



(12) **DEMANDE DE BREVET CANADIEN  
CANADIAN PATENT APPLICATION**

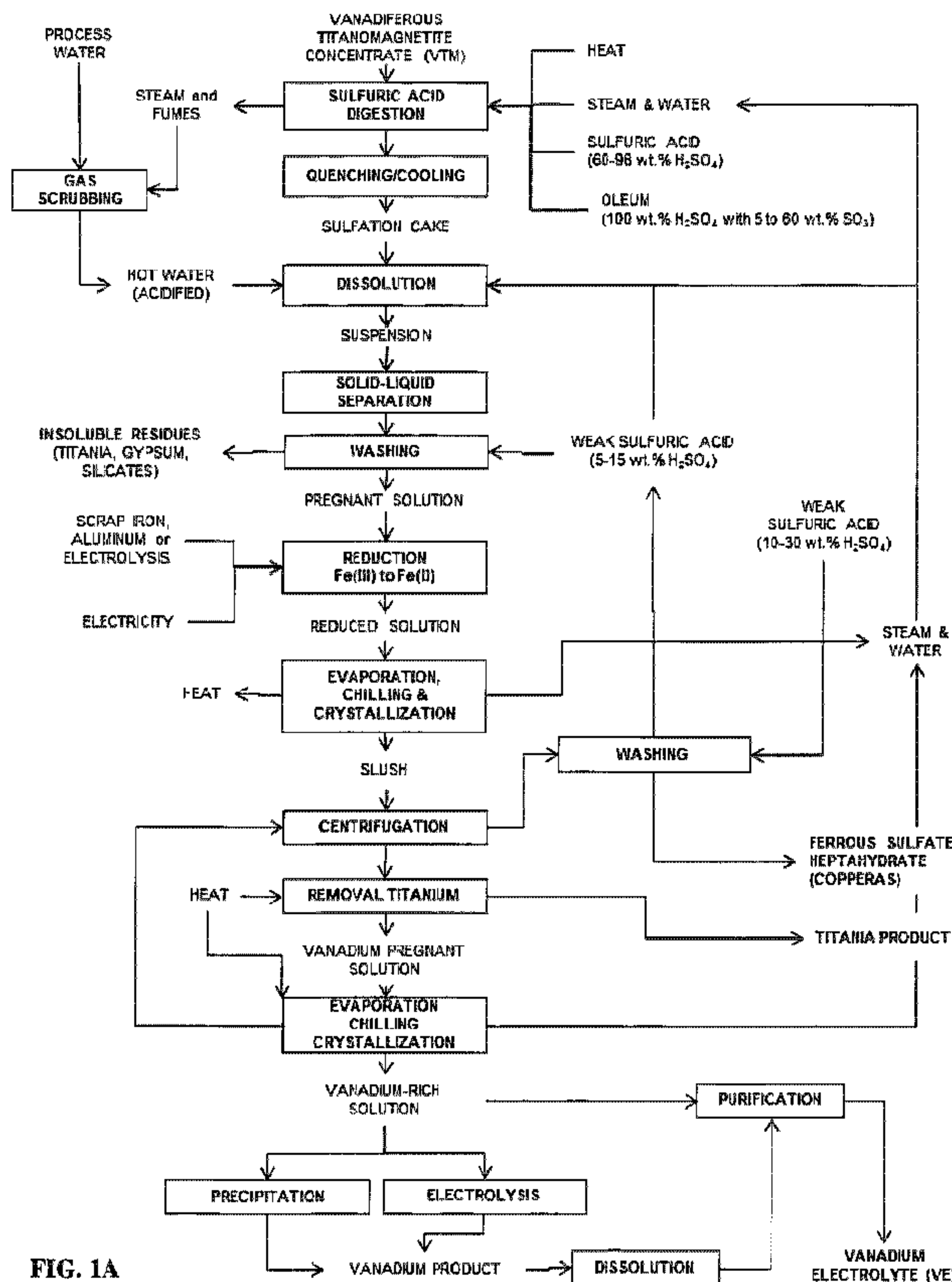
(13) **A1**

(86) Date de dépôt PCT/PCT Filing Date: 2018/02/21  
(87) Date publication PCT/PCT Publication Date: 2018/08/30  
(85) Entrée phase nationale/National Entry: 2019/01/29  
(86) N° demande PCT/PCT Application No.: CA 2018/050196  
(87) N° publication PCT/PCT Publication No.: 2018/152628  
(30) Priorités/Priorities: 2017/02/24 (US62/463,411);  
2017/11/06 (US62/582,060)

