Abstract: A method (10) for the hydrometallurgical processing of rare earth and uranium containing ores and concentrates, the method comprising the steps of: (i) Passing a rare earth ore to a concentration step in which is produced a rare earth phosphate concentrate (12); (ii) Passing the rare earth phosphate of step (i) to a first atmospheric leach step (16) in which the rare earth phosphate concentrate is leached in weak acid; (iii) Passing the product of step (ii) to a first solid liquid separation step (18); (iv) Passing the liquid product of step (iii) to a uranium recovery circuit (20); and (v) Passing the solids product of step (iii) to second atmospheric leach step (24) in which the solids are leached in strong acid and in which substantially all the rare earth elements present precipitate as sodium rare earth double sulphates, wherein the conditions of the first and second leach steps (16, 24) are controlled such that substantially no silica gelling occurs.
"Processing of Rare Earth and Uranium Containing Ores and Concentrates"

TECHNICAL FIELD

[0001] The present invention relates to the processing of rare earth and uranium containing ores and concentrates. More particularly, the present invention relates to a method for the hydrometallurgical processing of rare earth and uranium containing ores and concentrates.

[0002] The method of the present invention is intended to provide relatively efficient separation of rare earth elements from the uranium present in the ore or concentrate.

BACKGROUND ART

[0003] It is generally understood that the effective and efficient processing of a rare earth ore is dependent in large part upon the ability to separate the desired rare earth metal products from what might be termed nuisance elements, some of which are radioactive. Chief amongst these "nuisance" elements are the metals iron, thorium and uranium. Of course, one or more of these so-called nuisance elements may add value to any operation that targets primarily the rare earth elements.

[0004] Typically, a hard rock rare earth element containing ore will require acid leaching of the ore and a subsequent multitude of separation steps, making the processing of ores to recover rare earth elements particularly costly and time consuming. In particular, acid consumption has traditionally been high. In addition, the minerals hosting the target rare earth metals typically also contain silica that is readily acid soluble also. Unless the leach conditions are controlled very carefully the leaching of silica may result in the precipitation of silica gels.

[0005] One object of the present invention is to substantially overcome the abovementioned problems of the prior art, or to at least provide a useful alternative thereto.

[0006] The preceding discussion of the background art is intended to facilitate an understanding of the present invention only. The 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.

[0007] Throughout this specification, 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.

SUMMARY OF INVENTION

[0008] In accordance with the present invention there is provided a method for the
hydrometallurgical processing of rare earth and uranium containing ores and
concentrates, the method comprising the steps of:

(i) Passing a rare earth ore to a concentration step in which is produced a rare
earth phosphate concentrate;

(ii) Passing the rare earth phosphate of step (i) to a first atmospheric leach step
in which the rare earth phosphate concentrate is leached in weak acid;

(iii) Passing the product of step (ii) to a first solid liquid separation step;

(iv) Passing the liquid product of step (iii) to a uranium recovery circuit; and

(v) Passing the solids product of step (iii) to second atmospheric leach step in
which the solids are leached in strong acid and in which substantially all the
rare earth elements present precipitate as sodium rare earth double
sulphates,

wherein the conditions of the first and second leach steps are controlled such that
substantially no silica gelling occurs.

[0009] Still preferably, the first and second leach steps are conducted with sulphuric
acid.
[0010] Still further preferably, the combined residence time of the first and second leach steps is greater than about 16 hours.

[0011] Yet still preferably, the combined residence time of the first and second leach steps is about 18 hours.

[0012] The first leach step is preferably conducted at a temperature of greater than about 80°C but less than boiling.

[0013] The first leach step is still preferably conducted at a temperature of about 95°C.

[0014] The second leach step is preferably conducted at a temperature of greater than about 80°C but less than boiling.

[0015] The second leach step is still preferably conducted at a temperature of about 95°C.

[0016] The first leach step is preferably conducted at a pH of about 2 to 3. The first leach step is still preferably conducted with a free acid concentration of less than 1 gpl.

[0017] The second leach step is preferably conducted at a pH of less than about 1. The second leach step is still preferably conducted with a free acid concentration of between 30 to 80 gpl.

[0018] The method preferably further comprises:

Passing the product of step (v) to a second solid liquid separation step.

[0019] The method still preferably further comprises:

Passing the liquid product of the second solid liquid separation step to the first atmospheric leach step; and

Passing the solids from the second solid liquid separation step to a metathesis step in which those solids are contacted with a strong caustic solution to produce a residue containing rare earth element hydroxides.
Preferably, the caustic solution of the metathesis step is a sodium hydroxide solution.

