



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : B03D 1/008, 1/02	A1	(11) International Publication Number: WO 91/12080 (43) International Publication Date: 22 August 1991 (22.08.91)
(21) International Application Number: PCT/AU91/00041 (22) International Filing Date: 7 February 1991 (07.02.91) (30) Priority data: PJ 8505 7 February 1990 (07.02.90) AU (71) Applicant (for all designated States except US): COMMON-WEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION [AU/AU]; Limestone Avenue, Canberra, ACT 2602 (AU). (72) Inventors; and (75) Inventors/Applicants (for US only) : SENIOR, Geoffrey, David [AU/AU]; 3 Dominion Avenue, Glen Waverley, VIC 3150 (AU). TRAHAR, William, John [AU/AU]; 326 Balwyn Road, North Balwyn, VIC 3104 (AU). CREED, Michael, Denis [AU/AU]; 19 Bedford Road, Ringwood, VIC 3154 (AU).		(74) Agents: KILBORN, Paul, A. et al.; Sirotech Limited, 580 Church Street, Richmond, VIC 3121 (AU). (81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US. Published <i>With international search report.</i>
(54) Title: PROCESSING OF MINERAL DEPOSITS		
(57) Abstract <p>A process for the recovery of zircon from a particulate zircon-containing material. The process involves contacting the zircon-containing material with a soap solution followed by at least one water wash and at least one acid wash. The acid washed product is then subjected to flotation whereby zircon is floated. The feed material to the process may be a pre-concentrate which is produced by flotation. In a further aspect of the invention titanium containing minerals which are depressed during the zircon flotation stage may be recovered by flotation using an anionic collector such as carboxylate, phosphonate or sulphonated fatty acid. A sulphosuccinamate is preferred.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LJ	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

Processing of Mineral Deposits

Technical Field

This invention relates to the processing of mineral deposits and is particularly concerned with the processing of heavy mineral deposits.

Background Art

Heavy mineral deposits can contain as little as a few percent of valuable heavy minerals in a mixture with gangue minerals of varying composition. Most of these gangue minerals have a specific gravity (S.G.) less than 2.96 while the valuable minerals have S.G.'s above 3.3. Common heavy minerals are zircon ($ZrSiO_4$), the rare earth minerals monazite and xenotime and the titanium minerals rutile, anatase, ilmenite and leucoxene. Other valuable heavy minerals including alteration products of the primary minerals are also common in some deposits.

Heavy mineral sand processing currently involves a stage of wet gravity concentration to recover the heavy minerals and a separation stage involving dry concentration methods. In some cases additional wet concentration (either by gravity or magnetic methods) is necessary to produce products of high grade. Differences in the settling rates of minerals are used to achieve a separation in gravity concentration. Various types of equipment are used, including jigs, spirals, cones, pinched sluices and tables. Dry concentration methods are those of magnetic and electrostatic separation which separate the heavy minerals on the basis of their magnetic susceptibilities and electrical conductivities. For example, a good separation of zircon from rutile can be made using an electrostatic separator if the minerals are clean and of a suitable size because zircon is a poor conductor and rutile is a good conductor.

In principle, the surface properties of some heavy minerals differ enough for a separation to be made using flotation. A flotation method (the hot soap method) was developed in the 1930's to separate coarse zircon from rutile after wet gravity concentration but commercial use of this process ceased sometime in the late 1960's. No other commercial operator is believed to have used a flotation process on a commercial scale owing to the development after 1935 of electrostatic separation (Dunkin, 1953; Blaskett and Hudson, 1965).

Both wet gravity and dry separation methods operate efficiently on coarse (75 to 300 μ m) particles but are inefficient at fine (less than 75 μ m) sizes. Therefore they are not well suited for the processing of fine heavy minerals. We have found that flotation can be efficiently used to separate zircon from fine particles. This discovery allows for the treatment of heavy minerals which are much finer than those now mined. Such deposits are a valuable resource that is not currently exploited.

Disclosure of the Invention

Accordingly, in one aspect, the present invention provides a process for the recovery of zircon from a particulate zircon-containing material said process including

providing

(a) a zircon-containing material, said material having a particle size less than about 75 μ m; and

(b) a soap;

(c) contacting said zircon-containing material with a solution of said soap in the presence of an alkali at a temperature in the range 40°C to the boiling point of the solution to produce a soap-treated product;

(d) subjecting said soap-treated product to at least one water wash to form a water-washed product;

- (e) subjecting said water-washed product to at least one acid wash to form an acid-washed product; and
- (f) floating zircon from said acid-washed product.