(51) Cl.Int./Int.Cl. *C22B 3/08* (2006.01),  
*C01B 33/12* (2006.01), *C01G 23/00* (2006.01),  
*C01G 31/00* (2006.01), *C22B 3/44* (2006.01),  
*C22B 34/22* (2006.01), *C22B 7/00* (2006.01)  
(71) Demandeurs/Applicants:  
VANADIUMCORP RESOURCES INC., CA;  
ELECTROCHEM TECHNOLOGIES & MATERIALS INC.,  
CA  
(72) Inventeur/Inventor:  
CARDARELLI, FRANCOIS, CA  
(74) Agent: BENOIT & COTE INC.

(54) Titre : PROCÉDES METALLURGIQUES ET CHIMIQUES DE RECUPERATION DE VALEURS DE CONCENTRATION EN VANADIUM ET EN FER A PARTIR DE TITANOMAGNETITE VANADIFERE ET DE MATIERES PREMIERES VANADIFERES

(54) Title: METALLURGICAL AND CHEMICAL PROCESSES FOR RECOVERING VANADIUM AND IRON VALUES FROM VANADIFEROUS TITANOMAGNETITE AND VANADIFEROUS FEEDSTOCKS



(57) Abrégé/Abstract:

The present disclosure broadly relates to a process for recovering vanadium, iron, titanium and silica values from vanadiferous feedstocks. More specifically, but not exclusively, the present disclosure relates to a metallurgical process in which vanadium, iron,

(57) **Abrégé(suite)/Abstract(continued):**

titanium and silica values are recovered from vanadiferous feedstocks such as vanadiferous titanomagnetite, iron ores, vanadium slags and industrial wastes and by-products containing vanadium. The process broadly comprises digesting the vanadiferous feedstocks into sulfuric acid thereby producing a sulfation cake; dissolving the sulfation cake and separating insoluble solids thereby producing a pregnant solution; reducing the pregnant solution thereby producing a reduced pregnant solution; and crystallizing ferrous sulfate hydrates from the reduced pregnant solution, producing an iron depleted reduced solution. The process further comprises removing titanium compounds from the iron depleted reduced solution thereby producing a vanadium-rich pregnant solution; concentrating vanadium and recovering vanadium products and/or a vanadium electrolyte.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization

International Bureau

(43) International Publication Date  
30 August 2018 (30.08.2018)(10) International Publication Number  
**WO 2018/152628 A1**

## (51) International Patent Classification:

C22B 3/08 (2006.01) C22B 3/44 (2006.01)  
C01B 33/12 (2006.01) C22B 7/00 (2006.01)  
C01G 23/00 (2006.01) C22B 34/22 (2006.01)  
C01G 31/00 (2006.01)

## (21) International Application Number:

PCT/CA2018/050196

## (22) International Filing Date:

21 February 2018 (21.02.2018)

## (25) Filing Language:

English

## (26) Publication Language:

English

## (30) Priority Data:

62/463,411 24 February 2017 (24.02.2017) US  
62/582,060 06 November 2017 (06.11.2017) US

## (71) Applicants: VANADIUMCORP RESOURCES INC.

[CA/CA]; Suite 400, 1505 West 2nd Avenue, Vancouver, British Columbia V6H 3Y4 (CA). ELECTROCHEM TECHNOLOGIES & MATERIALS INC. [CA/CA]; 2037 Aird Avenue, Suite 201, Montreal, Québec H1V 2V9 (CA).

## (72) Inventor: CARDARELLI, François; 2037 Aird Avenue,

Suite 201, Montreal, Québec H1V 2V9 (CA).