The method still yet preferably further comprises:

Passing the hydroxide residue of the metathesis step to an acid re-leach step in which substantially all the rare earth hydroxides are re-dissolved; and

Passing the re-dissolved rare earth elements containing solution to rare earth precipitation step.

Preferably, the acid re-leach step is conducted with hydrochloric acid.

BRIEF DESCRIPTION OF THE DRAWINGS

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 hydrometallurgical processing of a rare earth ore or concentrate in accordance with the present invention; and

Figure 2 is a graphical representation of acid demand relative to pH for the leaching of Kvanefjeld ore;

Figure 3 is a graphical representation of the effect of pH on silica dissolution during leaching of Kvanefjeld ore at differing temperatures; and

Figure 4 is a graphical representation of pH relative to silica concentration in solution at differing particle sizes.
DESCRIPTION OF EMBODIMENTS

[0024] In Figure 1 there is shown a method 10 for the hydrometallurgical processing of rare earth ores and concentrates. The method 10 comprises the passing of a rare earth phosphate concentrate 12 to a re-pulp stage 14 in which is produced a concentrate slurry. The concentrate 12 is produced initially by way of a conventional crushing and milling circuit from a run of mine rare earth ore (not shown). The run of mine ore is first tipped into a gyratory crusher and ultimately fed to a SAG mill in which the ore is ground to a P80 of 75 μm.

[0025] The ground ore is passed to a concentration step, for example a froth flotation step (not shown), in which selected flotation reagents are utilised whereby phosphitic minerals become selectively hydrophobic allowing their effective separation and the production of the rare earth phosphate concentrate 12.

[0026] Rare earth phosphate flotation occurs within tank cells (not shown) with forced air addition to control froth rate. A first stage consists of short residence time rougher flotation with the concentrate produced reporting to the final concentrate thickener. The grade of this concentrate is high enough that cleaning of the concentrate is not warranted. The tails from the rougher flotation stage proceed to the scavenger flotation in which flotation occurs for an additional 10 minutes. The scavenger concentrate is not of suitable grade to be considered final concentrate. Therefore cleaning of the concentrate is required. The flotation tailings are thickened in a high rate thickener with the overflow water recovered for use as process water.

[0027] From the re-pulp stage 14 the concentrate slurry is passed to a first atmospheric leach step 16 in which it is leached with weak sulphuric acid solution at a temperature of at least about 80°C but without boiling, for example 90 to 95°C, preferably 95°C, and a density of about 15% solids. The first atmospheric leach step has a residence time of at least about 6 hours, for example about 10 hours, and the leach has a pH of between about 2 to 3, preferably 2.2, and a free acid concentration of less than about 1 gpl. A slurry from the leach step 16 is then passed to a first solid liquid separation step, utilising for example a thickener 18, in which leach liquor is separated from leach solids.
[0028]  The leach liquor, or pregnant leach solution (PLS) is passed to a uranium recovery circuit 20. The leach solids, or concentrate slurry, is passed to a second atmospheric leach step 22 in which it is leached with strong sulphuric acid solution at a temperature of at least about 80°C but without boiling, for example 90 to 95°C, preferably 95°C, and at a pH of less than about 1. The leach step 22 is operated at a density of about 32% solids over a residence time of at least about 6 hours, preferably about 8 hours, with a free acid concentration of between about 30 to 80 gpl.

[0029]  During the leaching steps 16 and 22 the uranium and rare earths present are initially leached from the concentrate into solution. However, the significant majority of the rare earths precipitate from solution as sodium-rare earth-double sulphates. In effect, the uranium reports to the pregnant leach solution or liquor whilst the rare earths report to the solids residue, thereby separating the rare earth elements from the substantial majority of the contaminants. However, a minor amount of uranium, also forms a stable sulphate precipitate in the leach stages 16 and 22 and thereby reports to the leach residue. For example, it is understood that about 0.5% of the uranium present reports to the residue in this manner.

[0030]  The relatively long combined leach residence time and relatively high temperature employed in the leach steps 16 and 22 ensures, together with the gradual dosing of acid, that the rate of silica precipitation is greater than the rate of silica leaching. In this manner the silica precipitates without significant formation of gels, reporting to the leach residue. The silica is consequently not reactive throughout the remainder of the method 10 once precipitated and reports ultimately to tailings.

