental concerns are becoming of increasing importance to those wishing to establish new mineral processing operations and those processes that require roasting more often than not emit products that have an overwhelmingly negative environmental impact.

Hydrometallurgical options for the extraction and recovery of vanadium from its ores have not been explored to date, as a rule, as a result of difficulties in both the leach step and the recovery step. With regard to leach and recovery, iron is typically co-extracted with the vanadium, and titanium is often also present, such as may be found in titanomagnetite type ores.

This results in concerns regarding selectivity of any leach and recovery processes. Iron is co-extracted with vanadium in the acid leaching since vanadium is locked as solid solution within the titanomagnetite matrix. Minimising the dissolution of iron in acid leaching is often a challenge without sacrificing the extraction efficiency of vanadium.

Solvent extraction requires that the solution pH be adjusted prior to the solvent extraction step. This often results in the co-precipitation of iron and vanadium.

Remya *et al* (Remya *et al.*, *Solvent Extraction and Ion Exchange*, Vol. 21., No. 4. pp. 573-589, 2003) conducted a study for solvent extraction of vanadium using Cyanex 923. However, there is no disclosure of a full process from leaching to purification step by solvent extraction and stripping and the recovery of vanadium by precipitation. Furthermore, multiple stripping agents are required which may involve extra processing cost in a full scale operation.

Additionally, any potential for economic viability of a hydrometallurgical route for the extraction and recovery of vanadium, and any associated valuable metals, has not been demonstrated.

The method of the present invention has as one object thereof to overcome substantially the abovementioned problems of the prior art, or to at least provide a useful alternative thereto.

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

Throughout the specification and claims, unless the context requires otherwise, the word "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 method for the extraction and recovery of vanadium from its ores, the method characterised by the steps of:

- (i) Acid leaching of an ore containing vanadium and iron to extract vanadium and iron into solution;

- (ii) Passing the product of the leach step (i) to a solid/liquid separation step;
 - (iii) Passing the liquid product of separation step (ii) to a solvent extraction step in which vanadium and iron are extracted into an organic extractant from that liquid product;
- 5 (iv) Passing the loaded organic extractant produced in step (iii) to a stripping step in which acid is used to selectively and sequentially strip the vanadium and iron from the organic extractant; and
- (v) Passing the vanadium containing strip solution of step (iv) to a recovery step.

- 10 In one form of the present invention the ore contains titanium in addition to vanadium and iron.

The acid leaching of step (i) is preferably conducted using hydrochloric acid (HCl).

More preferably, the concentration of HCl is within the range of about 20% to 32% (w/w).

- 15 Still preferably, the acid leaching is conducted in the range of about 25°C to 80°C under atmospheric pressure. The residence time of the acid leaching is preferably between about 30 to 360 minutes. The solids content during acid leaching is preferably about 20% w/w.

Preferably, the organic extractant of step (iii) contains a phosphine oxide.

- 20 Still preferably, the phosphine oxide is Cyanex 923™.

Yet still preferably, the extractant comprises about 40% v/v Cyanex 923™ and 60% v/v organic solvent.

Preferably, the aqueous to organic ratio during the solvent extraction step (iii) is between about 1:1 to 1:20. More preferably, the aqueous to organic ratio during the solvent extraction step (iii) is about 1:5.

5 Still preferably, the stripping step (iv) is conducted in a counter-current manner whereby vanadium is stripped from the loaded organic extractant prior to the stripping of iron from that solution.

10 Preferably, the acid used in the strip of step (iv) is hydrochloric acid. The hydrochloric acid is preferably in a concentration of between about 2 to 4 M when stripping vanadium. The hydrochloric acid is preferably in a concentration of about 0.01 M when stripping iron.

The purity of the vanadium solution produced is preferably between about 76% to 95%. The purity of the iron solution produced is preferably about 99%.

Description of the Drawings

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

Figure 1 is a flow sheet depicting a method for the extraction and recovery of vanadium from its ores in accordance with the present invention;

20 Figure 2 is a graph of the extraction of iron, vanadium and titanium over various leach times with 10% w/w solids content, temperature of 80°C and 36% w/w HCl;

Figure 3 is a graph of the extraction of iron, vanadium and titanium over various leach times with 20% w/w solids content, temperature of 25°C and 32% w/w HCl;

Figure 4 is a graph of the extraction of iron, vanadium and titanium over various leach times with 20% w/w solids content, temperature of 80°C and 20% w/w HCl;

5 Figure 5 is a graph of the effect of A:O ratio on the extraction efficiency of iron, titanium and vanadium by 20% v/v Gyanex 923™/80% v/v kerosene;

Figure 6 is a graph of the effect of HCl acidity on the purity of vanadium product recovered from loaded organic of Cyanex 923™; and

Figure 7 is a graph of the effect of HCl acidity on the stripping efficiency of iron and vanadium.

10 Best Mode(s) for Carrying Out the Invention

In Figure 1 there is shown a method 10 for the extraction and recovery of vanadium from its ores in accordance with the present invention. The method 10 comprises a leach step 12, solvent extraction step 14, vanadium stripping step 16 and iron stripping step 18.

15 Prior to the leach step 12 there are provided both a crushing circuit 20 and a beneficiation circuit 22. The purpose of the crushing and beneficiation circuits 20 and 22 are to produce a crushed ore with a size that is amenable for hydrometallurgical processing.

20 A run-of-mine (ROM) material 24 is delivered by front end loader 26 and dumped onto a 600 mm aperture static grizzly 28 mounted over a ROM bin 30. Oversize material is scalped on the grizzly 28. Scalped ROM ore is discharged from the bin 30 using a variable speed apron feeder 32 and directed to a jaw crusher 34.

25 The jaw crusher 34 reduces the top-size of the incoming material to about -250 mm. The crushed ore is discharged onto a crusher discharge conveyor 36, which extends underneath the apron feeder 32 to collect any spillages therefrom.

The crushed ore is then conveyed into a cone crusher 38 equipped with a feed bin 40 and vibrating feeder 42. The crushed ore from the cone crusher 38 is then transported to a stockpile 44, with a capacity of 24 hours, by way of a feed bin 46, vibrating feeder 48 and a screen 50. Crushed ore is drawn from the stockpile 44
5 by a stockpile discharge conveyor 52 and transported to two high pressure grinding rolls (HPGR) 54 and 56, arranged in series.

The use of the HPGR is understood to produce micro-cracks in the ore particles which allows for a significant increase in subsequent lixiviant penetration and metal recovery in leaching over conventional milling.

- 10 The final stage of HPGR 56 is operated in closed circuit with a screen 58 cutting at 1 mm. The oversize from the screen 58 is returned to a feed bin 60 for further grinding to improve the liberation of the valuable minerals. The screen undersize material is transferred into a feed hopper 62 for a subsequent counter current rougher magnetic separator 64, being a part of the beneficiation circuit 22.
- 15 Process water is added and the slurry is pumped to the rougher magnetic separator 64. The crushed ore is beneficiated using counter current magnetic separator before the concentrate is pumped to the leaching step 12.

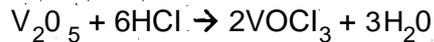
It is envisaged that an additional grinding step may be utilised to produce a product that is about minus 150 μm , depending upon the level of titanium
20 preferred in the residue of the leaching step 12. The smaller the ore is when passed to the leaching step 12 the higher the relative level of titanium in the leach residue.

Tails 66 from the rougher magnetic separator 64 are pumped to a tailings thickener 68 where process water is recovered for reuse. The slurry is thickened
25 to 60% solids by weight. Thickener overflow 70 gravitates to a process water tank 72 while underflow 74 is pumped to tailings 76. The magnetic concentrate is pumped to the leaching circuit for the extraction of vanadium and iron.

- 7 -

The purpose of the leach step 12 is to extract the valuable metal species of vanadium and iron into solution. The leaching step 12 is conducted in rubber lined, epoxy coated, agitated steel tanks arranged in series. The slurry is cascaded through the acid leach train. Hydrochloric acid is added to a first tank to adjust the pulp density to 20% solid by weight. The acid leaching is conducted at a temperature of between about 25°C to 85°C, for example 80°C, under atmospheric pressure or above, and for a residence time of between about 30 to 360 minutes. The initial HCl concentration is maintained at between about 20% to 32% w/w, for example at 20% w/w. The leach temperature is able to be controlled at about 80 to 85°C through insulation and capping of the leach tanks.

The leaching reactions are represented by the equation below:



A slurry 78 from the leach step 12 is pumped to a leach thickener 80 in which the slurry is thickened to 50% solids by weight. An overflow solution 82 is gravitated to an agitated metal extraction feed tank 84. An underflow solution 86 is pumped to a feed tank 88 and in turn to two horizontal belt filters 90 arranged in parallel. Here the leach residue is washed in a counter current manner using fresh water.

Mother liquor and wash filtrate from the filters 90 are pumped to a wash water tank 92 before it is transferred to the metal extraction feed tank 84 and the solvent extraction step 14. The leach residue cake from the filters 90 is stockpiled 94 and it is envisaged that this leach residue cake may be used as an ilmenite concentrate.

This purpose of the solvent extraction step 14, the vanadium stripping step 16 and iron stripping step 18 are to extract the valuable metal units from the leach solution in a sequential manner using the appropriate extractant and stripping agents.

From the metal extraction feed tank 84, the pregnant solution is fed to the solvent extraction step 14 in which it mixed with an organic extractant, for example a phosphine oxide. Specifically, the extractant is provided in the form of a mix of 40% v/v Cyanex 923™ in 60% v/v kerosene. The extraction is conducted at an organic to aqueous (O:A) ratio of between about 1:1 to 20:1, for example 5:1. In this step, vanadium and iron are co-extracted onto the organic phase. It should be noted that about 61% of the iron is loaded onto the organic. A barren effluent 96, which carries the remaining iron solution, is transferred to an acid regeneration plant 98.

10 A metals loaded organic 100 is then transferred into a stripping plant, in which the vanadium and iron are selectively separated. The stripping is conducted in a sequential manner involving selective stripping of vanadium followed by iron.