The zircon-containing material may have an average diameter of about 50 μ m.

Preferably the temperature of the soap solution is near boiling.

The zircon-containing material may be a heavy-mineral-containing beach sand type deposit. Alternatively the zircon-containing material may be a pre-concentrate.

Although many types of soap may be used, soaps of fatty acids are preferred. Alkali metal soaps of unsaturated fatty acids are particularly preferred. A mixture of fatty acid soaps may be used.

We have found that a soap concentration less than 0.25 percent may be used whereas prior art methods employ 0.25 to 0.75 percent soap (Anon, 1949, Subramanya, 1960). Preferably the soap concentration is less than 0.1 percent. A soap concentration of 0.05 percent is particularly preferred. The adaptation of the hot soap method to the process of the present invention by a more appropriate range of soap concentrations is an important extension of the previous technology.

The alkali concentration in the soap treatment step depends on the soap used and the sample. Alkali may be regarded as a depressant for any titanium containing minerals and/or monazite contained in the material. The alkali used may be NaOH. The pH of the soap treatment stage is preferably greater than pH 11.

Sulphuric acid may be used in the acid wash step. The concentrations of acid used may be in the range 0.1 to 0.25 percent. The volume of acid solution may be between 0.5 and 5 litres per kilogram of solids

Any suitable frother may be used in the flotation step, for example, Cyanamid Aerofroth 65. Preferably flotation is carried out at a pH around 1.9.

We have found that the flotation of zircon is rapid and is usually complete within about 4 minutes.

We have further demonstrated that the hot soap method can be used to separate zircon from a heavy mineral flotation pre-concentrate.

Accordingly, in a second aspect, the present invention provides a process for treating zircon-containing particulate material said process including

(a) subjecting said zircon-containing material to flotation whereby zircon and any other heavy minerals contained in said material are floated from gangue to form a pre-concentrate;

(b) contacting said pre-concentrate with a soap solution in the presence of an alkali at a temperature in the range 40°C to the boiling point of the solution to produce a soap-treated product;

(c) subjecting said soap-treated product to at least one water wash to form a water-washed product;

(d) subjecting said water-washed product to at least one acid wash to form an acid-washed product; and

(e) floating zircon from said acid-washed product.

The first flotation step of the second aspect of the invention may be carried out using soap type collectors.

The soap used in the first flotation step may be the same as one of the soaps used in the soap treatment step. The soap concentration in zircon conditioning stage (b) is adjusted so as to allow for residual soap from step (a). Preferably the soap concentration in the pre-float concentrate is less than that called for in conditioning step (b) for zircon flotation. For example, if the concentration of soap in the pre-float concentrate was 0.04 per cent and the soap concentration required in step (b) was 0.05 per cent one would then add sufficient soap to increase the concentration from 0.04 percent to 0.05 percent. Preferably the first flotation is carried out at a pH between 5 and 7 although satisfactory separations can probably be made between pH 2 and 10. When gangue minerals are more difficult to separate, reagents containing fluorine can be used to improve the efficiency. The fluorine containing agent may be sodium fluosilicate.

The soap collector may be sodium oleate. The collector may be present in an amount of 20 g/t to 200 g/t. Excellent separation has been found with addition of the equivalent of 100 g/t of sodium fluosilicate before 200 g/t of sodium oleate.

The feed to the first flotation stage can be either as-mined material or a concentrate of heavy minerals produced by wet gravity methods. Where slimes (say, less than 20 μ m particles) are present, it may be necessary to de-slime the flotation feed using known techniques. As for conventional heavy mineral sand processing the object of the first flotation stage is to concentrate the heavy minerals by rejecting a large proportion of the gangue minerals. A much smaller plant is then required for subsequent separation steps.

We have found that, surprisingly, titanium minerals which have been strongly depressed in a previous zircon flotation stage can be floated with good selectivity in a further flotation stage.

Accordingly, in yet a third aspect, there is provided a process for recovering zircon and titanium minerals from a particulate material containing said minerals comprising

(a) contacting said mineral-containing material with a soap solution in the presence of an alkali at a temperature in the range 40°C to the boiling point of the solution to produce a soap-treated product;

(b) subjecting said soap-treated product to at least one water wash to form a water-washed product;

(c) subjecting said water-washed product to at least one acid wash to form an acid-washed product; and

(d) subjecting said acid-washed product to flotation treatment whereby zircon is floated and titanium-containing minerals and, if present, monazite, are depressed; and

(e) subjecting said depressed minerals to flotation treatment whereby titanium-containing minerals and, if present, monazite, are floated.

