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(54) Title of the Invention: **Extraction of elements from carbonate - containing minerals**
Abstract Title: **A method of extracting rare earth elements from carbonate-containing minerals**

(57) A method for extraction of rare earth elements from carbonate-containing minerals is disclosed which comprises crushing the mineral to particles, submerging the crushed mineral in water, injecting CO₂ into the water until the alkaline and alkaline earth carbonates are dissolved, separating the remaining solid particles from the liquid phase. discharge the liquid phase, and submerging the remaining solid particles in water and add a mineral acid until the particles are dissolved, separation and precipitation of the ionic rare earth elements as oxides by use of conventional hydrometallurgical methods. The liquid phase carbonate may be treated to release carbon dioxide which may be recycled to the dissolution step. The method may also be applied to recover titanium hafnium and zirconium.

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Method for extraction of elements from carbonate-containing minerals

This invention relates to a method for extraction of elements from carbonate-containing minerals with limited use of mineral acid and small discharges of CO₂.

Background

Carbonate minerals comprise among others calcite (CaCO₃), dolomite (CaMg(CO₃)₂), and ankerite (Ca(Fe,Mg,Mn)(CO₃)₂). These minerals often also contain other elements, e.g. rare earth elements, in lower abundances than the main elements listed. They may also be found in matrixes together with abrasive minerals like hematite.

These elements may be extracted by dissolving the carbonate containing mineral in a mineral acid to form an aqueous solution of the elements, and then recovering the element of interest by use of hydrometallurgical method.

Hydrometallurgical methods have been developed since the second world-war for almost every element and for a huge number of possible chemical environments. The two main methods for industrial separations are liquid-liquid (or solvent) extraction and ion-exchange. During the last decades a large number of new liquid extractants and ion-exchange resins have emerged. There are more liquid extractants commercially available than ion-exchange resins.

Industrial solvent extraction (SX) processes are usually run in continuous mode where the aqueous and organic phases are moving counter-currently. For metal extractions mixer-settlers are usually employed, but also columns with mixing and separation sections are used. Each mixer-settler represents one separation stage, but equilibrium may not have to be achieved in each stage. An SX process may contain 100 stages or more. SX processes are known to sustain high loads and being robust in operation conditions. Various kinds of mixers and settlers and their combinations have been developed. The need of the specific process will determine what kind of mixer and settler to be chosen as well as the number of stages.

Ion-exchange (IX) processes are most often based on an aqueous phase percolating through a column packed with a non-dissolvable resin. To avoid clogging of the resin the liquid must be free of solid particles. Also, precipitation or gas emission in the column must be avoided. There are several modes of operation, but most industrial IX processes are semi-continuous. There is one true continuous IX-technology, the CAC – Continuous Annular Chromatograph. The concept of this device is to transform the time used in traditional chromatography to an angle at which the eluent is continuously collected. This is

developed in two versions, one where the packed bed of particles are moving (Carta et al. 1989 [1]; Byers and Williams 1996 [2]), having a static injection point and static exit collection positions, and another, where the injection point and exit collectors are moving while the bed is static (Navratil et al 1992 [3]). The latter version will be easier to use if a long column is needed. The CAC is particularly suited for elution chromatography. It can also be used in "reversed mode" for coarse separations, e.g. separation of groups of elements.

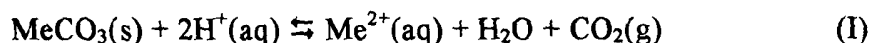
The simulated moving bed (SMB) is a semi-continuous mode with the advantage that the column can be very long. This method is used in very difficult separations where a huge number of theoretical plates are needed, i.e. very long column. SMB is particularly suited for affinity chromatography.

The advantage of IX over SX is the number of stages obtainable. In IX the term "theoretical plate" is used as there is a continuous separation along the column in contrast to SX where each stage is a physical unit. This also implies that it is better to use IX when high purity products are desired as the pure part of the exiting peak can be removed, while for SX all from the final stage must be used.

To achieve the best of each method it has been proved that solvent extraction agents may be absorbed into inert, porous polymer supports in the form of particles. Such impregnated resins behave like other kind of IX-resins without any loss of extractant [4]. Then there are a huge number of selective extractants are available also for the high purity separations. Still this kind of resins requires the same absence of solids in the feed solution.

Then the advantage of a continuous process can be obtained by using a CAC or SMB.

However, the use of dissolving the carbonate containing mineral in a mineral acid will lead to formation and release of CO₂. Also, in addition to the environmentally undesirable emission of CO₂, this is an expensive process as two moles of hydrogen ions, H⁺, is consumed per mole carbonate. A general reaction for a divalent metal ion (Me²⁺) can be written:



There is thus a need for an improved method for extracting elements from carbonate containing minerals, which avoids excessive use of mineral acid and which may avoid discharging formed CO₂.