Stripping is conducted in a counter-current fashion within each step 16 and 18. The vanadium is stripped from the metal loaded organic using HCl of between about 2.5M to 5M, for example 4M HCl. This produces a vanadium enriched solution 102 having a purity of about 81%. The vanadium enriched solution is then pumped to a recovery step, for example a vanadium precipitation circuit 104 for the production of vanadium pentoxide (V_2O_5).

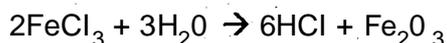
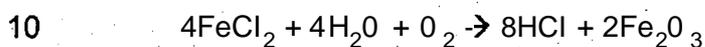
20 Metal loaded organic 106 from the vanadium stripping step 16 is then contacted with HCl of between about 0.01 M to 0.05M, for example 0.01 M HCl, in the iron stripping step 18. An iron enriched solution 108 at a purity of about 99% is recovered. The iron enriched solution 108 is pumped to the acid regeneration plant 98, while regenerated organic extractant 110 is recycled 110 back to the metal extraction step 14 for reuse.

25 Ammonium chloride is used as the precipitating agent in the vanadium precipitation circuit 104, Vanadium is precipitated as ammonium metavanadate:



After a filtration step 112, the ammonium metavanadate is calcined using a rotary kiln 114 operating at about 500-550°C, to dry the product, removing the water of crystallisation and to convert the filter cake to vanadium pentoxide (V₂O₅). The dry vanadium pentoxide is then packaged for transportation. Filtrate 116 from the filter step 112 is pumped into the process water tank for reuse.

The barren effluent 96 from the solvent extraction step 14 together with the iron enriched solution 108 from the iron stripping step 18 is pumped into the acid regeneration plant 98. The acid regeneration process utilises pyrohydrolysis and is understood to proceed according to the following reactions:



It is to be understood that other processes for the regeneration of acid may be utilised without departing from the scope of the present invention.

Regenerated acid at a strength of 20% w/w is collected and pumped back to the hydrochloric acid feed tank, while the iron oxide can be sold as a valuable product.

The method 10 of the present invention will now be described with reference to several non-limiting examples.

A metallurgical test work programme was based on an ore from the Mount Peake project in the Northern Territory of Australia, the project having an Inferred Resource of 140 Mt @ 0.30 % V₂O₅, 5.9% TiO₂ and 29% iron.

A vanadium rich concentrate (P₈₀ 150 µm, 75 µm and 45 µm) from a cleaner magnetic separation process was subjected to acid leaching to examine the impact of grind size, solids content and acid concentration. The composition of the vanadium rich concentrate is as depicted in Table 1:

Table 1

Grind Size (mm)	Concentrate Grade (%)						
	Fe	V ₂ O ₅	TiO ₂	SiO ₂	Al ₂ O ₃	P	S
150	51.7	1.10	15.8	5.30	3.0	0.013	0.03
75	55.3	1.19	16.5	2.07	2.5	0.004	0.03
45	55.4	1.18	16.3	2.12	2.4	0.005	0.03
Head Assay	34.5	0.54	9.2	22.9	5.0	0.08	0.03

The leaching in these tests was conducted at ambient or room temperature (about 25°C) using hydrochloric acid as the lixiviant.

- 5 To study the effect of HCl concentration, the lixiviant was set at 20 wt.% HCl and 10 wt.% HCl.

Unless stated, the initial solids content fixed at 20% w/w. The leach kinetics was allowed to take place for 4 hours. Samples were collected intermittently for assay analysis.

- 10 The vanadium rich concentrate was amenable to acid leaching yielding a vanadium extraction greater than 90%. Co-extraction of iron and titanium was also recorded at 77-81% and 16-19%, respectively. Reducing the grind size from P₈₀ 150 μm to 45 μm only affected the leach kinetics mildly, as can be seen with reference to Figures 2, 3 and 4.
- 15 These results showed that good control of the SiO₂ to Al₂O₃ mass ratio is not critical in the hydrometallurgical processing to achieve a high extraction of vanadium.

Analysis of the leach residue showed an upgrade in the TiO₂ grade from 16.6-16.8% to 38.3-43.5%.

- 20 The leaching of the P₈₀ 150 μm concentrate consumed comparatively less acid in comparison to leaching of the P₈₀ 45 μm concentrate, see Figure 5. At a P₈₀ of

150 μm it involves a reduction, not only in the reagent costs but also the grinding cost. It is understood that the grinding cost increases exponentially with the decrease in the grind sizes. Subsequent tests were conducted using P₆₀ 150 μm concentrate.

- 5 An increase in the pulp density from 20 wt.% solid to 30 wt.% solid reduced the acid consumption from 579 kg HCl/tonne feed ore to 480 kg HCl/tonne feed ore, as shown in Figure 6. Despite this, the vanadium extraction decreased from 90% to 75%, as shown in Figure 7. Similarly, the iron extraction also decreased from 77% to 61%, as shown in Figure 8. A decrease in the titanium extraction
10 was also observed, as shown in Figure 9.

The effect of HCl concentration on the vanadium extraction was also been investigated. A drastic decrease in the vanadium extraction was observed, following the decrease in the HCl concentration. Similarly, the iron and titanium extraction also decreased accordingly, as shown in Figures 10, 11 and 12,
15 respectively.

The poor extraction efficiencies are understood to be attributable to the relatively low acid strength in the solution, resulting in the leach proceeding very slowly. It is envisaged that heating the solution to 80°C may promote the dissolution of iron and vanadium, increasing thereby the leach kinetics. Heating of the solution to
20 80°C is understood to have improved vanadium extraction. A vanadium extraction at 97.5% has been successfully achieved using 20 wt.% HCl at 80°C.

A plot of extraction versus acid consumption was developed. The result is shown in Figure 13. A strong correlation is seen between the acid consumption and extraction. To achieve a vanadium extraction greater than 90% about 579 kg
25 HCl/tonne of feed ore is required.

A high dissolution of iron is required to achieve a high extraction of vanadium. This is understood to be due to the locking of vanadium with titanomagnetite.

The acid is consumed to attack the iron, unlocking the vanadium to promote its dissolution.

5 A separate test was conducted to study the amenability of a cobbing concentrate (-1 mm) generated from the use of high pressure grinding rolls (HPGR) to acid leaching. This test aimed to investigate the beneficial effect of HPGR processing, as well as the possibility of eliminating the need for fine grinding. The leaching was conducted at 80°C and pulp density of 20 wt.%. Concentrated HCl was used as the lixiviant. The reaction was allowed to take place for 6 hours. The leaching result is shown in Figure 14.

10 The leach kinetics increased with increasing leach time and reached equilibrium after 120 min. At 120 min about 97% of the vanadium was extracted. There was also 89% of iron and 55% of titanium being co-extracted. No apparent change in the extraction efficiency for iron, titanium and vanadium was observed after 120 min. However, the acid consumption increased from 596 kg HCl/tonne
15 feed ore to 772 kg HCl/tonne feed ore. The loss in acid is attributed to evaporation and/or being consumed to leach the remaining gangue minerals.

In comparison to the leach performance of the P₆₀ 45 µm and 150 µm concentrates, slower leach kinetics were observed with the -1 mm concentrate. This is expected since the P₆₀ 45 µm and 150 µm concentrates have higher
20 surface area to volume ratio than that of -1 mm concentrate. While the fastest leach kinetics were achieved at P₆₀ 45 µm, it is important to note that the grinding power increases exponentially at finer grind sizes.

The amount of acid consumed by the -1 mm concentrate was comparable to that of P₆₀ 45 µm and 150 µm concentrates. It is expected that the -1 mm concentrate
25 may consume higher amount of acid since it contained a higher level of gangue minerals than that in the P₈₀ 45 µm and 150 µm concentrates. The acid consumption is understood to be governed by the leaching of iron.

These results indicate that for some ore types, ball milling may be excluded from the method of the present invention. The elimination of ball milling is expected to lead to a reduction in the capital and operating expenditure.

5 A screening test was conducted to find the best performed extractant for the solvent extraction of vanadium. The extractants tested included:

- 20% v/v Cyanex 272™/80% v/v kerosene,
- 20% v/v Cyanex 923™/80% kerosene (Cyanex 923™) and
- 20% v/v DEHPA/15%v/v TBP/65% kerosene (TBP/DEHPA).

10 Amongst them, Cyanex 923™ gave the best extraction of vanadium. The Cyanex. 923™ extracted a cumulative 75% vanadium. The Cyanex 272™ and TBP/DEHPA only extracted a cumulative 39% and 48% vanadium, respectively.

Co-extraction of iron was observed. The Cyanex 923™ extracted a cumulative 99% iron.

15 Similarly, TBP/DEHPA also produced a cumulative extraction of 99% iron. By contrast, Cyanex 272™ only extracted a cumulative 94% iron. Since the vanadium is co-extracted with iron, it indicated that a selective stripping would be needed to separate the vanadium from iron.

20 A test work programme was designed to explore the use of Cyanex 923™ as the sole extractant for the extraction of iron, titanium and vanadium. Cyanex 923™ was chosen because it was demonstrated to be capable of extracting vanadium without the need for the pre-removal of iron.

The solvent extraction test programme was conducted using 20% v/v Cyanex 923™ in 80% v/v kerosene at A:O ratios of 1:1, 1:5, 1:10, 1:20. As shown in

Figure 15, the best performance was observed at an A:O ratio of 1:20. This is expected because an increase in the A:O ratio would increase the number of sites available for iron, titanium and vanadium to be loaded onto the organic.

5 Titanium was loaded more readily onto Cyanex 923™ in comparison to iron and vanadium. Complete extraction of titanium was achieved at an A:O ratio of 1:20. It is important to note that vanadium can be effectively loaded onto the organic even in the presence of significant amount of iron in solution. At an A:O ratio of 1:20, about 90% of the vanadium was also loaded onto the organic with 61% of the iron being co-extracted.

10 This option not only uses a single extractant but also eliminates the need for extra oxidant addition for the re-oxidation of Fe(II) to Fe(III).

The results showed that a stable emulsion was formed. Moreover, a third phase was observed during the phase separation. A modifier such as isodecanol can be added to prevent the emulsion and third phase formation.