We have found that where monazite is one of the minerals depressed in step (d), it too is floated with the titanium minerals from the gangue in step (e).

An anionic collector may be used in the titanium mineral flotation step. A carboxylate, phosphonate or sulphonated fatty acid may be employed.

We have discovered that a sulphosuccinamate may be used to float titanium. Alternatively a sulphosuccinate may be used.

Accordingly, in a fourth embodiment, the invention provides a process for the flotation of titanium minerals from particulate titanium-containing material which comprises subjecting said material to froth flotation in the presence of an alkyl sulphosuccinamate or alkyl sulphosuccinate.

Preferably the titanium flotation is carried out in the presence of an alkyl sulphosuccinamate. The alkyl group may have 8 or more carbon atoms. Preferably the alkyl group has about 18 carbon atoms.

The amount of succinamate depends on, for example, the amount of titanium in the material to be floated. The sulphosuccinamate may be present in an amount equivalent to about 50 g/t to 300 g/t. More preferably the sulphosuccinamate is present in amount equivalent to 100 g/t to 300 g/t.

We have found that the process of the third aspect of the invention is particularly advantageous when the heavy mineral-containing deposit is a flotation pre-concentrate. We have confirmed experimentally that the three flotation stages are compatible; that is, they can run in sequence. It is likely that the chemicals added upstream in any other flotation scheme will adversely affect the downstream separations. This is because of the persistent nature of these chemicals once they have adsorbed on mineral surfaces. When this occurs it will be necessary to remove the chemicals between the flotation stages which will complicate and increase the cost of any process. In this invention, the problem of compatibility is solved by using the same collector (carboxylate) in the first two stages and using in the third flotation stage, a collector that is compatible with carboxylates. This compatibility could not be predicted and had to be shown experimentally, especially

in view of the large pH changes. Suitable collectors other than carboxylates may be phosphonates or sulphonated fatty acids. The sulphosuccinamates may also be used.

Accordingly, in a fifth aspect, there is provided a process for treating a heavy-mineral-containing particulate material comprising:

(a) subjecting said heavy-mineral-containing material to flotation whereby heavy minerals contained in said material are floated from gangue to form a pre-concentrate;

(b) contacting said pre-concentrate with a soap solution in the presence of an alkali at a temperature in the range 40°C to the boiling point of the solution to produce a soap-treated product;

(c) subjecting said soap-treated product to at least one water wash to form a water-washed product;

(d) subjecting said water-washed product to at least one acid wash to form an acid-washed product; and

(e) subjecting said acid-washed product to flotation treatment whereby zircon is floated and titanium-containing minerals and, if present, monazite, are depressed; and

(f) subjecting said depressed minerals to flotation treatment whereby titanium-containing minerals and, if present, monazite are floated.

Preferably bulk flotation step (a) employs a soap as the collector. Conditions described in reference to the first flotation stage of the process of the second aspect may be used.

The three flotation stage process of the invention has a number of other important advantages:

- certain types of commercial soaps consist primarily of carboxylates. These soaps are widely available and are inexpensive. The first flotation stage which requires only a small addition of carboxylate (usually about 200 g/t) is therefore very attractive.

- all separations are done wet. This means that drying between stages is not required and this reduces processing costs.

When monazite is present, a process in which the heavy minerals are separated wet rather than dry is far more environmentally acceptable. Monazite can contain a radioactive component (thorium) which means that all dusts must be well contained in dry processing plants.

- the monazite is separated from the zircon which is otherwise a very difficult separation.

- both the zircon and the titanium/monazite concentrates can be upgraded further in cleaning processes.

- it is not necessary to get a near perfect rejection of gangue minerals in the first stage because those gangue minerals that remain are left as a residue in the third stage.

- where the same carboxylate (soap) is used in all three stages, it will not be necessary to keep separate process water in each stage. If environmental legislation or economics dictate that the process water be recycled, as is usual, then this can be done from a single tailings dam. A single dam will be less expensive to construct and operate than several separate dams.

Modes for Carrying out the Invention

In order that the invention may be more readily understood the following non-limiting examples are provided.