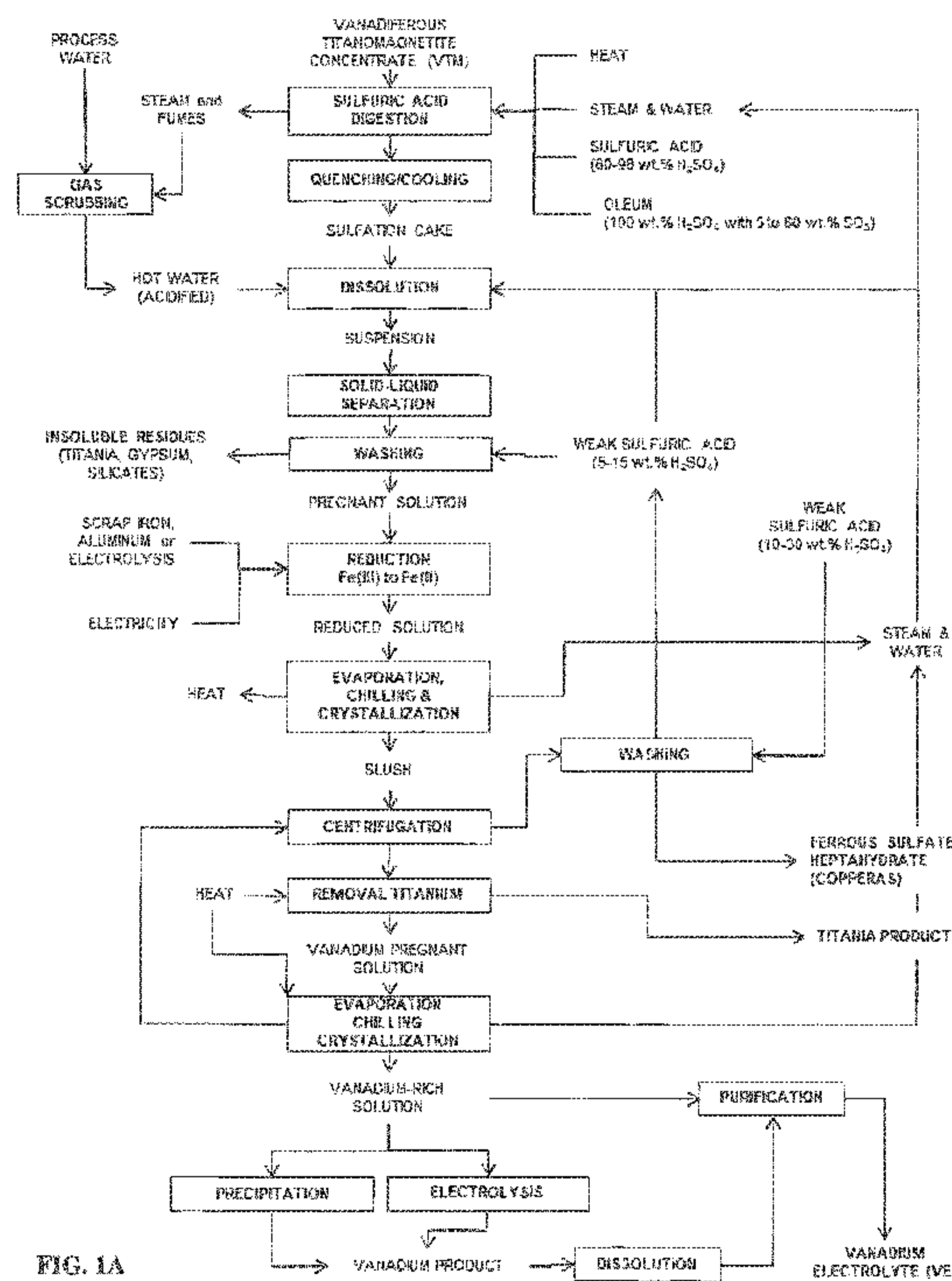
## (74) Agent: BENOÎT &amp; CÔTÉ INC.; 300-560 Cremazie Blvd.

East, Montreal, Québec H2P 1E8 (CA).

## (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, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP,

(54) Title: METALLURGICAL AND CHEMICAL PROCESSES FOR RECOVERING VANADIUM AND IRON VALUES FROM VANADIFEROUS TITANOMAGNETITE AND VANADIFEROUS FEEDSTOCKS



(57) Abstract: The present disclosure broadly relates to a process for recovering vanadium, iron, titanium and silica values from vanadiferous feedstocks. More specifically, but not exclusively, the present disclosure relates to a metallurgical process in which vanadium, iron, titanium and silica values are recovered from vanadiferous feedstocks such as vanadiferous titanomagnetite, iron ores, vanadium slags and industrial wastes and by-products containing vanadium. The process broadly comprises digesting the vanadiferous feedstocks into sulfuric acid thereby producing a sulfation cake; dissolving the sulfation cake and separating insoluble solids thereby producing a pregnant solution; reducing the pregnant solution thereby producing a reduced pregnant solution; and crystallizing ferrous sulfate hydrates from the reduced pregnant solution, producing an iron depleted reduced solution. The process further comprises removing titanium compounds from the iron depleted reduced solution thereby producing a vanadium-rich pregnant solution; concentrating vana-

[Continued on next page]

**WO 2018/152628 A1** 

KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, 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.