15 It is envisaged that changing the volumetric ratio of Cyanex 923™ to kerosene may also help to resolve these problems. Additionally, it is further envisaged that the introduction of a filtration step prior to solvent extraction, so as to remove undissolved solids, would reduce the impact of emulsion formation.

20 These tests aimed to determine if selective stripping of vanadium can be achieved from the metal loaded organics, and to evaluate the ability of the extractant to be regenerated for reuse. The main focus is to identify the best stripping solution to be used for separating vanadium from iron. It is not designed to optimise the stripping efficiency of vanadium and iron.

25 The Cyanex 923™, which has been loaded with iron and vanadium, was used as the feed solution for the stripping test. Two stripping solutions at 2M HCl and 1M HCl were evaluated for the stripping of vanadium, as shown in Figure 16.

The vanadium was initially stripped from the organic followed by the stripping of iron using 0.01 M HCl. The combined results are represented conveniently in Figure 17.

- 5 Stripping of vanadium by 2M HCl at an A:O ratio of 2:1 produced a vanadium solution with an average purity of 76%. When the stripping test was performed using 1M HCl at an A:O of 1:1, the selectivity between vanadium and iron decreased drastically. It yielded a vanadium solution with average purity of 12%.

Subsequently, when the loaded organic was mixed with 0.01 M HCl at an A:O of 1:1, it generated an iron solution with a purity of 99%.

- 10 A stripping test was also conducted on the Cyanex 923™ which has been loaded with 55% iron, 97% titanium and 70% vanadium. In this test, the stripping of vanadium was performed using a HCl solution at 4M HCl, 2.5M HCl and 2M HCl. It aimed to evaluate if the purity of the vanadium solution can be improved with increasing the acidity of the stripping solution.

- 15 Following the stripping of vanadium, the loaded organic was mixed with 0.01 M HCl for the recovery of the iron.

When the loaded organic was mixed with 4M HCl at an A:O ratio of 3:1, the vanadium was stripped from the loaded organic, producing a vanadium solution with a purity of 95%.

- 20 Subsequently, mixing of the loaded organic with 0.01 M HCl produced an iron solution with a purity of 99%.

The test results clearly demonstrated that the vanadium can be selectively separated from iron.

- 25 The purity of the vanadium solution can be tuned by manipulating the acidity of the stripping solution.

- 16 -

A separate test work programme, conducted using the sole extractant of Cyanex 923™, showed that the vanadium, titanium and iron can be loaded efficiently on the extractant without the requirement of pre-treatment.

5 The extraction efficiencies of iron, titanium and vanadium increased as the A:O ratio increased from 1:1 to 1:20. At an A:O ratio of 1:20, complete extraction of titanium was achieved with about 90% of vanadium and 61% of iron being co-extracted.

10 Stripping test performed on metals loaded Cyanex 923™ showed that the vanadium can be selectively stripped from the organic using HCl at a concentration 2-4 M. Depending on the acidity of the stripping solution, a vanadium solution with purity of 76% to 95% can be produced. An iron solution with a purity of 99% can be recovered from the loaded organic using 0.01 M HCl as the stripping solution.

15 Further solvent extraction test work was conducted using the HPGR product described hereinabove. The leach slurry was filtered to remove the residue solid before subjected to the solvent extraction.

20 Cyanex 923™ was used the extractant. As described immediately above, this extractant has been previously found to extract iron, vanadium and titanium effectively. The extraction was carried out using 40 vol.% Cyanex 923™ in 60 vol.% kerosene at an O:A ratio of 1:1, 5:1, 8.5:1, 9:1, 10:1, and 12.5:1.

As shown in Figure 18, the extraction of vanadium, iron and titanium increased with the O:A ratio. This is attributed to the increase in the organic concentration at higher O:A ratio, improving the number of adsorption sites for the loading of iron, titanium and vanadium onto Cyanex 923.

25 McCabe Thiele diagrams were constructed to determine the number of stages required for the extraction of vanadium, iron and titanium. These are illustrated in Figures 19 to 24. At an O:A of 5:1, it was determined that titanium can be

extracted efficiently in a single stage of contact. Complete extraction of vanadium was achieved after two stages of contact. For iron, it required 6 stages of contact to achieve an extraction of 88%.

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

Claims

1. A method for the extraction and recovery of vanadium from its ores, the method characterised by the steps of:
 - 5 (i) Acid leaching of an ore containing vanadium and iron to extract vanadium and iron into solution;
 - (ii) Passing the product of the leach step (i) to a solid/liquid separation step;
 - (iii) Passing the liquid product of separation step (ii) to a solvent extraction step in which vanadium and iron are extracted into an organic extractant from that liquid product;
 - 10 (iv) Passing the loaded organic extractant produced in step (iii) to a stripping step in which acid is used to selectively and sequentially strip the vanadium and iron from the organic extractant; and
 - (v) Passing the vanadium containing strip solution of step (iv) to a recovery step.
- 15 2. A method according to claim 1, wherein the ore contains titanium in addition to vanadium and iron.
3. A method according to claim 1 or 2, wherein the acid leaching of step (i) is conducted using hydrochloric acid.
4. A method according to claim 3, wherein the concentration of HCl is within the
20 range of about 20% to 32% w/w.
5. A method according to any one of the preceding claims, wherein the organic extractant of step (iii) contains a phosphine oxide.

6. A method according to any one of the preceding claims, wherein the acid leaching is conducted in the range of about 25°C to 80°C under atmospheric pressure.
7. A method according to any one of the preceding claims, wherein the residence time of the acid leaching is between about 30 to 360 minutes.
8. A method according to any one of the preceding claims, wherein the solids content during acid leaching is about 20% w/w.
9. A method according to any one of the preceding claims, wherein the organic extractant of step (iii) contains a phosphine oxide.
10. A method according to claim 9, wherein the phosphine oxide is Cyanex 923™.
11. A method according to claim 9 or 10, wherein the extractant comprises about 40% v/v Cyanex 923™ and 60% v/v organic solvent.
12. A method according to any one of the preceding claims, wherein the aqueous to organic ratio during the solvent extraction step (iii) is between about 1:1 to 1:20.
13. A method according to any one of the preceding claims, wherein the aqueous to organic ratio during the solvent extraction step (iii) is about 1:5.
14. A method according to any one of the preceding claims, wherein the stripping step (iv) is conducted in a counter-current manner whereby vanadium is stripped from the loaded organic extractant prior to the stripping of iron from that solution.
15. A method according to any one of the preceding claims, wherein the acid used in the strip of step (iv) is hydrochloric acid.

- 20 -

16. A method according to claim 15, wherein the hydrochloric acid is provided in a concentration of between about 2 to 4 M when stripping vanadium.
17. A method according to claim 15 or 16, wherein the hydrochloric acid is provided in a concentration of about 0.01 M when stripping iron.
- 5 18. A method according to any one of the preceding claims, wherein the purity of the vanadium solution produced in the recovery step (v) is between about 76% to 95%.
19. A method according to any one of the preceding claims, wherein the purity of the iron solution produced in the recovery step (v) is about 99%.
- 10 20. A method for the extraction and recovery of vanadium from its ores substantially as hereinbefore described with reference to any one or more of the accompanying Figures.
21. A method for the extraction and recovery of vanadium from its ores substantially as hereinbefore described with reference to any one or more of
15 the Examples.