[0031]  A residue slurry from the leach step 22 is passed to a second solid liquid separation step, for example a filtration step 24. The filtration step 24 is conducted using, for example, a belt filter, washing with barren sodium sulphate wash water from the uranium recovery circuit 20 and then with raw water to remove dissolved contaminants from filter cake. Liquids from the filtration step 24 are returned to the leach step 16.

[0032]  Filter cake from the filtration step 24 is re-pulped and passed to a metathesis step 26 in which it is contacted with a strong caustic solution, for example sodium hydroxide, whereby the sodium-rare earth element-double sulphates are converted into rare earth element hydroxides. The sodium hydroxide is dosed to achieve a pH of
greater than 9.5, the residence time is about 2 hours, and the temperature is in the
range of about 10 to 70°C. It is envisaged that other alkalis may be utilised in the
metathesis step 26, including sodium carbonate, calcium hydroxide and magnesium
oxide. The rare earth element (REE) hydroxides are amenable to subsequent mild
leaching with hydrochloric acid.

[0033] The metathesis reaction is understood to occur according to the following
reaction:

\[ \text{NaREESO}_4 \cdot xH_2O + 3\text{NaOH} \rightarrow \text{REE(OH)}_3 + 2\text{Na}_2\text{SO}_4 + xH_2O \]

[0034] The metathesis step 26 is conducted in a series of three continuously stirred
tank reactors (not shown) for 2 hours at ambient temperature. The metathesis slurry is
thickened, filtered and washed. The resulting filter cake is advanced to a mild acid re-
leach step 28. The spent metathesis solution is recycled with a bleed sent to effluent
treatment.

[0035] The mild acid re-leach step 28 involves the leaching of the residue or filter
cake from the metathesis step 26 with hydrochloric acid at a pH in the range of about 1
to 4. The re-leach step 28 is preferably conducted so as to minimise aluminium and
iron re-dissolution, achieved using a pH of about 3. The filter cake from the metathesis
step 26 is re-pulped to 30% w/w solids in barren liquor and pumped to a metathesis re-
leach circuit in which the re-leach step 28 is conducted. The re-leach circuit comprises
three agitated tanks which provide a total of 1 hour residence time. Concentrated
hydrochloric acid is added to either of the first two tanks to achieve a desired discharge
pH of 3.0. The resultant slurry is pumped to a re-leach thickener (not shown) where
flocculant is added and solids are thickened to 25% w/w solids and pumped to a filter
feed tank which provides surge capacity.

[0036] Thickened slurry is dewatered and washed with barren liquor in a plate-and-
frame filter press (not shown) to remove soluble rare earth elements. Filter cake at 55%
w/w solids is re-pulped in a re-pulp tank (not shown) before being sent to a residue
storage facility 30. Filtrate is returned to the re-leach thickener.

[0037] Re-leach thickener overflow, or chloride product liquor, is collected in a tank
that provides surge capacity and is pumped to an impurity removal step 32. In the
impurity removal step 32 lime and barium salts are utilised to precipitate iron, radionuclide and aluminium impurities that pass to effluent treatment 34.

[0039] In the impurity removal step 32, the chloride product liquor from the metathesis step 26 cascades through two trains of three agitated tanks (not shown) which provide a total of 6.0 hours residence time. Lime slurry is added to either of the first two tanks to achieve the desired discharge pH of 3.0. The resultant slurry is pumped to a thickener (not shown) where flocculant is added and solids are thickened to 25% w/w solids. Half of this material is re-circulated to the first agitated tank as seed, whilst the remainder is pumped to the filter feed tank.

[0040] Thickened slurry is dewatered and washed with barren liquor in a plate-and-frame filter press to recover contained soluble rare earth elements. Filter cake at 50% w/w solids is discharged into a re-pulp tank (not shown) and then pumped to effluent treatment 34. Filtrate is returned to the thickener.

[0041] Thickener overflow is forwarded to an ion exchange step 36 in which uranium and thorium are substantially removed from the chloride product liquor. This recovers uranium to produce additional product and prevents contamination of rare earth products.

[0042] The ion exchange step 36 employs ion exchange to selectively extract the uranium and thorium from solution in known manner. The functional group for one suitable resin for uranium and thorium removal in such a step is Pyridinium (available in one form under the commercial name CleanTeq R-304™). It is envisaged that other anion exchange resins may also be used in this step. The remaining chloride product liquor is passed to a lead removal step 38. The lead removal step 36 utilises a sulphiding circuit (not shown). A small amount of uranium recovered in the ion exchange step 26 is recycled to the leach step 16.