Example 1 Production of Zircon and Titanium/Monazite Concentrates from a Gravity Sample

The sample used a gravity concentrate containing 63 percent heavy (+3.3 S.G.) minerals all with an average grain size of about 50 μ m. The deposit from which the concentrate was produced contained about 3 percent heavy minerals. The heavy minerals in the highest concentrations were zircon, monazite and various titanium minerals of which rutile, ilmenite, leucoxene and anatase were identified. The most magnetic of the titanium minerals were removed by wet magnetic separation after gravity concentration. However, it was still not possible to make a pure TiO₂ concentrate without separating the less pure titanium minerals or without processing them chemically.

The hot soap stage involved the following steps: to a 1 litre solution containing 15 mls of 5 percent NaOH solution was added 2.5 grams of a 50/50 mixture of sodium oleate and sodium stearate. The temperature was raised to near boiling and 500 grams of the gravity concentrate was added. After 20 minutes agitation the hot soap solution was decanted. The solids were then washed three times with 1 litre volumes of water and finally rinsed with a litre of 0.2 percent H₂SO₄ solution. The zircon was then floated in a standard laboratory cell using Aerofroth 65 as frother. The pH of flotation was 1.9.

After 4 minutes almost all the zircon had been floated and 100 g/t of sodium fluosilicate was added and conditioned for 2 minutes. The equivalent of 105 g/t of a commercial sulphasuccinamate (Cyanamid Aero 830) was added, conditioned

for 2 minutes and froth concentrates taken. No change in the pH was needed.

Results:

First Stage - Zircon Rich Product

	ZrO ₂	TiO ₂	CeO ₂	-2.96 S.G. gangue
Assay (%)	58.5	5.5	0.11	1.24
Recovery(%)	98.5	14.3	9.30	1.39

Second Stage - Titanium and Monazite Rich Product

	TiO ₂	CeO ₂	-2.96 S.G. gangue
Assay (%)	72.4	2.2	2.2
Recovery (%)	91.7	83.7	1.1

Example 2 - Production of Zircon and Titanium/Monazite Concentrates After Pre-concentration Using Flotation

The same sample as in Example 1 was used except that it was pre-concentrated by flotation. The pre-concentration stage involved floating the heavy minerals from the bulk of the gangue minerals using sodium oleate (which is one of the preferred soaps for zircon flotation). A standard laboratory flotation cell was used and the equivalent of 20 g/t of sodium oleate was added, conditioned for 2 minutes and froth concentrates taken.. The pH was 5.5 and the time of flotation was 4 minutes.

The hot soap procedure was the same as in Example 1 except that the addition of the 50/50 soap mixture was reduced to 0.25 grams to compensate for any soap that might have been carried over from the pre-concentrate stage.

After zircon flotation, 200 g/t of sodium fluosilicate was added and conditioned for 2 minutes. The equivalent of 110 g/t of commercial sulphosuccinamate (Cyanamid Aero 830) was added. No change in pH was needed.

Results:

First Stage - Flotation Pre-concentrate

Heavy Liquid Fractions

+3.3 S.G. -3.3+2.96 S.G. -2.96 S.G.

	+3.3 S.G.	-3.3+2.96 S.G.	-2.96 S.G.
Assay (%)	75.2	2.85	21.9
Recovery (%)	97.8	96.4	46.8

Second Stage - Zircon Rich Product

ZrO ₂	TiO ₂	CeO ₂	-2.96 S.G. gangue
Assay (%)	57.4	4.16	0.25
Recovery (%)	96.2	10.9	20.2

Assay (%)	57.4	4.16	0.25	0.37
Recovery (%)	96.2	10.9	20.2	0.90

Third Stage - Titanium and Monazite Rich Product

TiO ₂	CeO ₂	-2.96 S.G. gangue
Assay (%)	71.0	2.05
Recovery (%)	98.9	99.6

Assay (%)	71.0	2.05	2.69
Recovery (%)	98.9	99.6	3.13

Example 3 - Zircon Concentrate using a Soap Concentration of 0.05 percent

The hot soap stage of Example 1 was repeated using a 0.5 gram addition of the soap mixture. The concentration of the soap solution was therefore 0.05 percent which is much lower than that described in the prior art.