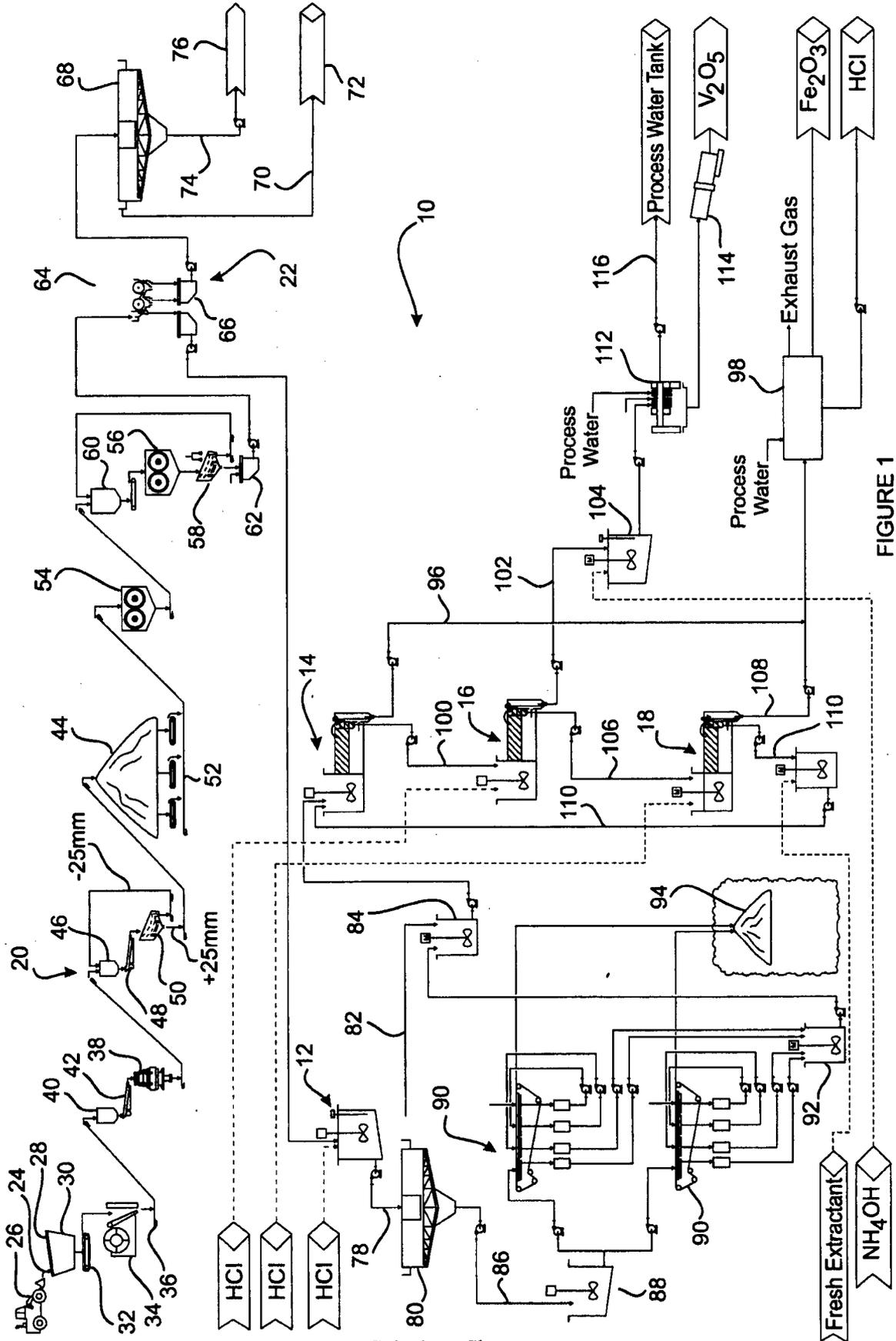


FIGURE 1

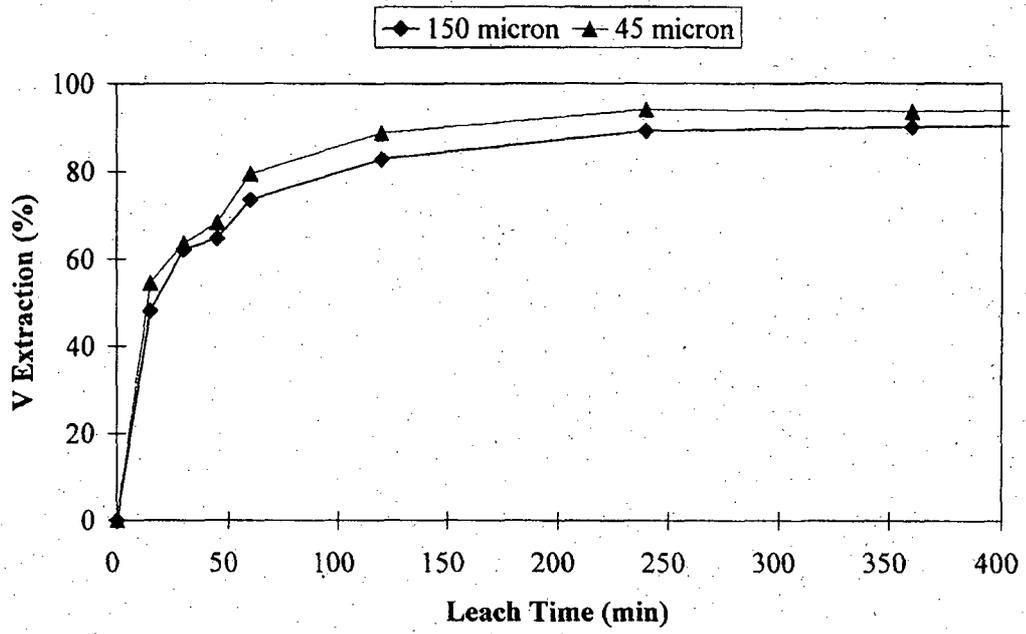


Figure 2

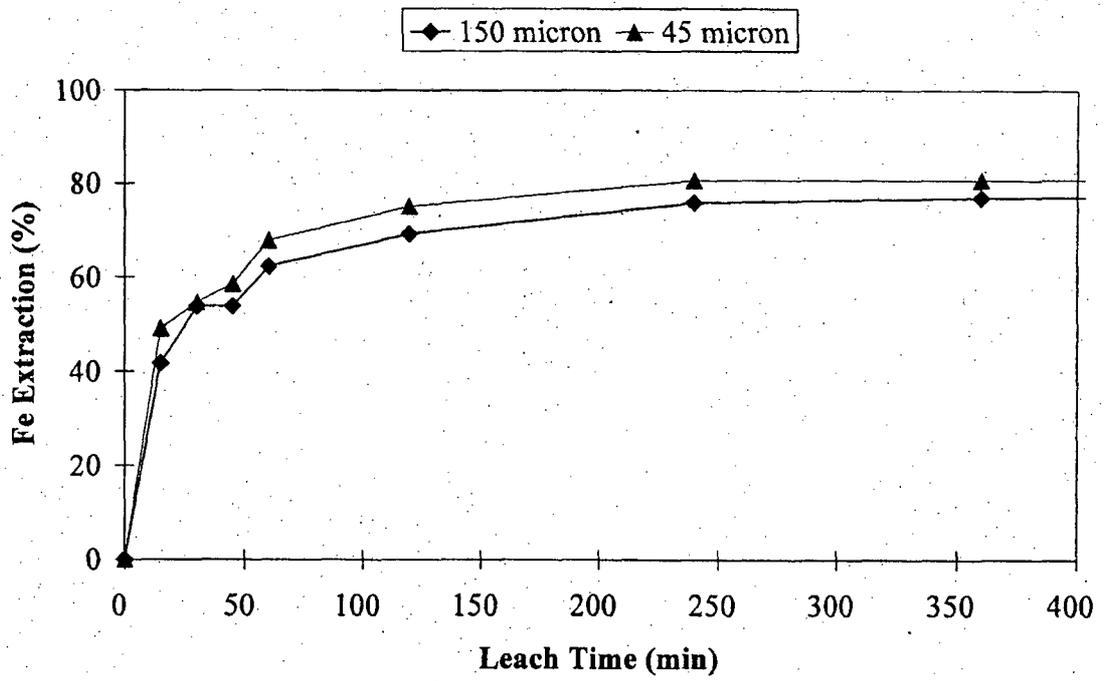


Figure 3

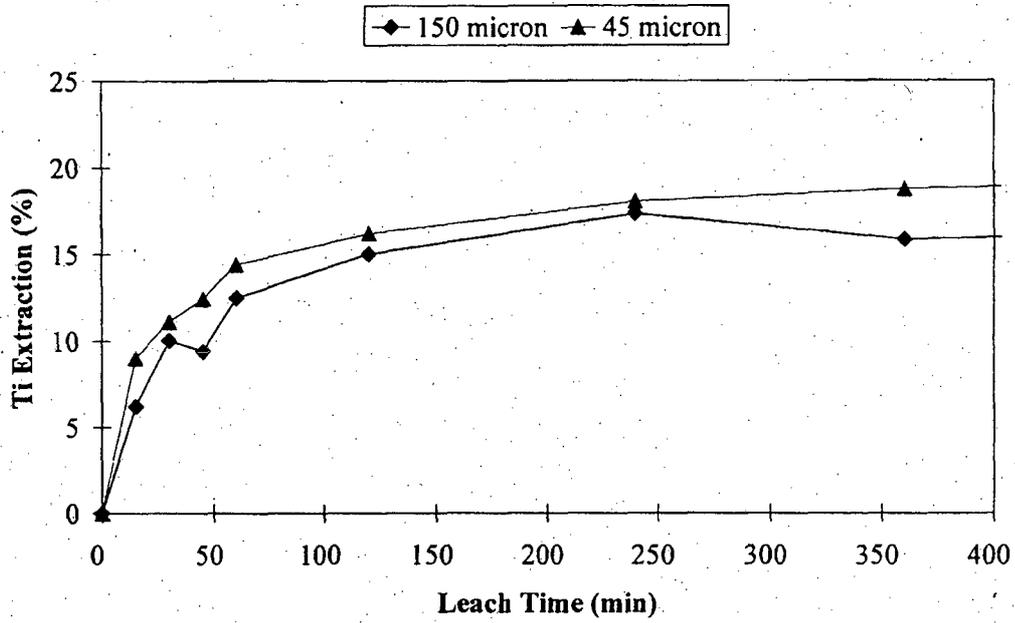


Figure 4

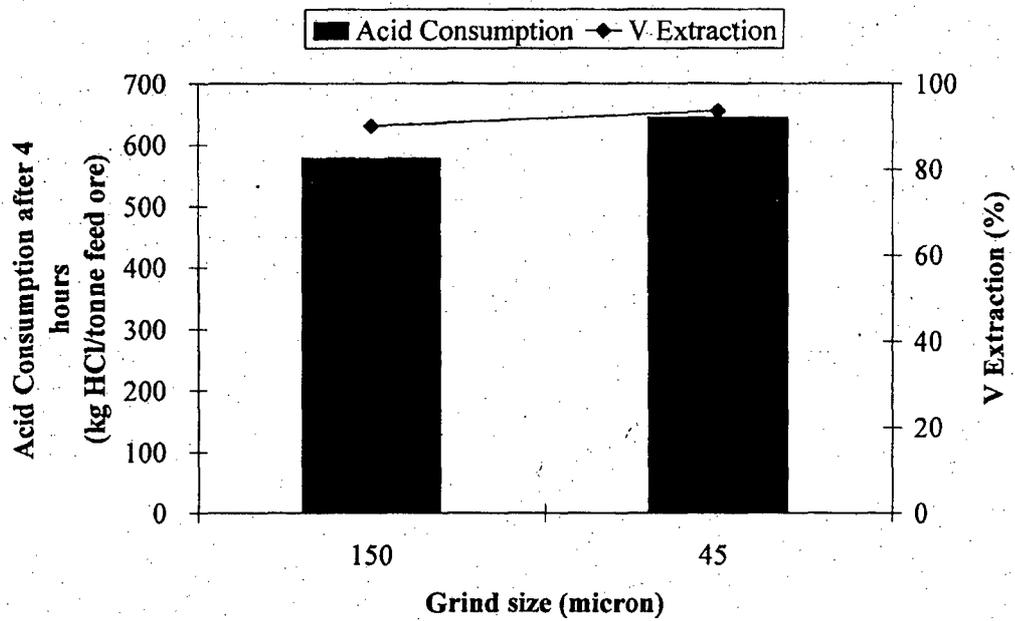


Figure 5

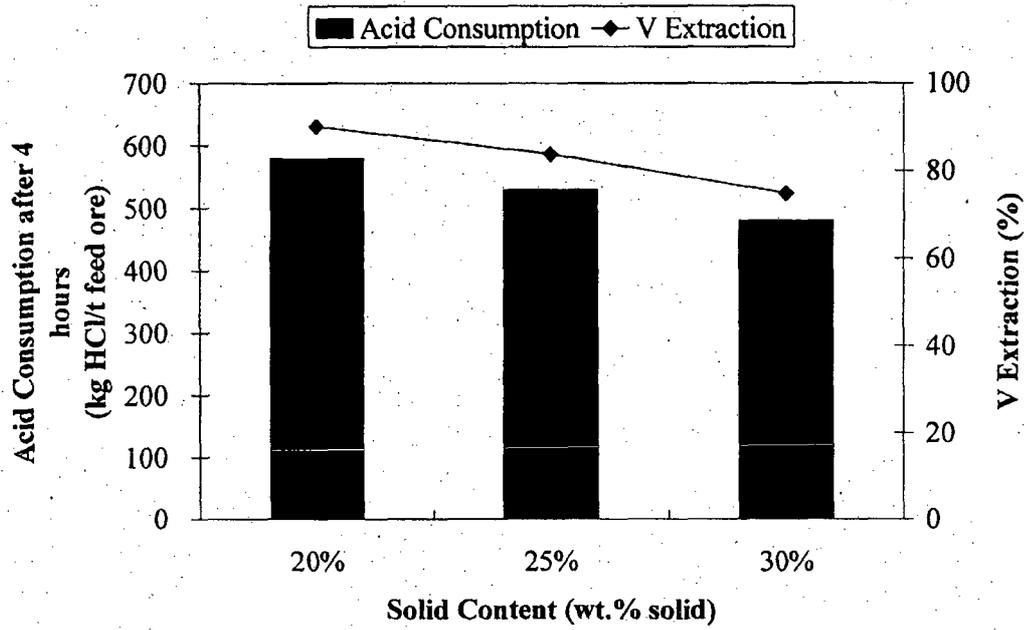


Figure 6

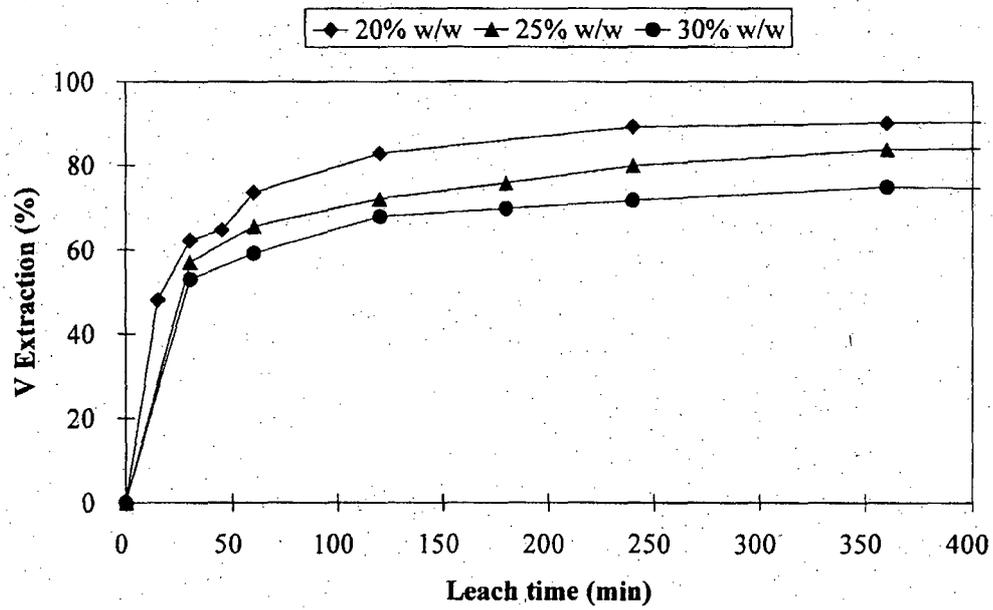


Figure 7

- 5/13-

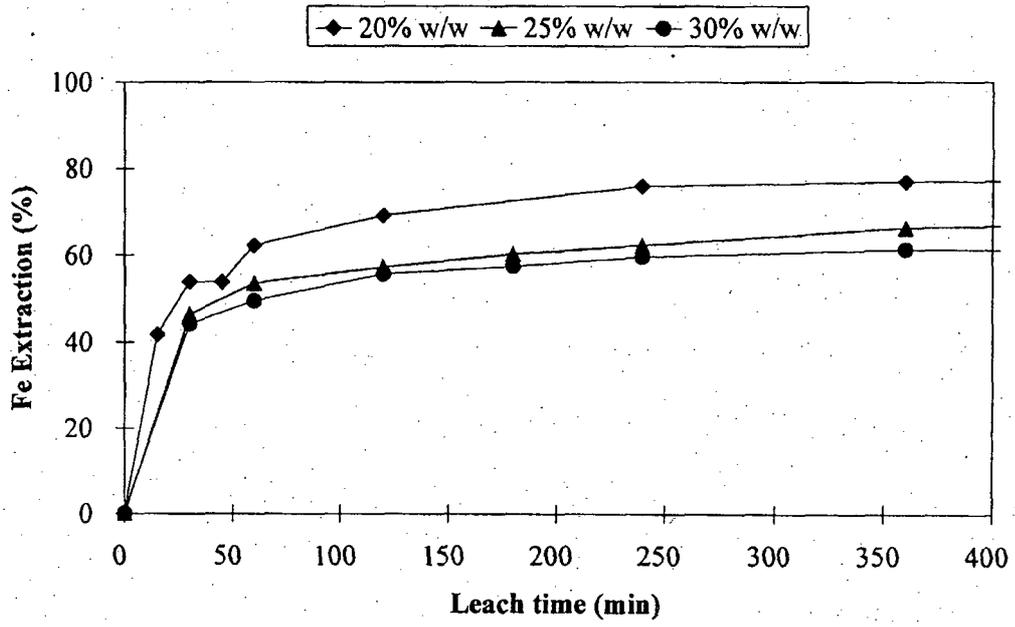


Figure 8

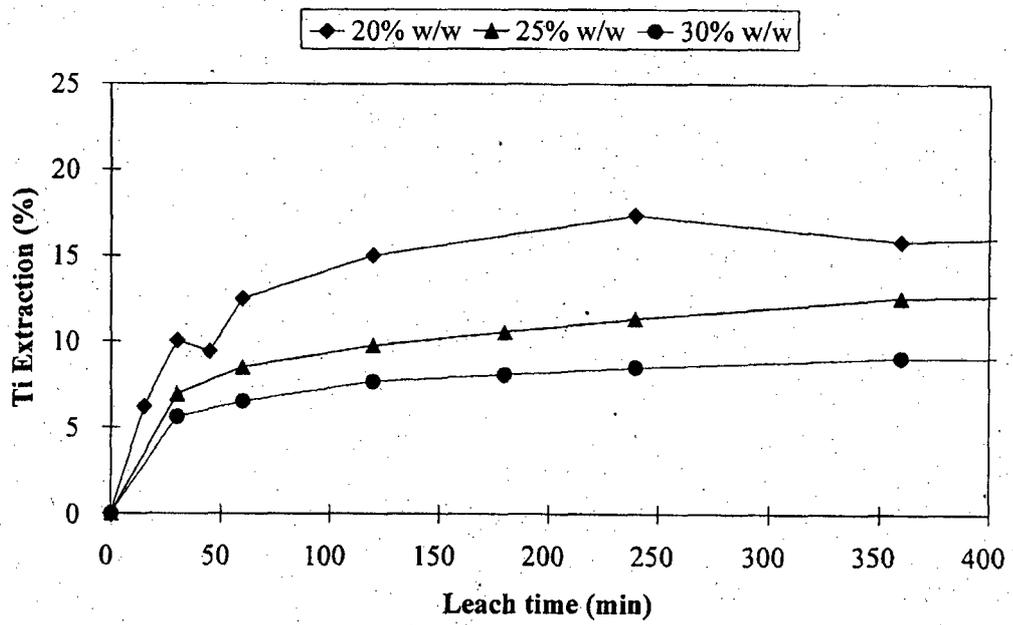


Figure 9

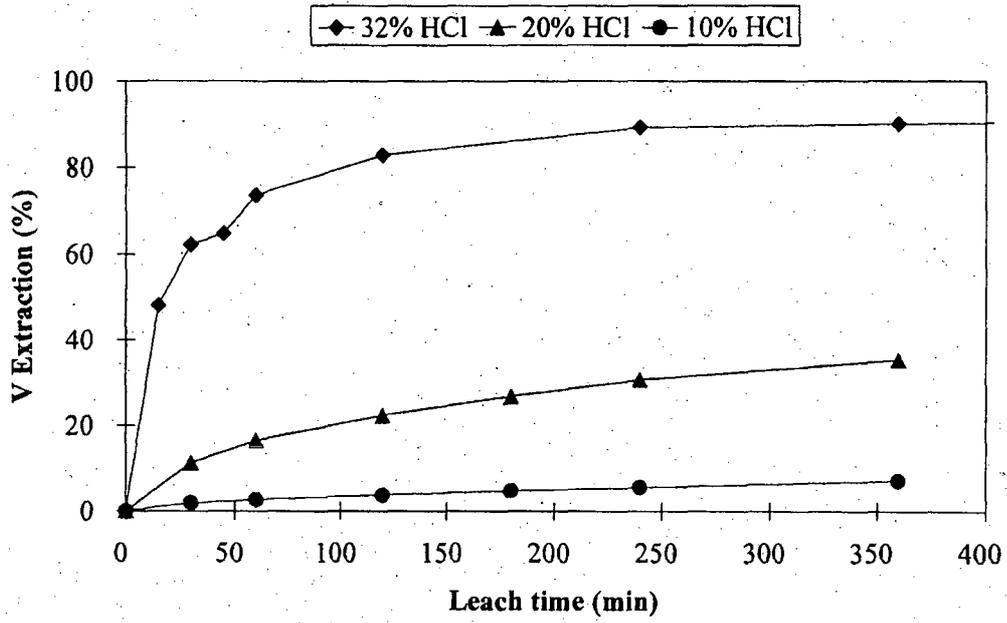


Figure 10

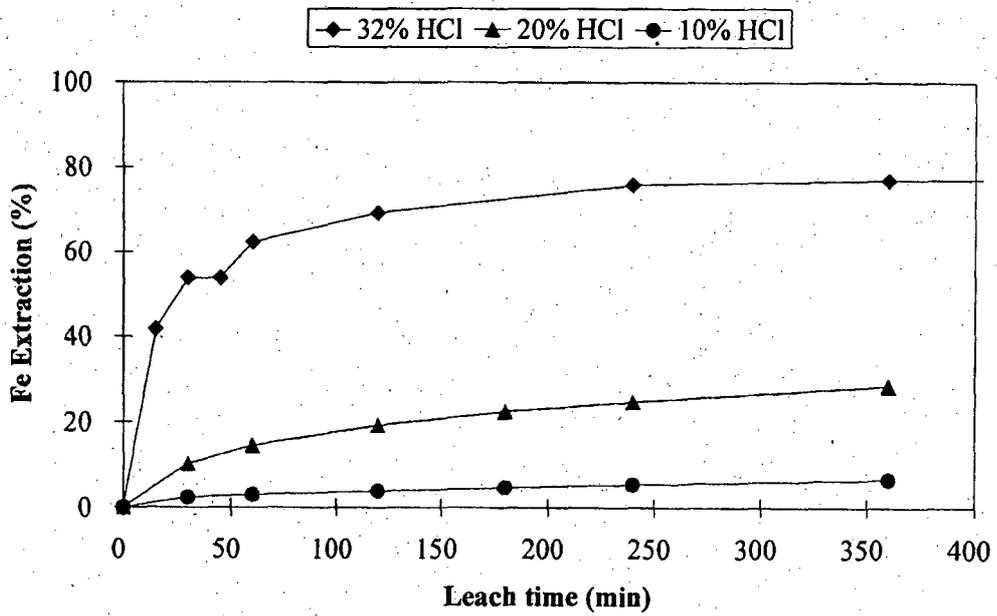


Figure 11

- 7/13-

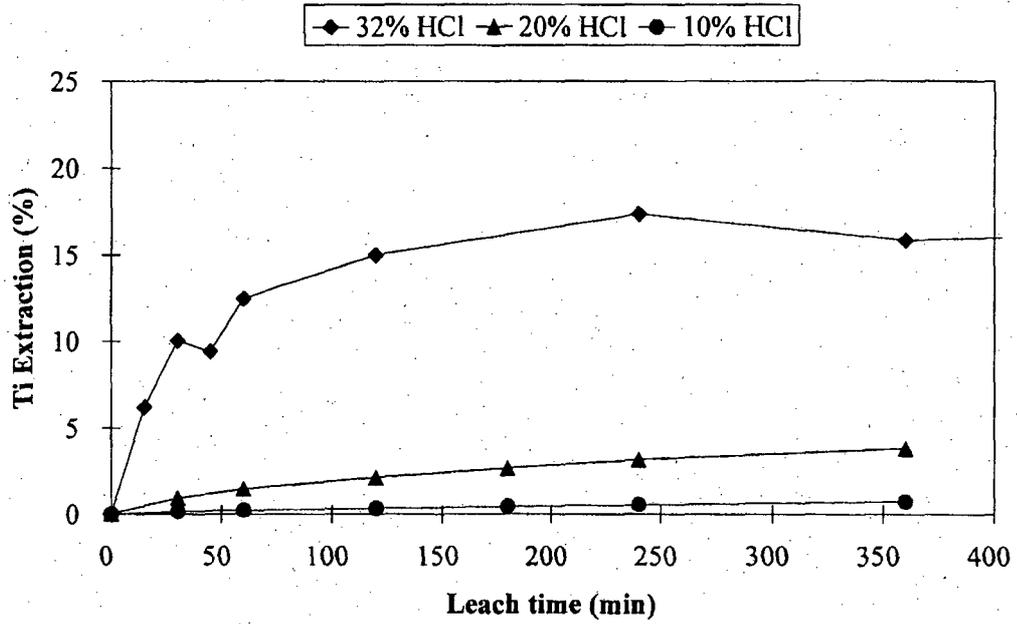


Figure 12

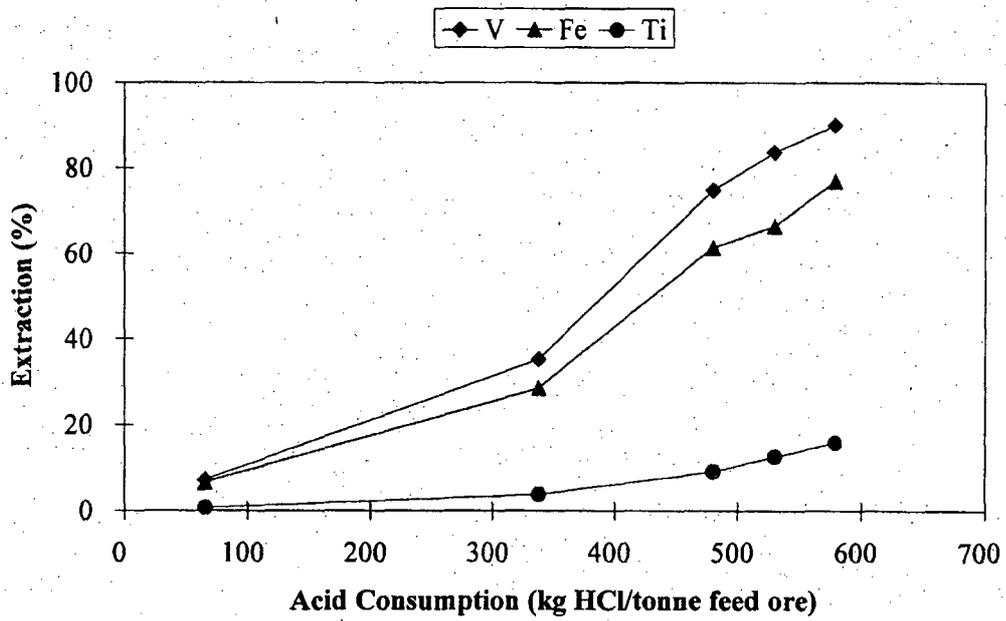


Figure 13

- 8/13-

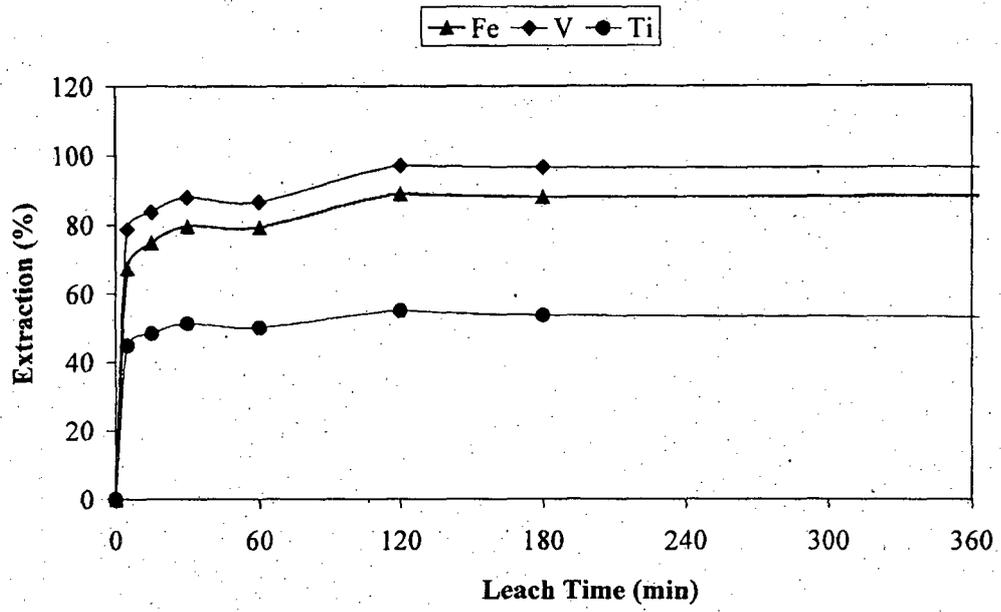


Figure 14