[0043] In the lead removal step 38 the chloride product liquor from the ion exchange step 36 cascades through a train of three agitated tanks (not shown) which provide a total of 15 minutes residence time. Sodium hydrosulphide solution is added to either of the first two tanks. It is envisaged that other sulphide precipitants may be utilised in this step, including Na₂S, (NH₄)₂S and H₂S. The resultant slurry is pumped to a thickener (not shown) where flocculant is added and solids are thickened. A majority of this
material (~75%) is re-circulated to the first sulphiding reactor as seed, whilst the remainder is pumped to a filter feed tank (not shown) that provides surge capacity.

[0044] Thickened slurry is dewatered and washed with water in a plate-and-frame filter press to recover contained soluble rare earth elements. Filter cake at 75% w/w solids is discharged into 2 m³ lined bulka bags which are containerised for shipment off-site. Filtrate is returned to the sulphiding thickener.

[0045] Sulphiding thickener overflow is collected in a tank and is pumped through the Sulphiding polishing filter to remove fine solids contaminants from downstream processes.

[0046] Rare earth elements are subsequently precipitated from the chloride product liquor as carbonate in a mixed rare earth element precipitation step 40.

[0047] In the precipitation step 40 the chloride product liquor is treated in a series of three continuously stirred tank reactors (not shown). Sodium carbonate solution is dosed to control the pH at approximately 7.5 which results in the precipitation of rare earths as rare earth element carbonate. A total of three hours residence time is provided. It is envisaged that rare earth precipitants other than sodium carbonate may be utilised, including calcium hydroxide, sodium hydroxide, ammonia, magnesia, oxalic acid, sodium oxalate and the like.

[0048] The precipitated rare earth element carbonate solids are separated from the barren chloride product liquor in a thickener (not shown) to produce a thickened underflow. This underflow is further dewatered in a carbonate product filter (not shown) to produce a filter cake. The filter cake is washed with water to reduce chloride levels in a final rare earth element carbonate product 42, and is prepared for sale.

[0049] A polishing filter removes any fine rare earth carbonate solids from the rare earth element carbonate product thickener overflow to produce a barren chloride liquor. Most of the barren chloride liquor is recycled back to the re-leach step 28 with the excess sent to effluent treatment 34.
The present invention will now be further described with reference to the following non-limiting examples relating to various aspects of the present invention:

EXAMPLES

Ore Mineralogy

The testwork discussed hereinafter and the method of the present invention described above have been conducted on and developed respectively for a multi-element rare earth and uranium ore found in the Northern Ilimaussaq Intrusive Complex of the Kvanefjeld deposit in Greenland. Steenstrupine is the most important host to both rare earth elements and uranium in the lujavrite hosted multielement deposits. It is a complex sodic phospho-silicate mineral. Mineralogical studies suggest that steenstrupine commonly contains between 0.2% and 1% U$_3$O$_8$, and likely hosts over half of the uranium contained within the deposits.

Within the black lujavrite, the grain size of the steenstrupine commonly ranges from 75 pm to over 500 $\mu$m, whilst in the MC lujavrite, grain size can exceed 1mm. Other minerals that are important hosts to REEs include the phosphate mineral vitusite and, to a lesser extent, britholite and minor monazite. Aside from steenstrupine, uranium is also hosted in unusual zirconium silicate minerals of the lovozerite and eudialyte groups. In these zirconium-silicates a portion of the zirconium is substituted by several hundred ppm each of uranium, yttrium, HREE and tin. Zinc is hosted in the sulphide mineral sphalerite, which is the dominant sulphide throughout the deposit. Lovozzerite group minerals coexist with steenstrupine, whereas eudialyte group minerals are present at deeper, lower grade levels of the deposits.

The table below contains details of the significant ore minerals found in lujavrite. HREE refers to heavy rare earth elements whilst LREE refers to light rare earth elements:
[0056] In the upper, higher grade portions of Kvanefjeld (>300 ppm $U_3O_8$) phosphate bearing minerals (e.g. steenstrupine) are the dominant hosts to REEs and uranium, with the zirconium silicates being of secondary importance. However, at greater depth, the zirconium silicates become increasingly important hosts to uranium. The mine schedule established for the Study is focussed in greater than 300 ppm $U_3O_8$ resource material that dominates the upper level of the Kvanefjeld deposit.

[0057] Lujavrite gangue minerals consist of 60% sodium aluminosilicates and 40% sodium iron pyriboles. The total ore minerals typically comprise 5 - 10% of the rock volume as disseminated grains. Trace components of the rock also include water soluble sodium silicate and sodium phosphate minerals together with humic material. Uranium, REE, and zinc mineralisation is orthomagmatic, having crystallised from the lujavrite melt along with the silicate gangue.

[0058] It is important to note that the five (5) main gangue minerals make up approximately 86% of the mass, hence the majority of the uranium and REEs are locked in a very small quantity of material.
The Table below contains details of the lujavrite gangue mineralogy:

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Type</th>
<th>Class</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nesquehine</td>
<td>Pyroxene</td>
<td>Na₂Fe₅Si₆O₁₆</td>
<td>Trace refractory Li, P</td>
</tr>
<tr>
<td>Amphibole</td>
<td>Nesquehine</td>
<td>Na₂Fe₃Si₅O₁₆</td>
<td>Trace refractory Li, P</td>
</tr>
<tr>
<td>Naujaite</td>
<td>Pyroplagioclase</td>
<td>Na₂Fe-Mn Alumino-silicate</td>
<td>Trace refractory Li, P</td>
</tr>
<tr>
<td>Blötte</td>
<td>Pyroplagioclase</td>
<td>K-Fe Alumino-silicate</td>
<td>Trace refractory Li, P</td>
</tr>
<tr>
<td>Microlite</td>
<td>Feldspar (Na-K)</td>
<td>Alumino-silicate</td>
<td></td>
</tr>
<tr>
<td>Albite</td>
<td>Feldspar (Na)</td>
<td>Alumino-silicate</td>
<td></td>
</tr>
<tr>
<td>Neophite</td>
<td>Feldspathid (Na-K)</td>
<td>Alumino-silicate</td>
<td>Acid susceptible</td>
</tr>
<tr>
<td>Sodalite</td>
<td>Feldspathid (Na)</td>
<td>Alumino-silicate</td>
<td>Acid susceptible</td>
</tr>
<tr>
<td>Analcime</td>
<td>Zeolite (Na)</td>
<td>Hydrated Alumino-silicate</td>
<td>Acid susceptible</td>
</tr>
<tr>
<td>Natrolite</td>
<td>Zeolite (Na)</td>
<td>Hydrated Alumino-silicate</td>
<td>Acid susceptible</td>
</tr>
<tr>
<td>Usingerite</td>
<td>Zeolite (Na)</td>
<td>Hydrated Alumino-silicate</td>
<td>Acid susceptible</td>
</tr>
</tbody>
</table>

[0060] Rare Earth Phosphate Flotation

[0061] The Rare Earth Phosphate (REP) flotation is an important part of the method of the present invention as it allows the concentration of the majority of target values in approximately 10% of the original mass of the whole of ore.

[0062] Treating this concentrate, rather than whole of ore, dramatically reduces the capital and operating costs of the resulting hydrometallurgical process plant.

[0063] Flotation is performed with commercially available reagents which include sodium silicate and hydroximates. The flotation circuit consists of roughing, scavenging and cleaning of the concentrate. Extensive laboratory testwork also included pilot plant campaigns. The blended concentrate derived from the pilot plant was used as the main feed source for the leaching investigations. Further bench scale testwork has indicated the concentrate produced is likely to be lower grade than that expected in a commercial operation due to sub-optimal pilot plant performance. Nonetheless it still provides a good example of the likely commercial concentrate derived from Kvanefjeld.

[0064] The ore type used for the pilot plant testwork was from an area designated as "Domain A" within the Kvanefjeld deposit. The leach response of concentrates derived from other "Domains" and areas of the Kvanefjeld deposit were also investigated to determine their variability.
The Table below provides a comparison of Domain A ore and rare earth phosphate concentrate composition:

<table>
<thead>
<tr>
<th>Element</th>
<th>Al</th>
<th>Ce</th>
<th>Fe</th>
<th>P</th>
<th>Si</th>
<th>U</th>
<th>Y</th>
<th>Zn</th>
<th>Zr</th>
<th>REO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore %</td>
<td>6.19</td>
<td>0.593</td>
<td>10.1</td>
<td>0.29</td>
<td>24.2</td>
<td>0.037</td>
<td>0.121</td>
<td>0.3</td>
<td>0.061</td>
<td>1.41</td>
</tr>
<tr>
<td>Con %</td>
<td>4.42</td>
<td>4.19</td>
<td>8.58</td>
<td>7.38</td>
<td>18.8</td>
<td>0.150</td>
<td>0.66</td>
<td>1.10</td>
<td>0.281</td>
<td>11.3</td>
</tr>
</tbody>
</table>

In the Kvanefjeld ores, cerium can be used as a proxy for the upgrade of light rare earth elements while yttrium can be used as a proxy for the upgrade of heavy rare earth elements.

Leaching

Studies on the Kvanefjeld deposit by the Danish government department Ris0 in the 1970’s recommended the use of high temperature carbonate pressure leaching to extract the uranium from the ore. Historically acid leaching of ore was eliminated as a viable option due to silica gel formation and high acid consumption. The issues of silica leaching from the ore and precipitating rapidly to produce silica gels was well established for the ore which contained 24.2% silicon in a variety of alkaline minerals. The challenge for the metallurgical team was to develop acid leaching conditions which allowed the values to be leached from the concentrate while controlling the silica to prevent gelation. The concentrate still contained high silicon levels which also made it a candidate for silica gel formation during leaching.

Sodium Rare Earth Element Double Sulphate Formation

All lanthanides form sparingly soluble sodium-REE double salts in sulphate solutions. This reaction occurs according to the following equation 1:

\[ \text{Na}^+ + \text{RE}^{3+} + 2\text{SO}_4^{2-} + x\text{H}_2\text{O} = \text{NaRE}((\text{SO}_4)_2.x\text{H}_2\text{O} (1) \]

The double salt solubility increases with increasing lanthanide atomic weight. Light rare earth elements (La to Nd) are almost insoluble, middle rare earths (Sm to Gd) have limited solubility while heavy rare earths (Tb-Lu including Y) are sparingly soluble. Increased temperature and concentration of reactants shifts the reaction (1) equilibrium...
strongly to the right. Under certain conditions it is possible to precipitate nearly all heavy rare earth elements from solution as double sulphates in addition to all of the light and middle rare earth elements.

[0073] It is possible to recover the rare earth elements from the double sulphates by washing with water or by alkaline metathesis. The use of alkaline metathesis converts the rare earth elements from double sulphate to hydroxides according to the following equation 2.

[0074] \[
\text{NaRE(SO}_4\text{)}_2\cdot x\text{H}_2\text{O} + 3\text{NaOH} = \text{RE(OH)}_3 + 2\text{Na}_2\text{SO}_4 + x\text{H}_2\text{O} \quad (2)
\]

[0075] Preliminary tests showed that sulphuric and hydrochloric acid gave similar leach recoveries at equivalent acid doses. For much of the leach amenability testwork hydrochloric acid was used as it does not result in the precipitation of rare earth elements. Sulphuric acid leaching is possible for the concentrate however it requires an additional stage to recover the rare earth elements from the leach residue.

[0076] **Leachability Tests**

[0077] Hydrochloric acid was selected for this testwork and other amenability testwork due to the limited solubility of light rare earth elements in sulphate solutions containing alkalis.

[0078] Bench scale laboratory tests were performed for initial evaluation of the concentrate as no previous leaching tests had been performed. The first part of the evaluation determined the pH at which the gangue element leaching occurs while monitoring pH. Concentrate was reacted in a continuously stirred laboratory scale reactor at ambient temperature. Figure 2 shows that acid demand increases significantly between pH 3.5 and 4.0. This buffer point indicates the pH at which significant amounts of minerals leach.

[0079] **Silica Stability Testing**

[0080] Previous testwork has indicated a tendency for silica gel formation during acid leaching of ores and concentrates. Silica gels will lead to a loss of agitation, poor solid-liquid separation and crud formation in solvent extraction. Conditions needed to
be identified where high extraction of values (uranium and rare earth elements) is achieved whilst avoiding silica gel formation.

[0081] Testwork was focused on the formation of granular silica precipitates and how this differs from the formation of gels. Silica is soluble in solution as monosilicic acid (Si(OH)₄) produced from leaching silicate minerals (i.e. feldspar and feldsparthoid). Silica gels can form when supersaturated silica solutions become unstable and polymerisation reactions occur. Monosilic acid polymerises via a condensation type reaction between silanol groups (Si-OH) for form a siloxane bond according to the reaction:

\[ 2\text{Si(OH)}_4(\text{aq}) \rightarrow \text{0(Si(OH)}_3\text{)}_2(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \] (3)

[0082] This reaction forms long chained dimers which grow and encapsulate water. Variables known to influence silica precipitation include: time, temperature, pH, seeding, fluoride, ferric and aluminium ions in solution. Essentially conditions need to be controlled to allow heterogeneous precipitation of silica to occur, forming crystalline solids rather than gels.