Results:

Zircon Rich Product

	ZrO ₂	TiO ₂	CeO ₂	-2.96 S.G. gangue
Assay (%)	59.6	1.38	0.20	0.47
Recovery (%)	96.2	3.29	15.7	0.53

The results show that for the fine heavy minerals an even more selective separation of zircon from titanium minerals can be made with a more dilute solution than conventionally used.

Example 4 - Pre-concentration of Heavy Minerals Using One of the soaps from the Hot Soap Method

The sample used was an as-mined sample that had been de-slimes partially at nominally 20µm in a circuit with two cyclones. The sample assayed 6.5 percent heavy (+3.3 S.G.) minerals all with an average grain size of about 50µm. No chemicals were added during the de-slimes.

A 500 gram lot of the sample was pulped in a laboratory cell and 0.1 gram of sodium oleate was added and

conditioned for 2 minutes. The heavy minerals were then floated from the gangue minerals at pH 5.5. Cyanamid Aerofroth 65 was used as the frother and the time of flotation was 8 minutes.

The results were as follows:

	Heavy Liquid Fractions		
	+3.3 S.G.	-3.3+2.96 S.G.	-2.96 S.G.
Assay (%)	32.6	7.67	59.7
Recovery (%)	99.0	94.9	12.7

Ninety nine percent of the heavy minerals were recovered while 87.3 percent of the gangue minerals were rejected. Such a result demonstrates that flotation with sodium oleate can be used to concentrate the fine heavy minerals. Further it was found that the result could be improved by adding sodium fluosilicate before the collector. For example, when the test was repeated and 0.05 gram sodium fluosilicate was added and conditioned for 2 minutes before the collector was added the results were as follows:

	Heavy Liquid Fractions		
	+3.3 S.G.	-3.3+2.96 S.G.	-2.96 S.G.
Assay (%)	59.2	11.5	29.2
Recovery (%)	99.5	93.4	3.48

Importantly, the soap addition for pre-concentration is less than has to be added in our zircon flotation stage and it is possible to compensate for any soap that is carried over, as has been shown in Example 2.

It will be appreciated that various modifications and/or alterations may be made without departing from the spirit and scope of the present invention.

References:

Anon 1949, "Flotation of Zircon", Chemical Engineering and Mining Review, May, pp 283-285

Subramanya, G.V., 1960, "Selective Flotation of Zircon from Beach Sands", Journal of Mines, Metals and Fuels, July, pp 47-48

Dunkin, 1953, "Concentration of Zircon, Rutile Beach Sands: In: Ore Dressing Methods in Australia and Adjacent Territories, Fifth Empire Milling and Metallurgical Congress, Australia and New Zealand, Publication Volume III, Editors: Dunkin H.H and McKeown M.R., Australasian Institute of Mining and Metallurgy, Melbourne, pp. 260-263

Blaskett K.S., and Hudson, S.B., 1965, "Beach Sand Minerals" In: The Australian Mining, Metallurgical and Mineral Industry, Eighth Commonwealth Mining and Metallurgical Congress, Australia and New Zealand, Publication Volume 3, Editors: Woodcock J.T. and Madigan R.T., Australasian Institute of Mining and Metallurgy, Melbourne, pp 313-340.

CLAIMS

1. A process for the recovery of zircon from a particulate zircon-containing material, said process including:

providing

(a) a zircon-containing material, said material having a particle size less than about 75 μ m; and

(b) a soap:

(c) contacting said zircon-containing material with a solution of said soap in the presence of an alkali at a temperature in the range 40°C to the boiling point of the solution to produce a soap-treated product;

(d) subjecting said soap-treated product to at least one water wash to form a water-washed product;

(e) subjecting said water-washed product to at least one acid wash to form an acid-washed product; and

(f) floating zircon from said acid-washed product.

2. A process according to claim 1 wherein the concentration of said soap in step (c) is less than 0.25 percent.

3. A process according to claim 2 wherein the concentration of said soap is less than 0.1 percent

4. A process according to claim 3 wherein the concentration of said soap is in the range of about .025 to about 0.05 percent.

5. A process according to any one of claims 1 to 4 wherein said soap is a fatty acid soap or a mixture of fatty acid soaps.

6. A process according to claim 5 wherein said soap is an alkali metal soap of an unsaturated fatty acid.

7. A process according to any one of claims 1 to 6 wherein step (c) is carried out at a pH >11.

8. A process according to any one of claims 1 to 7 wherein said alkali is NaOH.

9. A process according to any one of claims 1 to 8 wherein the concentration of said acid in step (e) is in the range 0.1 to 0.25 percent.