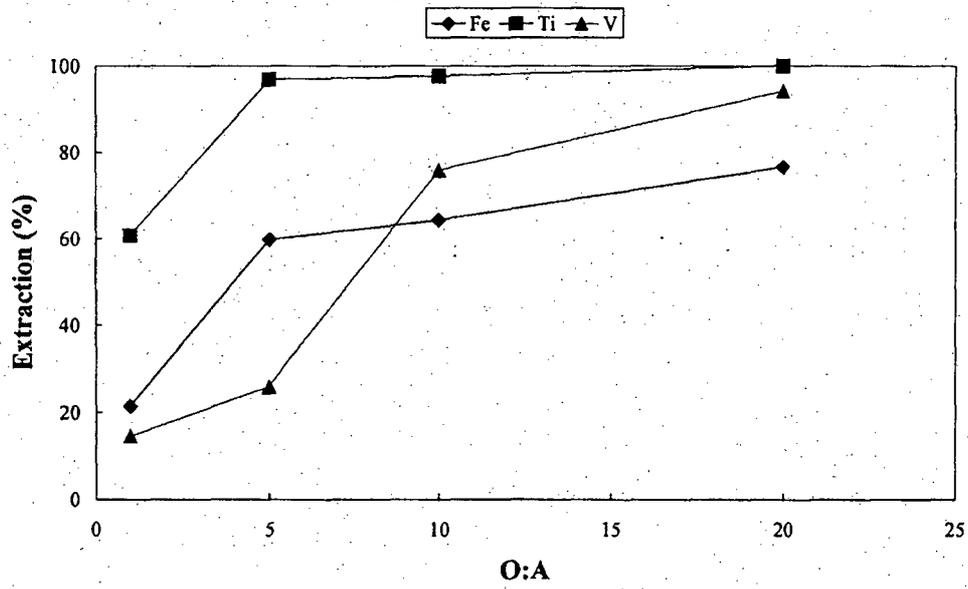


Figure 15

- 9/13-

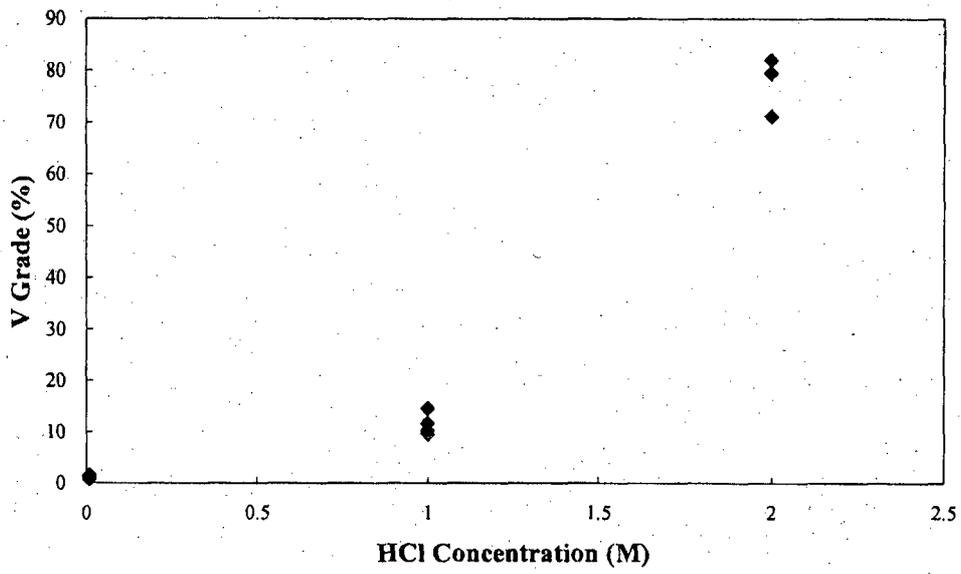


Figure 16

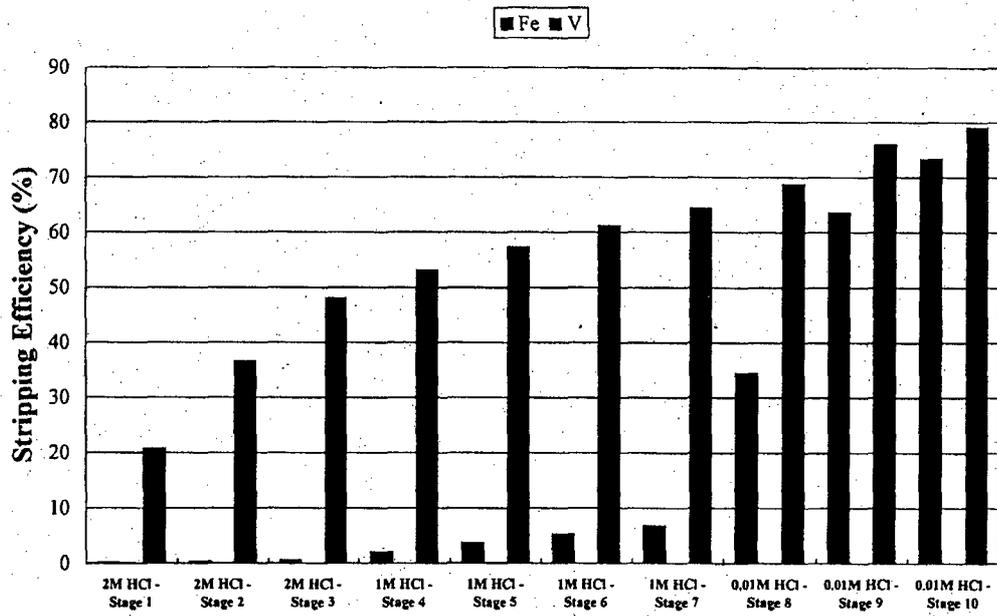


Figure 17

- 10/13-

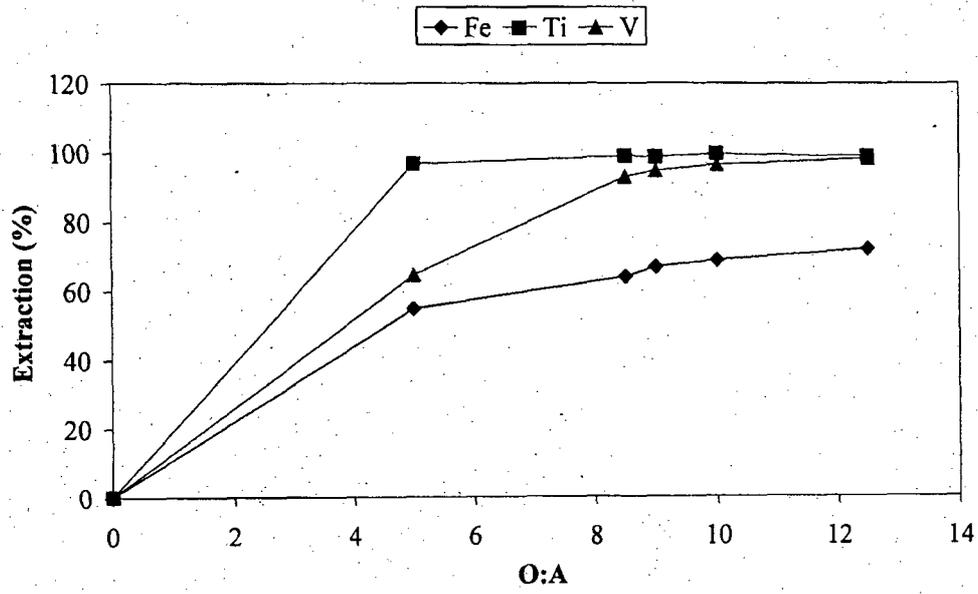


Figure 18

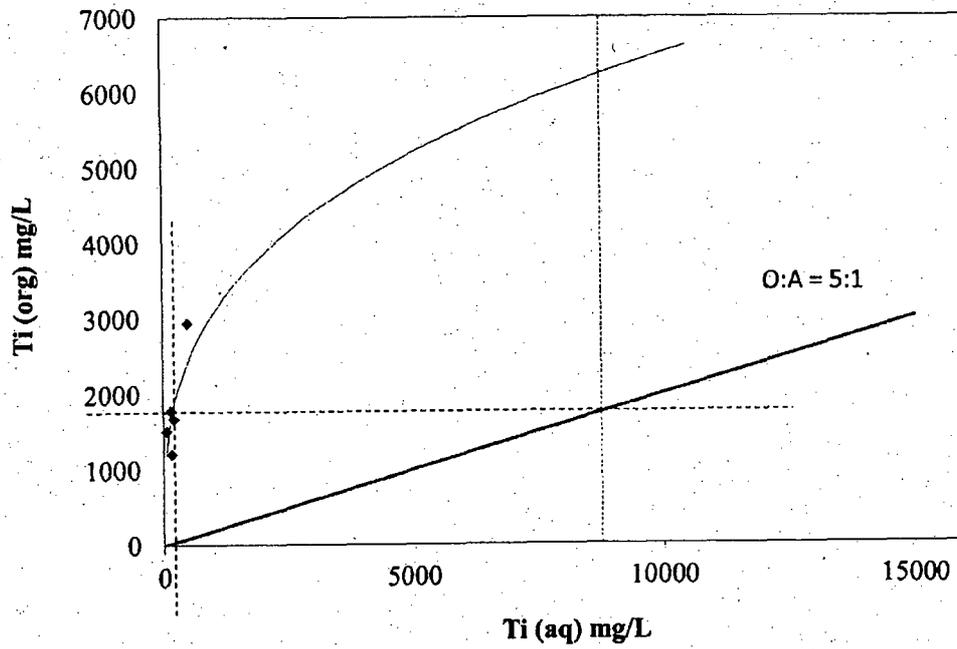


Figure 19

-11/13-

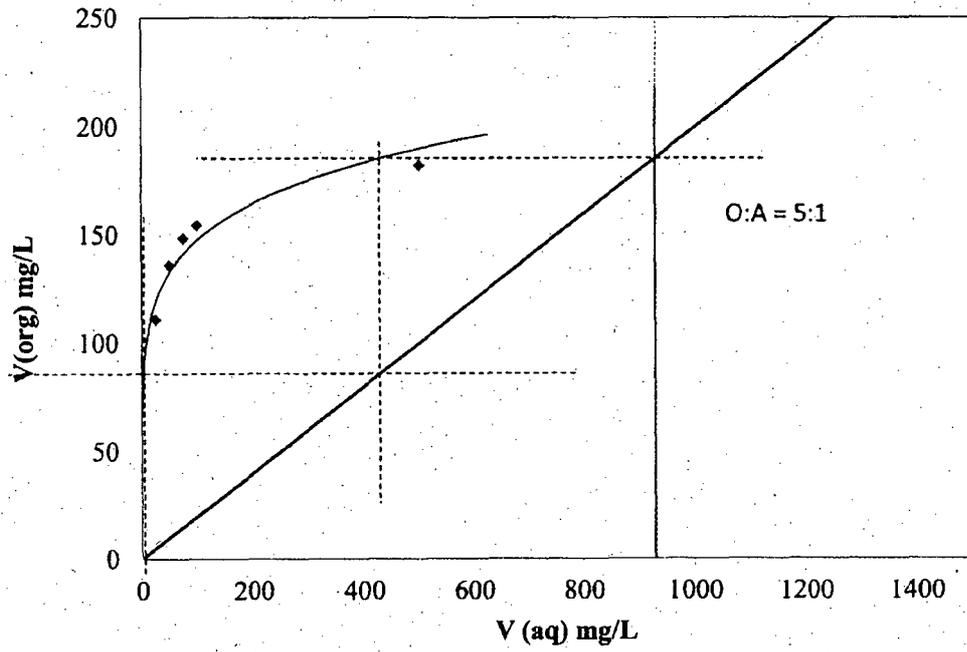


Figure 20

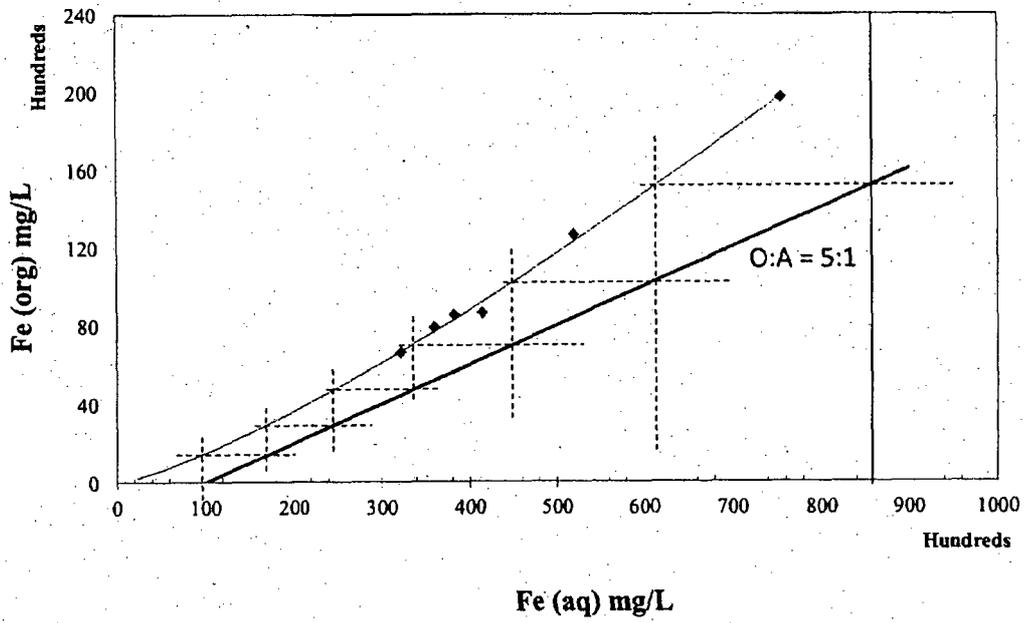


Figure 21

-12/13-

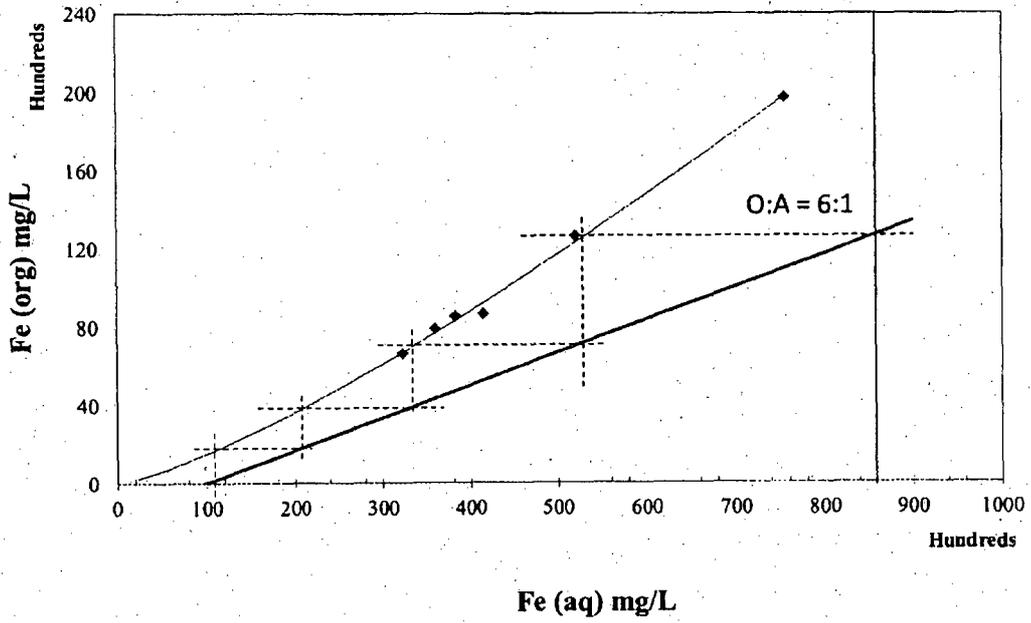


Figure 22

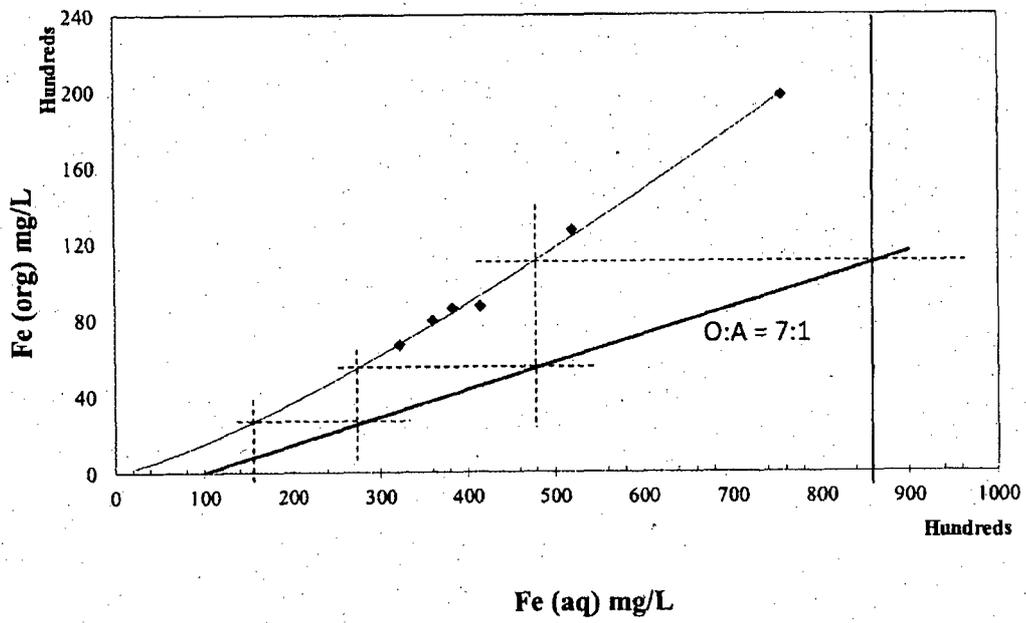


Figure 23

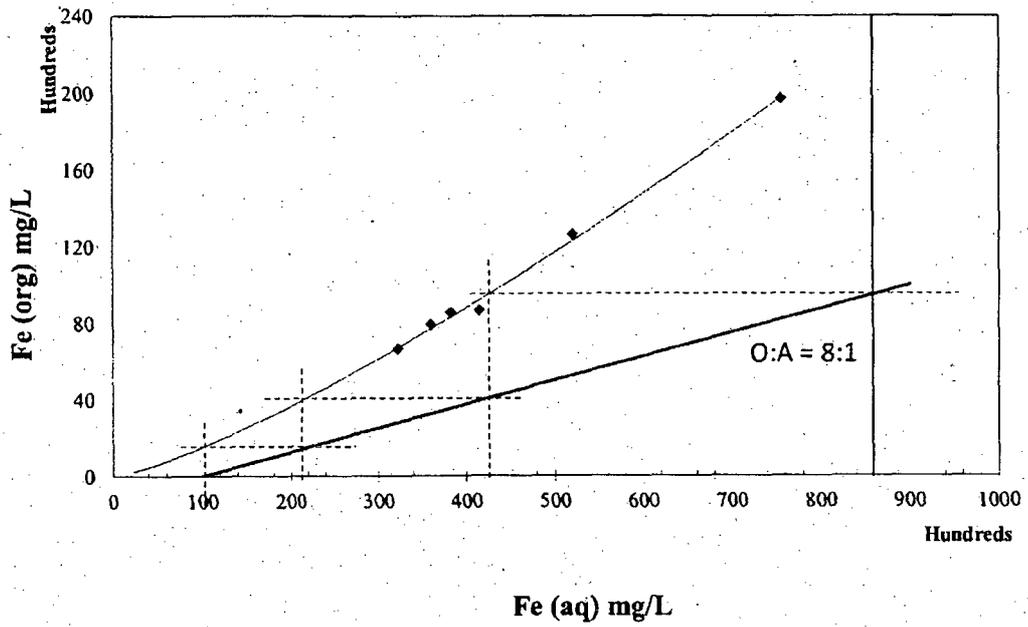


Figure 24

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU20 11/0005 19

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl.		
C22B 3/10 (2006.01) C22B 34/22 (2006.01)		
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)		