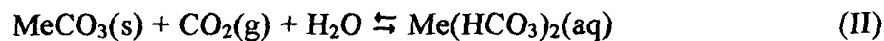
Objective of the invention

The main objective of the invention is to provide a cost effective method for extracting elements from carbonate containing minerals.

A further objective of the invention is to provide a method which minimises the use of mineral acid.

Description of the invention

The invention is based on the realisation that when CO_2 is injected into water, there is formed a weak acid, carbonic acid, which will dissolve carbonates of alkaline and alkaline earth elements in the form of bicarbonates, but generally not carbonates of elements other than the alkaline and alkaline earth elements, such as for instance Group IV elements, rare earth elements and other. Carbonates from these elements will often remain as a solid carbonate phase in the weak acid solution formed by carbonic acid. The general reaction for dissolving the carbonates in the case of a divalent metal may be written:



Also, since the major fraction of carbonate minerals comprises calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), and ankerite ($\text{Ca}(\text{Fe},\text{Mg},\text{Mn})(\text{CO}_3)_2$), the injection of CO_2 may be employed in a closed cycle process where the rare earth carbonates are separated from the major fraction of the carbonate mineral without using the relatively expensive mineral acid. Thus, the main objective of the invention may be obtained by a method as follows:

In a first aspect, the present invention relates to method for extracting elements from carbonate containing minerals, where the method comprises:

- 1) crushing the mineral to particles,
- 2) submerging the crushed mineral in water,
- 3) injecting CO_2 into the water until the alkaline and alkaline earth carbonates are dissolved,
- 4) separating the remaining solid particles from the liquid phase,
- 5) discharge the liquid phase,
- 6) submerging the remaining solid particles in water and add a mineral acid until the particles are dissolved, and
- 7) separation and precipitation of the ionic rare earth elements as oxides by use of conventional hydrometallurgical methods.

By the term "particles" we mean relatively small bits of crushed mineral rock. The mean particle diameter should typically be about 0.5 mm, but any other mean particle diameters may also be applied. The invention will function with almost any mean particle diameter, but smaller diameters will favour the reaction kinetics of the dissolution reactions.

Hydrometallurgical methods for selectively precipitating rare earth elements from the dissolution made in step 7) of the method according to first aspect of the invention are well known to a skilled person. There is no need for describing such methods. Also, any suitable hydrometallurgical method may be applied since the inventive feature of the first aspect is the use of carbonic acid to selectively dissolve the alkaline and alkaline earth carbonates and thus allow use of liquid-solid separation techniques for separating out the non-dissolvable remaining rare earth carbonates of the mineral. The method may for example also be applied for extracting Group 4 elements – Ti, Zr, Hf, which will have great value and can be dissolved by using much less acid compared to dissolving the whole mineral.

The method according to the first aspect of the invention solves the problem of excessive use of mineral acid since the mineral acid is not used to solve the major fraction of the carbonate mineral, but only the carbonates of interest.

In cases where the dissolved alkaline and alkaline earth bicarbonates formed in step 3) of the method according to the first aspect of the invention may be discharged in a waste disposal or in the sea, the method obtains another benefit in that it consumes CO₂. In this case the method becomes CO₂ negative and may be employed to extract CO₂ from other CO₂-forming processes.

However, in cases where waste disposal of the bicarbonate solution is not available, the method according to the invention may be made CO₂-neutral by including a precipitation step of the alkaline bicarbonates as solid carbonates with capture and reuse of the CO₂ in step 3).

In a second aspect, the invention relates to a method for extracting elements from carbonate containing minerals, where the method comprises:

- 1) crushing the mineral to particles,
- 2) submerging the crushed mineral in water,
- 3) injecting CO₂ into the water until the alkaline and alkaline earth carbonates are dissolved,
- 4) separating the remaining solid particles from the liquid phase,
- 5) submerging the remaining solid particles in water and add a mineral acid until the particles are dissolved,
- 6) separation and precipitation of the ionic rare earth elements as oxides by use of conventional hydrometallurgical methods,
- 7) increase the pH of the liquid phase from step 4) by adding a base until the alkaline and alkaline earth elements are precipitated as solid carbonates,
- 8) collecting the CO₂ formed in step 7) and re-cycle the gas to step 3), and
- 9) separating the precipitated carbonates from step 8) and discharge them.

The precipitation of the alkaline and alkaline earth metals may be given as reaction II above in the case of a divalent metal, but in reverse. The discharge of the precipitated carbonates may be in a waste disposal.