10. A process according to claim 9 wherein said acid is sulphuric acid.

11. A process according to any one of claims 1 to 10 wherein said zircon-containing material is a heavy-mineral-containing beach sand or a pre-concentrate.

12. A method according to any one of the preceding claims wherein said zircon-containing material has an average particle diameter of about 50µm.

13. A process for treating a particulate zircon-containing material said process including:

(a) subjecting said zircon-containing material to flotation whereby zircon and any other heavy metals contained in said material are floated from gangue to form a pre-concentrate;

(b) contacting said pre-concentrate with a soap solution in the presence of an alkali at a temperature in the range 40°C to the boiling point of the solution to produce a soap treated product;

(c) subjecting said soap-treated product to at least one water wash to form a water-washed product;

(d) subjecting said water-washed product to at least one acid wash to form an acid-washed product; and
(e) floating zircon from said acid-washed product.

14. A process according to claim 13 wherein said zircon-containing material has a particle size less than about 75 μm .

15. A process according to claim 13 or 14 wherein said flotation step (a) is carried out using a soap type collector.

16. A process according to claim 15 wherein said collector is the same soap as that used in step (b).

17. A process according to claim 16 wherein said collector used in step (a) is present in an amount of 20 g/t to 200 g/t.

18. A process according to any one of claims 13 to 17 wherein step (a) is carried out at a pH between 2 and 10, preferably between 5 and 7.

19. A process according to any one of claims 13 to 18 wherein step (a) is carried out in the presence of a fluorine containing agent.

20. A process according to claim 19 wherein the fluorine containing agent is sodium fluosilicate.

21. A process according to any one of claims 13 to 20 wherein the concentration of said soap in step (b) is less than 0.25 percent.

22. A process according to claim 21 wherein the concentration of said soap is less than 0.1 percent

23. A process according to claim 22 wherein the concentration of said soap is in the range of about .025 to about 0.05 percent.

24. A process according to any one of claims 13 to 23 wherein said soap is a fatty acid soap or a mixture of fatty acid soaps.

25. A process according to claim 24 wherein said soap is an alkali metal soap of an unsaturated fatty acid.

26. A process according to any one of claims 13 to 25 wherein step (b) is carried out at a pH >11.

27. A process according to any one of claims 13 to 26 wherein said alkali is NaOH.

28. A process according to any one of claims 13 to 27 wherein the concentration of said acid in step (d) is in the range 0.1 to 0.25 percent.

29. A process according to claim 28 wherein said acid is sulphuric acid.

30. A process according to any one of claims 13 to 29 wherein said zircon-containing material is a heavy-mineral-containing beach sand or a pre-concentrate.

31. A process for recovering zircon and titanium minerals from a particulate material containing said minerals said process comprising:

(a) contacting said mineral-containing material with a solution of a soap in the presence of an alkali at a temperature in the range 40°C to the boiling point of the solution to produce a soap-treated product;

(b) subjecting said soap-treated product to at least one water wash to form a water-washed product;

(c) subjecting said water-washed product to at least one acid wash to form an acid-washed product; and

(d) subjecting said acid-washed product to flotation treatment whereby zircon is floated and titanium-containing minerals and, if present, monazite, are depressed; and

(e) subjecting said depressed minerals to flotation treatment whereby said titanium-containing minerals and, if present, monazite, are floated.

32. A process according to claim 31 wherein said particulate material has a particle size less than about 75 μ m.

33. A process according to claim 31 or 32 wherein an anionic collector is used in step (e).

34. A process according to claim 33 wherein said anionic collector is a carboxylate, phosphonate or sulphonated fatty acid.

35. A process according to claim 31 or 32 wherein said titanium mineral is floated using a sulphosuccinamate or sulphosuccinate as the collector.

36. A process according to claim 35 wherein the collector is an alkyl sulphosuccinamate wherein the alkyl group has 8 or more carbon atoms, preferably about 18 carbon atoms.

37. A process according to claim 36 wherein said sulphosuccinamate is present in an amount equivalent to about 50 g/t to 300 g/t, preferably 100 g/t to 300 g/t.

38. A process according to any one of claims 30 to 37 wherein said mineral-containing material is a heavy-mineral-containing beach sand or a pre-concentrate.