**(84) Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, 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, KM, ML, MR, NE, SN, TD, TG).

**Published:**

- *with international search report (Art. 21(3))*
- *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

**CLAIMS**

1. A process for recovering vanadium, iron, titanium and silica values from vanadiferous feedstocks, the process comprising:
  - digesting the vanadiferous feedstocks into sulfuric acid thereby producing a sulfation cake;
  - dissolving the sulfation cake and separating insoluble solids thereby producing a pregnant solution;
  - reducing the pregnant solution thereby producing a reduced pregnant solution;
  - crystallizing ferrous sulfate hydrates from the reduced pregnant solution, producing an iron depleted reduced solution; and
  - removing titanium compounds from the iron depleted reduced solution thereby producing a vanadium-rich pregnant solution.
2. The process of claim 1, further comprising treating the vanadium-rich pregnant solution to recover vanadium products and/or a vanadium electrolyte.
3. The process of claim 1 or 2, wherein the vanadiferous feedstocks comprise materials containing vanadium in various oxidation states.
4. The process of any one of claims 1 to 3, wherein the vanadiferous feedstocks comprise vanadiferous titanomagnetite, iron ores, industrial wastes and/or industrial by-products.
5. The process of claim 4 wherein the iron ores comprise hematite, magnetite, wustite, siderite, ankerite and/or taconite.
6. The process of claim 4 wherein the by-products comprise vanadium bearing metallurgical slags and/or residues from iron making and/or steel making.
7. The process of any one of claims 1 to 6, wherein the sulfuric acid digestion comprises using an aqueous solution of sulfuric acid having a mass percentage from about 5 wt.% H<sub>2</sub>SO<sub>4</sub> to about 100 wt.% H<sub>2</sub>SO<sub>4</sub>.
8. The process of claim 7, wherein the aqueous solution of sulfuric acid has a mass percentage from about 15 wt.% H<sub>2</sub>SO<sub>4</sub> to about 99 wt.% H<sub>2</sub>SO<sub>4</sub>.

9. The process of claim 7 or 8, wherein the aqueous solution of sulfuric acid has a mass percentage from about 30 wt.% H<sub>2</sub>SO<sub>4</sub> to about 98 wt.% H<sub>2</sub>SO<sub>4</sub>.
10. The process of any one of claims 1 to 9, wherein the sulfuric acid digestion further comprises the use of oleum.
11. The process of claim 10, wherein the oleum comprises substantially 100 wt.% H<sub>2</sub>SO<sub>4</sub> and an excess of up to 65 wt.% of dissolved SO<sub>3</sub>.
12. The process of any one of claims 1 to 11, wherein the sulfuric acid digestion further comprises the addition of ammonium or alkali-metal sulfates of general formula M<sub>2</sub>SO<sub>4</sub> to the sulfuric acid, wherein M is NH<sub>4</sub><sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup> or K<sup>+</sup>.
13. The process of any one of claims 1 to 6, wherein the vanadiferous feedstocks are ground to a particle size of less than about 0.500 millimeter.
14. The process of claim 13, wherein the vanadiferous feedstocks are ground to a particle size of less than about 0.125 millimeter.
15. The process of claim 13 or 14, wherein the vanadiferous feedstocks are ground to a particle size of less than about 0.050 millimeter.
16. The process of any one of claims 1 to 15, wherein the vanadiferous feedstocks are oven dried prior to being processed to remove residual moisture.
17. The process of claim 16, wherein the vanadiferous feedstocks are fed into the sulfuric acid at a temperature ranging from 20°C to 400°C and stirred.
18. The process of claim 16, wherein the vanadiferous feedstocks are mixed with the sulfuric acid to produce a suspension, a slurry or a paste and heating the suspension, slurry or paste to a temperature ranging from 50°C to 250°C.
19. The process of claim 16, wherein the vanadiferous feedstocks are mixed with the sulfuric acid to produce a suspension, a slurry or a paste and water and/or steam are injected into the

suspension, slurry or paste to raise the temperature of the suspension, slurry or paste to a temperature ranging from 50°C to 250°C.