[0083] Laboratory testwork was performed to assess the silica stability in the leach process and identify conditions where silica gelling is minimised. In order to assess the impact of temperature, silica stability tests were performed at 22°C, 60°C and 95°C. The tests involve measuring the silica concentration in solution with varying acid addition. The type of dissolved silica is characterised by filtering the leach solution through different pore sized filter papers. The selected filter papers were 15 µm and 0.45 µm. In addition the filtration rate of the solution was also measured which provides an indication of the extent of gel formation.

[0084] Figure 3 shows that silica starts to leach significantly into solution at approximately pH 3.0. The concentration of fine silica in solution is higher with low temperature and considerably lower with high temperature of 95°C. This indicates the rate of silica precipitation was much faster at high temperature. Both lower temperature solutions resulted in gel formation. At 95 °C the rate of silica precipitation and leaching were such that low supersaturation levels were maintained thus avoiding significant silica gelling.
This is an important point for leaching the concentrate without producing a gel. Note that without the increased temperature silica gelling occurred.

Figure 4 shows that silica particle growth started to occur significantly at pH 2.2 as evidenced by the difference between filtrate concentrations. As the pH was decreased further there was an increase in the rate of silica dissolution from the minerals. Four hours was allowed for the silica to reach equilibrium at all pH points and this was not enough time for the silica to precipitate. Nonetheless, continued particle growth was observed which suggests heterogeneous (self seeded) precipitation was occurring.

Atmospheric leaching is made particularly relevant for the Kvanefjeld deposit by virtue of the unusual nature of the rare earth element and uranium-bearing minerals. The value minerals (ore minerals) were formed in a highly alkaline environment and are not completely stable when removed from such an environment. Importantly, these unique minerals have not been altered to more common, yet much more refractory rare earth element and uranium-bearing minerals. When contacted with acidic solution the Kvanefjeld ore minerals disintegrate, liberating the rare earths and uranium into solution. This leads to high extractions of >85% for heavy rare earths and >90% for uranium within an atmospheric leach.

The conditions in the leach are carefully controlled in order to:

(i) Manage the precipitation of gangue elements such as silica;

(ii) Reduce acid consumption by about 25% compared with prior art processes through use of a two-stage leach,

(iii) Effectively separate rare earth elements from uranium by precipitating the rare earth elements as sodium rare earth element double sulphate salts, while uranium remains in solution; and

(iv) Produce residues which settle and filter well.

The atmospheric leach conditions are managed to drive rare earth elements into the leach residue as salts. This cleanly separates the REEs from uranium that
remains stable in solution. The residue is treated with caustic soda, rendering it amenable to a mild re-leach, the re-leach producing a rare earth element chloride solution. A single mixed rare earth element product is then precipitated from this chloride solution. Because of the clean initial separation from the gangue elements, very low post leach losses are experienced.

[0091] Uranium is recovered from the atmospheric leach solution by means of a highly selective solvent extraction process. Solvent extraction has been successfully tested at bench scale and, as a proven technology for uranium extraction, is considered low risk and straightforward to engineer. A final uranium oxide product is produced at this stage.

[0092] The method of the present invention is able to achieve high extractions of valuable rare earth elements and uranium from a mineral concentrate in an atmospheric leach.

[0093] A high quality mixed rare earth oxide product can be produced which is suitable for rare earth separation refineries. The mixed rare earth oxide product is low in radionuclides and contains significant quantities of heavy rare earth elements.

[0094] Modifications and variations such as would be apparent to the skilled addressee are considered to fall within the scope of the present invention.
CLAIMS

1. A method for the hydrometallurgical processing of rare earth and uranium containing ores and concentrates, the method comprising the steps of:

   (i) Passing a rare earth ore to a concentration step in which is produced a rare earth phosphate concentrate;

   (ii) Passing the rare earth phosphate of step (i) to a first atmospheric leach step in which the rare earth phosphate concentrate is leached in weak acid;

   (iii) Passing the product of step (ii) to a first solid liquid separation step;

   (iv) Passing the liquid product of step (iii) to a uranium recovery circuit; and

   (v) Passing the solids product of step (iii) to second atmospheric leach step in which the solids are leached in strong acid and in which substantially all the rare earth elements present precipitate as sodium rare earth double sulphates,

   wherein the conditions of the first and second leach steps are controlled such that substantially no silica gelling occurs.