39. A process according to claim 38 wherein said pre-concentrate is produced by flotation of a heavy-mineral-containing particulate material whereby heavy minerals contained in said material are floated from gangue.

40. A process according to claim 39 wherein the collector used in the flotation of said heavy-mineral-containing material is a soap.

41. A process according to claim 40 wherein said soap used to form said pre-concentrate is the same soap as that used in step (a).

42. A process according to any one claim 31 to 41 wherein the concentration of said soap in step (a) is less than 0.25 percent.

43. A process according to claim 42 wherein the concentration of said soap is less than 0.1 percent

44. A process according to claim 43 wherein the concentration of said soap is in the range of about .025 to about 0.05 percent.

45. A process according to any one of claims 31 to 44 wherein said soap is a fatty acid soap or a mixture of fatty acid soaps.

46. A process according to claim 45 wherein said soap is an alkali metal soap of an unsaturated fatty acid.

47. A process according to any one of claims 31 to 46 wherein step (a) is carried out at a pH >11.

48. A process according to any one of claims 31 to 47 wherein said alkali is NaOH.

49. A process according to any one of claims 31 to 48 wherein the concentration of said acid in step (c) is in the range 0.1 to 0.25 percent.

50. A process according to claim 49 wherein said acid is sulphuric acid.

51. A process according to any one of claims 31 to 50 wherein said particulate material has an average particle diameter of about 50 μ m.

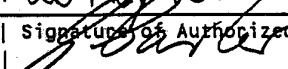
52. A process for the flotation of titanium minerals from particulate titanium-containing material which process includes subjecting said material to froth flotation in the presence of an alkyl sulphosuccinamate or alkyl sulphosuccinate as the collector.

53. A process according to claim 52 wherein the collector is an alkyl sulphosuccinamate wherein the alkyl group has 8 or more carbon atoms, preferably about 18 carbon atoms.

54. A process according to claim 53 wherein said sulphosuccinamate is present in an amount equivalent to 50 g/t to 300 g/t, preferably 100 g/t to 300 g/t.

INTERNATIONAL SEARCH REPORT

International Application No. **PCT/AU 91/00041**

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. ⁵ B03D 1/008, 1/02					
II. FIELDS SEARCHED					
Minimum Documentation Searched 7					
Classification System	Classification Symbols				
IPC	B03D 1/008, 1/02				
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched 8					
AU: IPC as above					
III. DOCUMENTS CONSIDERED TO BE RELEVANT 9					
Category*	Citation of Document, ¹¹ with indication ¹² where appropriate, of the relevant passages	Relevant to Claim No 13			
A	GB,A, 2159138 (BILSING) 27 November 1985				
A	Derwent Soviet Inventions Illustrated, Volume V, No. 21, Issued 28 June 1974, Chemical Engineering P.8, SU 390835 (MINERAL RESOURCES INST) 21 December 1974 (21.12.74)				
<p>* Special categories of cited documents: 10</p> <table style="width: 100%; border: none;"> <tr> <td style="width: 45%; border: none;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </td> <td style="width: 5%; border: none; text-align: center; vertical-align: top;"> <p>"T"</p> <p>"X"</p> <p>"Y"</p> <p>"&"</p> </td> <td style="width: 50%; border: none;"> <p>Later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>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.</p> <p>document member of the same patent family</p> </td> </tr> </table>			<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T"</p> <p>"X"</p> <p>"Y"</p> <p>"&"</p>	<p>Later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>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.</p> <p>document member of the same patent family</p>
<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T"</p> <p>"X"</p> <p>"Y"</p> <p>"&"</p>	<p>Later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>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.</p> <p>document member of the same patent family</p>			
IV. CERTIFICATION					
Date of the Actual Completion of the International Search 9 May 1991 (09.05.91)	Date of Mailing of this International Search Report 20 May 1991				
International Searching Authority Australian Patent Office	Signature of Authorized Officer  G CARTER				

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE 1

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

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

2. Claim numbers ..., 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:

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

VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING 2

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

Claims 1-51 Describe a process for the recovery of Zircon but
 Claims 52-54 describe a process for floatation of titanium

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. 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 claim numbers:

4. As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- The additional search fees were accompanied by applicant's protest.
 No protest accompanied the payment of additional search fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON
INTERNATIONAL APPLICATION NO. PCT/AU 91/00041

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 Members		
GB 2159138	AU 42764/85 IN 164826	CA 1274024 CN 85104474	DD 237482

END OF ANNEX