20. The process of claim 15, wherein the vanadiferous feedstocks comprise a moisture content from about 0.5 wt.% up to about 60 wt.%.
21. The process of claim 20, wherein the vanadiferous feedstocks are fed into the sulfuric acid and stirred.
22. The process of any one of claims 1 to 21, wherein the sulfuric acid digestion is performed at temperatures ranging from about 20°C to about 400°C.
23. The process of claim 22, wherein the sulfuric acid digestion is performed at temperatures ranging from about 50°C to about 300°C.
24. The process of claim 22 or 23, wherein the sulfuric acid digestion is performed at temperatures from about 75°C to about 250°C.
25. The process of claim 1, wherein the vanadiferous feedstocks are pre-reduced using a thermal reduction process prior to the sulfuric acid digestion.
26. The process of claim 25, wherein the thermal reduction process comprises the use of a reductant chosen from at least one of anthracite, sub-bituminous coal, bunker oil, natural gas, methane, carbon monoxide, hydrogen gas, water gas or smelter gas.
27. The process of claim 1, wherein the vanadiferous feedstocks are pre-oxidized or roasted using a thermal process prior to the sulfuric acid digestion.
28. The process of claim 27, wherein the thermal process is performed in air or oxygen enriched air.
29. The process of claim 1, wherein the sulfuric acid digestion is performed with a solution of sulfuric acid (L) and a mass of vanadiferous feedstocks (S) having a mass ratio (L-to-S) not exceeding twenty to one (20:1 or 20 kg/kg).

30. The process of claim 29, wherein the mass ratio (L-to-S) is not exceeding ten to one (10:1 or 10 kg/kg).
31. The process of claim 29 or 30, wherein the mass ratio (L-to-S) is not exceeding five to one (5:1 or 5 kg/kg).
32. The process of any one of claims 29 to 31, wherein the mass ratio (L-to-S) is not exceeding two to one (2:1 or 2 kg/kg).
33. The process of claim 1, wherein the sulfuric acid digestion is performed with a mass of pure sulfuric acid (100 wt.% H<sub>2</sub>SO<sub>4</sub>) (A) and a mass of vanadiferous feedstocks (S) having a mass ratio (A-to-S) not exceeding twenty to one (20:1 or 20 kg/kg).
34. The process of claim 33, wherein the mass ratio (A-to-S) is not exceeding five to one (5:1 or 5 kg/kg).
35. The process of claim 33 or 34, wherein the mass ratio (A-to-S) is not exceeding three to one (3:1 or 3 kg/kg).
36. The process of any one of claims 33 to 35, wherein the mass ratio (A-to-S) is not exceeding two to one (2:1 or 2 kg/kg).
37. The process of claim 1, wherein the sulfuric acid digestion is performed with pure sulfuric acid (100 wt.% H<sub>2</sub>SO<sub>4</sub>) (A) and a mass of vanadiferous feedstocks (S) having a mass ratio (A-to-S) of two to one (2:1 or 2 kg/kg).
38. The process of claim 1, wherein the sulfuric acid digestion is performed over a period ranging from about five (5) minutes up to about twenty-four (24) hours.
39. The process of claim 38, wherein the sulfuric acid digestion is performed over a period ranging from about ten (10) minutes up to about fifteen (15) hours.
40. The process of claim 38 or 39, wherein the sulfuric acid digestion is performed over a period ranging from about fifteen (15) minutes up to about ten (10) hours.



41. The process of any one of claims 38 to 40, wherein the sulfuric acid digestion is performed over a period ranging from about thirty (30) minutes up to about six (6) hours.
42. The process of claim 1, wherein the sulfuric acid digestion is performed in air.
43. The process of claim 1, wherein the sulfuric acid digestion is performed under an inert atmosphere.
44. The process of claim 1, wherein the sulfuric acid digestion is performed at atmospheric pressure.
45. The process of claim 1, wherein the sulfuric acid digestion is performed under pressure.
46. The process of claim 45, wherein the sulfuric acid digestion is performed in an autoclave.
47. The process of claim 1, wherein the sulfuric acid digestion is performed batch wise.
48. The process of claim 47, wherein the sulfuric acid digestion is performed using a brick-lined digester or a corrosion resistant vessel.
49. The process of claim 1, wherein the sulfuric acid digestion is performed semi-continuously or continuously.
50. The process of claim 1, wherein the sulfuric acid digestion is performed using a rotary kiln or a rotary heart furnace.
51. The process of claim 22, wherein external heating is provided.
52. The process of claim 51, wherein the external heating is provided using a jacketed vessel comprising a hot circulation fluid, indirect flame heating, gas fired burners, gas heaters or electrical heaters.
53. The process of claim 22, wherein internal heating is provided.
54. The process of claim 53, wherein the internal heating is provided using direct flame heating, gas fired burners, radiant gas heaters, internal electrical heaters or Joule heating using immersed AC or DC electrodes.

55. The process of claim 22, wherein the sulfuric acid digestion is performed autogenously by injecting water or steam into a mixture comprising the sulfuric acid and the vanadiferous feedstocks pre-heated at a temperature ranging from about 40°C to about 110°C.
56. The process of claim 1, wherein the sulfuring acid digestion comprises agitating a mixture comprising the sulfuric acid and the vanadiferous feedstocks.
57. The process of claim 56, wherein the agitating is performed mechanically using motor-driven impellers.
58. The process of claim 56, wherein the agitating is performed by injecting compressed gas into the mixture.
59. The process of claim 58, wherein the injection of the compressed gas is performed through nozzles or porous plugs located at a bottom portion of a digester, a corrosion resistant vessel, a rotary kiln or a rotary heart furnace.
60. The process of claim 58, wherein the injection of the compressed gas is performed using a lance.
61. The process of claim 1, wherein the sulfuring acid digestion is performed in a temperature and corrosion resistant containment vessel or a digester.
62. The process of claim 61, wherein the containment vessel or digester comprises bulk metals or alloys.
63. The process of claim 62, wherein the bulk metals or alloys include high silicon cast iron or high nickel-alloys.
64. The process of claim 63, wherein the high silicon cast iron is Duriron®.
65. The process of claim 63, wherein the high nickel-alloys are Hastelloy® B2, or Hastelloy® C-276.
66. The process of claim 61, wherein the containment vessel or digester comprises composite metallic materials.

67. The process of claim 66, wherein the composite metallic materials include cast iron, steel, heat resistant stainless steels and high nickel alloys clad with an inner liner made of a corrosion resistant material.
68. The process of claim 67, wherein the corrosion resistant material includes tantalum, enamel, glass, or a polymeric material.
69. The process of claim 68, wherein the polymeric material includes at least one of TFE, PVDF, PTFE or PFA.
70. The process of claim 61, wherein the digester comprises a steel shell lined with at least one impervious layer and at least one refractory layer.
71. The process of claim 70, wherein the impervious layer comprises plastics, elastomers, lead or lead alloys.
72. The process of claim 70, wherein the refractory layer comprises high silica bricks assembled with an acid resistant mortar comprising silica and/or potassium silicate.
73. The process of claim 1, wherein the sulfation cake is dissolved into at least one of water, acidified water or weak sulfuric acid.
74. The process of claim 73, wherein the weak sulfuric acid comprises from about 1 g/L to about 300 g/L of H<sub>2</sub>SO<sub>4</sub>.
75. The process of claim 73 or 74, wherein the weak sulfuric acid comprises from about 5 g/L to about 150 g/L of H<sub>2</sub>SO<sub>4</sub>.
76. The process of any one of claims 73 to 75, wherein the dissolution of the sulfation cake is performed at a temperature ranging from about 20°C to about 100°C.
77. The process of any one of claims 73 to 76, wherein the dissolution of the sulfation cake is performed in multistage concurrent mode.
78. The process of any one of claims 73 to 76, wherein the dissolution of the sulfation cake is performed in multistage countercurrent mode.

79. The process of any one of claims 73 to 76, wherein the dissolution of the sulfation cake is performed in batch concurrent multiple contact mode.
80. The process of any one of claims 73 to 76, wherein the dissolution of the sulfation cake is performed in batch countercurrent multiple contact mode.
81. The process of claim 1, wherein the pregnant solution is at a pH below 2.0.
82. The process of claim 1, wherein the pregnant solution is kept at a temperature ranging from about 20°C to about 80°C.
83. The process of claim 73, wherein the dissolution of the sulfation cake is performed with a mass of the at least one of water, acidified water or weak sulfuric acid (W) and a mass of sulfation cake (B) having a mass ratio (W-to-B) not exceeding twenty to one (20:1 or 20 kg/kg).
84. The process of claim 83, wherein the mass ratio (W-to-B) is not exceeding ten to one (10:1 or 10 kg/kg).
85. The process of claim 83 or 84, wherein the mass ratio (W-to-B) is not exceeding five to one (5:1 or 5 kg/kg).
86. The process of any one claims 83 to 85, wherein the mass ratio (W-to-B) is not exceeding two to one (2:1 or 2 kg/kg).
87. The process of claim 73, wherein the dissolution of the sulfation cake is performed with a mass of the at least one of water, acidified water or weak sulfuric acid (W) and a mass of sulfation cake (B) having a mass ratio (W-to-B) of two to one (2:1 or 2 kg/kg).
88. The process of claim 1, wherein the insoluble residues are separated from the pregnant solution by solid-liquid separation techniques producing a filter cake.
89. The process of claim 88, further comprising recovering silica and/or titanium dioxide values from the filter cake.

90. The process of claim 1, wherein reducing the pregnant solution comprises reacting the pregnant solution with at least one of metallic iron, aluminum, magnesium, zinc or alloys thereof.
91. The process of claim 90, wherein the metallic iron, aluminum, magnesium, zinc or alloys thereof comprise scrap, powder, flakes or turnings.
92. The process of claim 1, wherein reducing the pregnant solution comprises reacting the pregnant solution with sulfur dioxide gas.
93. The process of claim 1, wherein reducing the pregnant solution comprises electrochemically reducing the pregnant solution.
94. The process of claim 93, wherein the electrochemical reduction is performed using an undivided electrolyzer comprising a cathode and a sacrificial anode.
95. The process of claim 94, wherein the sacrificial electrode comprises iron, steel, aluminum, zinc or alloys thereof.
96. The process of claim 94, wherein the cathode comprises a metallic cathode.
97. The process of claim 96, wherein the metallic cathode comprises at least one of iron, iron alloys, nickel, nickel alloys, copper, copper alloys, zinc, zinc alloys, titanium, titanium alloys, zirconium, zirconium alloys, lead, lead alloys, or austenitic stainless steels.
98. The process of claim 93, wherein the electrochemical reduction is performed using a divided electrolyzer.
99. The process of claim 98, wherein the divided electrolyzer comprises a catholyte consisting of the pregnant solution.
100. The process of claim 98 or 99, wherein the divided electrolyzer comprises a separator and mixed metal oxides (MMO) anodes or hydrogen depolarized anodes (HAD).
101. The process of claim 100, wherein the separator comprises a diaphragm or an ion exchange membrane.

102. The process of claim 1, further comprising concentrating the reduced pregnant solution.
103. The process of claim 102, further comprising cooling the concentrated pregnant solution to a temperature not exceeding about 10°C producing the crystallized ferrous sulfate hydrates.
104. The process of claim 103, wherein the concentrated pregnant solution is cooled to a temperature not exceeding about 5°C.
105. The process of claim 103 or 104, wherein the concentrated pregnant solution is cooled to a temperature not exceeding about 0°C.
106. The process of any one of claims 103 to 105, wherein the cooling is performed using a crystallizer.
107. The process of any one of claims 103 to 106, wherein the crystallized ferrous sulfate hydrates are isolated by solid-liquid separation producing the iron depleted reduced solution.
108. The process of claim 107, wherein the crystalline ferrous sulfate hydrates are rinsed with sulfuric acid.
109. The process of claim 1, further comprising heating the iron depleted reduced solution and adding an alkaline material to the iron depleted reduced solution to precipitate the titanium compounds.
110. The process of claim 109, wherein the alkaline material comprises at least one of an alkali-metal, an ammonium carbonate or an ammonium sulfate.
111. The process of claim 109 or 110, wherein the pH of the iron depleted reduced solution is adjusted to values ranging from about 0.5 to about 2.5.
112. The process of any one of claims 109 to 111, wherein the titanium compounds comprise compounds of at least formulas  $MTi_3(SO_4)_4(OH)_6$  and  $[Ti_2(SO_4)_3]_x[H_2SO_4]_y$ , wherein M is selected from the group consisting of  $H^+$ ,  $NH_4^+$ ,  $Na^+$  and  $K^+$ ; and x and y are independently selected integers ranging from 1 to 10.