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) WPI, EPODOC: IC/EC C22B 3/00, C22B 3/04/-, C22B 3/20/-, C22B 34/22, COIG 31/00 & Keywords (VANADINITE, IRON, TITANOMAGNETITE, VANADIUM, LEACHING, SOLVENT, EXTRACTION, HYDROCHLORIC, ACID) and like terms		
ESPACENET, USPTO, GOOGLE PATENTS & Keywords (VANADIUM, EXTRACTION, RECOVERY, ORE, IRON, LEACHING, SOLVENT) and like terms		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 15 1933 A (HAZEN WAYNE C et al) 6 October 1964 column 1, lines 14 - 27; column 3, lines 1 - 22; claim 1	1 - 4, 6 - 8, 12 - 19
Y	column 1, lines 14 - 27; column 3, lines 1 - 22; claim 1	5, 9 - 11
Y	CYANEX 923 Extractant - Solvent Extraction Reagent [retrieved on 9 June 2011] Retrieved from Internet < URL: http://www.cvtec.com/specialty-chemicals/PDFs/TransformationalSvnthetic/CYANEX%20923.pdf > published on 4 May 2009 page 3, column 1, lines 1 - 5	5, 9 - 11
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
* Special categories of cited documents:		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"
"E"	earlier application or patent but published on or after the international filing date	"X"
"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"
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"
"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 16 June 2011		Date of mailing of the international search report 29 JUN 2011
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustrialia.gov.au Facsimile No. +61 2 6283 7999		Authorized officer VIJAYA MATHE AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No : (02) 6225 6162

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU20 11/0005 19

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Re 29598 A (BARE et al) 28 March 1978 Abstract; claims 1- 32	

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU20 11/0005 19

Bpx No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: **20 - 21**
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
The claims do not comply with Rule 6.2(a) because they rely on references to the description and/or drawings,

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT**Information on patent family members**

International application No.

PCT/AU2011/000519

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
US 3151933	NONE
RE 29598	NONE

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX