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PATENT SPECIFICATION

NO DRAWINGS

1.039.621

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COMPLETE SPECIFICATION

Process for the Extraction of Metals

We, RIO TINTO FINANCE & EXPLORATION LIMITED, a British Company, of 9, Basinghall Street, London, E.C.2, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the extraction of metals by exchange reaction with a more basic metal.



where metal A is less basic than metal B. The term metal ion used herein includes the uranyl ion, UO_2^{++} .

The metals normally encountered in hydro-metallurgical processes can be arranged in the following order of increasing basicity:—

(a) Fe^{++} (b) UO_2^{++} (c) Sn^{++} (d) Al (e) Hg (f) Cu or Cd (g) Pb or Ag or Zn (h) Ni or Co or Fe^{++} (i) Mn (j) Ca or Mg.

The metal naphthenate of any metal in the above series will react, according to the above general equation, with all metals which are less basic, i.e. with metals which appear earlier in the series. Thus if the metal B is an alkaline earth metal, the exchange reaction will occur with all metals other than the alkaline and alkaline earth metals. If the metal B is nickel, the exchange reaction will occur, for example with Fe^{++} , Sn^{++} , Cu, Zn and somewhat less readily with Cd. The exchange reaction becomes more difficult as the two metals concerned become closer in the given series. However, even with adjacent members of the series, it is possible to obtain an exchange extraction by using an excess of the more basic metal in the organic phase.

The invention is illustrated by the following examples:—

[Price 4s. 6d.]

It has been found that metal values may be recovered from aqueous media containing them by extraction in accordance with the principle that a metal ion present as a salt of an oil-soluble organic acid in an organic phase can be replaced by a less basic metal ion in an aqueous phase, on contacting the aqueous and organic phases, according to the general equation.

EXAMPLE 1

The extraction of ferric iron with copper naphthenate.

25.0 mls of an aqueous solution, buffered at pH 2.1 and containing 4.58 g/l Fe was contacted with different volumes of a kerosene solution of copper naphthenate containing 13.5 g/l Cu. The two phases, at room temperature were mixed for $\frac{1}{2}$ hour by stirring and then allowed to separate and were analysed for Cu and Fe. During the exchange extraction reaction the pH of the aqueous phase tends to rise but this may be overcome by the controlled addition of acid during extraction or by buffering the aqueous solution. If the pH rises too high an insoluble precipitate of a hydrolysed iron compound, (e.g. basic sulphate or hydroxide), is formed. The results given in Table 1 attached, show that the removal of iron from the aqueous phase with a mole ratio of Cu:Fe = 2.124:2.05 is so complete that it can only be detected in the p.p.m. range.

EXAMPLE 2

The extraction of ferric iron with zinc naphthenate.

25 mls of an aqueous solution buffered to pH 1.9, and containing 4.66 g/l Fe was contacted with different volumes of a kerosene

solution of zinc naphthenate containing 28.0 g/l Zn. The two phases at room temperature were mixed for $\frac{1}{2}$ an hour by stirring and then allowed to separate and were analysed for Zn and Fe. In this system also it was necessary to prevent the pH rising too high during the exchange extraction reaction to avoid precipitation of insoluble iron compounds. The results given in Table II attached show that complete removal of iron is obtained with a mole ratio of Zn: Fe of 2.14:2.09.

EXAMPLE 3

The extraction of nickel with manganese naphthenate.

25 mls of an aqueous solution of pH 5.4 and

containing 2.92 g/l Ni was contacted with different volumes of a kerosene solution of manganese naphthenate containing 13.8 g/l Mn. The two phases, at room temperature, were mixed for $\frac{1}{2}$ an hour by stirring and then allowed to separate and analysed for Mn and Ni. With this system it was not necessary to control the pH during the exchange extraction reaction since insoluble precipitates were not formed. With this system larger quantities of the organic phase constituent are required for complete reaction than with the systems described in Examples 1 and 2. Thus the results in Table III attached show that a mole ratio of Mn: Ni = 6.28:1.24 is necessary to remove 94.17% of the nickel from the aqueous phase.

TABLE I

System Cu naphthenate/Fe⁺⁺⁺ aq., buffered at pH 2.1

Before Contact					
Organic Phase			Aqueous Phase		
Assay Cu	Vol. Used	Moles Cu	Assay Fe	Vol. Used	Moles Fe
13.5 g/l	5.00 mls	1.062 m moles	4.58 g/l	25.00 mls	2.05 m moles
	10.00	2.124			
	15.00	3.186			
	20.00	4.248			
	25.00	5.310			
	30.00	6.372			

After Contact				
Aqueous Phase			Organic Phase	
Assay		% Extn-Fe	Moles Cu stripped	% Cu stripped
Cu	Fe			
3.05 g/l	150 ppm	100	1.2 m. moles	100
4.15	10	100	1.635	77
4.09	10	100	1.61	50.5
4.20	10	100	1.65	38.9
4.20	10	100	1.65	31.1
4.15	10	100	1.635	25.7