- 113.** The process of claim **112**, wherein seeds of the compounds of formula  $MTi_3(SO_4)_4(OH)_6$  are added to the iron depleted reduced solution to trigger the precipitation.
- 114.** The process of any one of claims **109** to **113**, wherein the precipitate is isolated by solid-liquid separation producing the vanadium-rich pregnant solution.
- 115.** The process of claim **114**, further comprising washing and drying the precipitate.
- 116.** The process of claim **115**, further comprising oxidizing the precipitate.
- 117.** The process of claim **116**, further comprising leaching the precipitate using sulfuric acid producing a titanium dioxide product.
- 118.** The process of claim **1**, further comprising removing any residual titanium values from the vanadium-rich pregnant solution.
- 119.** The process of claim **114**, further comprising removing any residual titanium values from the vanadium-rich pregnant solution.
- 120.** The process of claim **118** or **119**, wherein the residual titanium values are removed by boiling and hydrolysis.
- 121.** The process of claim **1**, further comprising recovering vanadium values from the vanadium-rich pregnant solution.
- 122.** The process of claim **120**, further comprising recovering vanadium values from the vanadium-rich pregnant solution.
- 123.** The process of claim **121** or **122**, wherein the vanadium values are recovered by crystallization.
- 124.** The process of claim **121** or **122**, wherein the vanadium values are recovered by chemical precipitation of vanadium compounds.
- 125.** The process of claim **121** or **122**, wherein the vanadium values are recovered by chemical precipitation of hydrated oxides and/or hydroxides of vanadium (IV).

- 126.** The process of claim **125**, wherein the vanadium values are recovered by oxidation of the precipitated hydrated oxides and/or hydroxides of vanadium (IV) to vanadium (V) and caustic or alkaline leaching to extract vanadium (V) as a soluble alkali-metal vanadate.
- 127.** The process of claim **121** or **122**, wherein the vanadium values are recovered by oxidation of the vanadium-rich pregnant solution followed by chemical precipitation of oxides and/or hydroxides of vanadium (V) and iron (III).
- 128.** The process of claim **127**, further comprising caustic or alkaline leaching to extract vanadium (V) as a soluble alkali-metal vanadate.
- 129.** The process of claim **121** or **122**, wherein the vanadium values are recovered by removal of any remaining iron (II) by oxidation to iron (III) using ammonium persulfate and precipitation of the oxidized iron as natrojarosite or other jarosite type solids.
- 130.** The process of claim **126** or **127**, further comprising precipitating ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ).
- 131.** The process of claim **121** or **122**, wherein the vanadium values are recovered by electrolysis.
- 132.** The process of claim **1**, further comprising purifying the vanadium-rich pregnant solution producing a vanadium electrolyte.
- 133.** The process of claim **118**, further comprising purifying the vanadium-rich pregnant solution producing a vanadium electrolyte.
- 134.** The process of claim **119**, further comprising purifying the vanadium-rich pregnant solution producing a vanadium electrolyte.
- 135.** The process of any one of claims **126** to **133**, wherein the vanadium-rich pregnant solution is purified by ion exchange, solvent extraction, electrolysis, or electrodialysis.



- 136.** A process for recovering vanadium and iron values from vanadiferous feedstocks comprising digesting the vanadiferous feedstocks using sulfuric acid, producing vanadium pentoxide, and preparing a vanadium electrolyte.
- 137.** The process according to claim **136**, wherein the sulfuric acid digestion is performed at temperatures ranging from room temperature up to 400°C.
- 138.** The process according to claim **136** or **137**, wherein the vanadiferous feedstock is ground to a particle size below 0.500 millimeter.
- 139.** The process according to any one of claims **136** to **138**, wherein the vanadiferous feedstock is oven dried prior to being processed for removing the residual moisture.
- 140.** The process according to claim **139**, wherein the ground and oven dried vanadiferous feedstock is mixed with sulfuric acid in order to produce a suspension, a slurry or a paste and the temperature of the mixture is raised by heating the mixture until the operating temperature is reached.
- 141.** The process according to any one of claims **136** to **140**, wherein the sulfuric acid digestion is performed in air or inert atmosphere.
- 142.** The process according to any one of claims **136** to **140**, wherein the sulfuric acid digestion is performed at atmospheric pressure or under pressures in excess of atmospheric pressure.
- 143.** The process according to any one of claims **136** to **142**, wherein the vanadiferous feedstocks comprise materials containing vanadium in various oxidation states or a mixture thereof including vanadiferous titanomagnetite, iron ores such as hematite, magnetite, wustite, siderite, ankerite, taconite, vanadium slags, industrial wastes and by-products containing vanadium such as metallurgical slags from iron and steel making.