2. A method according to claim 1, wherein the first and second leach steps are conducted with sulphuric acid.

3. A method according to claim 1 or 2, the combined residence time of the first and second leach steps is greater than about 16 hours.

4. A method according to any one of claims 1 to 3, the combined residence time of the first and second leach steps is about 18 hours.

5. A method according to any one of the preceding claims, wherein the first leach step is conducted at a temperature of greater than about 80°C but less than boiling.
6. A method according to any one of the preceding claims, wherein the first leach step is conducted at a temperature of about 95°C.

7. A method according to any one of the preceding claims, wherein the second leach step is conducted at a temperature of greater than about 80°C but less than boiling.

8. A method according to any one of the preceding claims, wherein the second leach step is conducted at a temperature of about 95°C.

9. A method according to any one of the preceding claims, wherein the first leach step is conducted at a pH of about 2 to 3.

10. A method according to any one of the preceding claims, wherein the first leach step is conducted with a free acid concentration of less than 1 gpl.

11. A method according to any one of the preceding claims, wherein the second leach step is conducted at a pH of less than about 1.

12. A method according to any one of the preceding claims, wherein the second leach step is conducted with a free acid concentration of between 30 to 80 gpl.

13. A method according to any one of the preceding claims, wherein the method further comprises:

   Passing the product of step (v) to a second solid liquid separation step.

14. A method according to claim 13, wherein the method still further comprises:

   Passing the liquid product of the second solid liquid separation step to the first atmospheric leach step; and

   Passing the solids from the second solid liquid separation step to a metathesis step in which those solids are contacted with a strong caustic solution to produce a residue containing rare earth element hydroxides.
15. A method according to claim 14, wherein the caustic solution of the metathesis step is a sodium hydroxide solution.

16. A method according to claim 14 or 15, wherein the method further comprises:

   Passing the hydroxide residue of the metathesis step to an acid re-leach step in which substantially all the rare earth hydroxides are re-dissolved; and

   Passing the re-dissolved rare earth elements containing solution to rare earth precipitation step.

17. A method according to claim 16, wherein the acid re-leach step is conducted with hydrochloric acid.

18. A method for the hydrometallurgical processing of rare earth and uranium containing ores and concentrates, the method being substantially as hereinbefore described with reference to the figures.

19. A method for the hydrometallurgical processing of rare earth and uranium containing ores and concentrates, the method being substantially as hereinbefore described with reference to the examples.
Figure 1
The point at which gangue leaching rate begins is less well defined than for Washed Ore. Moderate increases in leaching rate are seen between pH 4 and pH 3.5. A sharp increase in gangue leaching rate at pH 3.2.

Dosing rate increased slightly over this period.

Figure 2

Figure 3
Figure 4
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

C22B 60/02 (2006.01)  C22B 59/00 (2006.01)  C22B 3/04 (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 database consulted during the international search (name of database and, where practicable, search terms used)

WPI and EPDOC: IPC/CC marks C22B60/02/-, C22B59/00/-, C22B3/04/-, C22B60/0221/- and keywords such as rare earth, Scandium, Yttrium, Lanthanum, Cerium, Praseodymium, Neodymium, Promethium, Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium, Lutetium, phosphate, leach, extract, etc and same keywords search through google patent and espacenet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>Documents are listed in the continuation of Box C</td>
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<tr>
<td>[X]</td>
<td>Further documents are listed in the continuation of Box C</td>
<td>[X] See patent family annex</td>
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* Special categories of cited documents:
  "A" document defining the general state of the art which is not considered to be of particular relevance
  "E" earlier application or patent but published on or after the international filing date
  "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)
  "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

"T" 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
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
11 February 2013

Date of mailing of the international search report
11 February 2013

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<td>GB 672347 A (FREDERICK THOMAS SEELYE AND THOMAS ATHOL RAFTER) 21 May 1952</td>
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<td>claims 1-10, Example</td>
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<td>A</td>
<td>US 2009/0272230 A1 (MACKOWSKI et al.) 05 November 2009</td>
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<td>abstract, claims 1-20, examples</td>
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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.: 18-19 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:
   
   See Supplemental Box

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)

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.
The claims 18-19 do not comply with Rule 6.2(a) because it/they rely on references to the description and/or drawings.
This Annex lists known 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.

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End of Annex

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

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