In a further aspect, the invention may be used for forming a valuable product, precipitated calcium carbonate (PCC). This may be obtained by including a separation step in step 6) for selectively precipitating the calcium carbonate. There are available conventional hydrometallurgical methods known to a skilled person for selectively precipitating calcium carbonate from a solution of mixed alkaline and alkaline earth elements, and where the colour, particle size and porosity can be controlled. This allows the precipitated calcium carbonate to be sold as PCC, Precipitated Calcium Carbonate; a highly priced commodity. Any such hydrometallurgical process may be applied by the invention.

Example:

Fen deposit in Ulefoss, Norway

This area has been known for its complex mineralogical composition for a century and there have been several mines in operation, in particular for iron and niobium. Fen is the site where the main Norwegian thorium deposits are found. The thorium minerals at Fen are known to be oxide and silicate, but experience obtained in the 1980's indicates that some is also abundant in carbonate rock. The Fen area has been surveyed for rare earth elements (REE), in particular scandium, and the total REE-containing rock, "rødberg and rauhaugitt" (hematite containing dolomite-calcite and ankerite ferrocarnatite) were estimated to 400 million tonnes with an average REE content of 0.9 % REO (rare earth oxide, Ln_2O_3). Thus, it is a huge deposit, but the rock is very inhomogeneous. Table 1 gives content of REE in one typical sample of Rødberg, and Table 2 indicates concentration of selected elements in hydrochloric leachates.

Table 1. Content of rare earth elements and thorium and niobium in rødberg, determined by different methods at different laboratories. All concentrations in ppm.

La	Ce	Nd	Sm	Eu	Lu	Y	Sc	Th	Nb
1800	4000	1800	300	60	25	200	70	600	450

Table 2. Leachates of rødberg with 5M HCl at 70°C. All figures in ppm.

Test	Ce	Nd	Eu	Y	Sc	Th	Ti	Zr
A	310	240	6	30	11	70	50	8
B	340	265	8	38	13	34	63	7

The data reported in Table 2 were obtained by traditional hydrochloric leaching with CO₂ emission. However, there are published reports indicating the possibility of using aqueous CO₂ as leaching agent [5]. The physical conditions for this particular ore would be temperature below 100 °C, pH between 5 and 7 and pressure of CO₂ in the range of 1 – 100 bars. These parameters must be determined specifically for each mineral.

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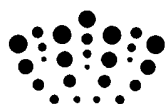
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CLAIMS

1. Method for extracting elements from carbonate containing minerals, where the method comprises:
 - 1) crushing the mineral to particles,
 - 5 2) submerging the crushed mineral in water,
 - 3) injecting CO₂ into the water until the alkaline and alkaline earth carbonates are dissolved,
 - 4) separating the remaining solid particles from the liquid phase,
 - 5) discharge the liquid phase,
 - 10 6) submerging the remaining solid particles in water and add a mineral acid until the particles are dissolved, and
 - 7) separation and precipitation of the ionic rare earth elements as oxides by use of conventional hydrometallurgical methods.

2. Method for extracting elements from carbonate containing minerals, where the method comprises:
 - 1) crushing the mineral to particles,
 - 2) submerging the crushed mineral in water,
 - 3) injecting CO₂ into the water until the alkaline and alkaline earth carbonates are dissolved,
 - 20 4) separating the remaining solid particles from the liquid phase,
 - 5) submerging the remaining solid particles in water and add a mineral acid until the particles are dissolved,
 - 6) separation and precipitation of the ionic rare earth elements as oxides by use of conventional hydrometallurgical methods,
 - 25 7) increase the pH of the liquid phase from step 4) by adding a base until the alkaline and alkaline earth elements are precipitated as solid carbonates,
 - 8) collecting the CO₂ formed in step 7) and re-cycle the gas to step 3), and
 - 9) separating the precipitated carbonates from step 8) and discharge them.

3. Method according to claim 2,
 - 30 where the method further comprises
 - separation of the solution formed in step 3) into a calcium bicarbonate solution and a second solution containing the remaining dissolved carbonates, and
 - selectively precipitate the calcium bicarbonate solution to form precipitated calcium carbonate, and then the second solution to form other alkaline or earth
 - 35 alkaline carbonates.



Application No: GB0819597.6
Claims searched: 1-3

Examiner: Nicholas Mole
Date of search: 9 March 2009

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
A		US 3857920 A (GRANTHAM) see esp. example 3
A		US 2001/0022952 A (RAU) see paras. 74-77

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^X:

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Worldwide search of patent documents classified in the following areas of the IPC

B01J; C01D; C01F

The following online and other databases have been used in the preparation of this search report

WPI EPODOC

International Classification:

Subclass	Subgroup	Valid From
C01F	0017/00	01/01/2006