TABLE II

System Zinc Naphthenate/Fe^{III} aq buffered at pH 1.9

Before Contact					
Organic Phase			Aqueous Phase		
Assay Zn	Vol. Used	Moles Zn	Assay Fe	Vol. Used	Moles Fe
28.0 g/l	2.50 mls	1.07 m moles	4.66 g/l	25.00 mls	2.09 m moles
	5.00	2.14			
	10.00	4.28			
	15.00	6.42			
	20.00	8.56			

After Contact					
Aqueous Phase				Organic Phase	
Assay		% Extn-Fe	pH	Moles Zn Stripped	% Zn Stripped
Zn	Fe				
3.40 g/l	0.89 g/l	80.9	3.2	1.297 m moles	100
6.22	N.D.*	100	4.3	2.375	100
8.17	N.D.	100	5.1	3.125	72.9
8.05	N.D.	100	5.2	3.07	47.8
8.17	N.D.	100	5.3	3.125	36.5

* the abbreviation N.D. used above means "not detected"

TABLE III

System Mn Naphthenate/Ni^{II} aq — NOT buffered

Before Contact					
Organic Phase			Aqueous Phase		
Assay Mn	Vol. Used	Moles Mn	Assay Ni	Vol. Used	Moles Ni
13.8 g/l	5.00 mls	1.256 m moles	2.92 g/l pH 5.4	25.00 mls	1.24 m moles
	10.00	2.512			
	15.00	3.768			
	20.00	5.024			
	25.00	6.280			
	30.00	7.536			

After Contact				
Aqueous Phase			Organic Phase	
Assay		% Extn. Ni	Moles Mn stripped	% Mn stripped
Mn	Ni			
1.84 g/l	1.01 g/l	65.4	0.838 m. moles	66.8
2.29	0.48	83.6	1.04	41.4
2.39	0.32	89.05	1.057	28.8
2.43	0.25	91.44	1.105	22.1
2.43	0.17	94.17	1.105	17.6
2.43	0.15	94.86	1.105	14.7

WHAT WE CLAIM IS:—

1. A method of recovering metal values from aqueous media, in which a metal ion as herein defined present as a salt of an oil-soluble organic acid, dissolved in an organic phase is contacted with the less basic metal ion in an aqueous phase, to exchange metal ions between the two phases.
2. A method as claimed in claim 1, in which a metal ion from one of the divisions (a) to (j) of the series (a) Fe⁺⁺⁺ (b) UO₂⁺⁺ (c) Sn⁺⁺ (d) Al (e) Hg (f) Cu or Cd (g) Pb or Ag or Zn (h) Ni or Co or Fe⁺⁺ (i) Mn (j) Ca or Mg is present in the organic phase and replaces a less basic metal ion from an earlier division, dissolved in the aqueous phase.
3. A method as claimed in claim 1 or 2 in which the organic acid is naphthenic acid.
4. A method as claimed in any one preceding claim, in which the organic phase is kerosene.
5. A method as claimed in any of claims 1 to 4 in which ferric iron is extracted from aqueous media by copper naphthenate.
6. A method as claimed in any of claims 1 to 4, in which ferric iron is extracted from aqueous media by zinc naphthenate.
7. A method as claimed in any of claims 1 to 4, in which nickel ions are extracted from aqueous media by manganese naphthenate.
8. A method as claimed in claim 1, substantially as herein described with reference to any of the Examples.

TABLE III

System Mn Naphthenate/ Ni^{++} aq — NOT buffered

Before Contact					
Organic Phase			Aqueous Phase		
Assay Mn	Vol. Used	Moles Mn	Assay Ni	Vol. Used	Moles Ni
13.8 g/l	5.00 mls	1.256 m moles	2.92 g/l pH 5.4	25.00 mls	1.24 m moles
	10.00	2.512			
	15.00	3.768			
	20.00	5.024			
	25.00	6.280			
	30.00	7.536			

After Contact				
Aqueous Phase			Organic Phase	
Assay		% Extn. Ni	Moles Mn stripped	% Mn stripped
Mn	Ni			
1.84 g/l	1.01 g/l	65.4	0.838 m. moles	66.8
2.29	0.48	83.6	1.04	41.4
2.39	0.32	89.05	1.057	28.8
2.43	0.25	91.44	1.105	22.1
2.43	0.17	94.17	1.105	17.6
2.43	0.15	94.86	1.105	14.7

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2. A method as claimed in claim 1, in which a metal ion from one of the divisions (a) to (j) of the series (a) Fe^{+++} (b) UO_2^{++} (c) Sn^{++} (d) Al (e) Hg (f) Cu or Cd (g) Pb or Ag or Zn (h) Ni or Co or Fe^{++} (i) Mn (j) Ca or Mg is present in the organic phase and replaces a less basic metal ion from an earlier division, dissolved in the aqueous phase.

3. A method as claimed in claim 1 or 2 in which the organic acid is naphthenic acid.

4. A method as claimed in any one preceding claim, in which the organic phase is kerosene.

5. A method as claimed in any of claims 1 to 4 in which ferric iron is extracted from aqueous media by copper naphthenate.

6. A method as claimed in any of claims 1 to 4, in which ferric iron is extracted from aqueous media by zinc naphthenate.

7. A method as claimed in any of claims 1 to 4, in which nickel ions are extracted from aqueous media by manganese naphthenate.

8. A method as claimed in claim 1, substantially as herein described with reference to any of the Examples.



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B.K.

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