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㉒ A method of purifying a substance by the selective alkaline carbonate leaching of said substance to remove uranium therefrom.

㉒ A method of purifying uranium-containing substances containing compounds of one or more of the metals aluminium, magnesium, calcium and iron by removing the uranium from said substances. The purification is effected by selective, alkaline carbonate leaching of the uranium. The substance is finely divided and slurried in an aqueous solution containing 0.3–1.5 mole/l of carbonate ions and having an oxidation potential of 0.3–1 V, and subsequent to the leaching process the leaching liquid has a pH of between 8.5 and 10.5 at a pressure of 0.2 to 2.0 MPa.

The substance may be finely-divided by wet-grinding, and the leaching solution used as the grinding liquid. The leaching is preferably effected in a tube reactor vessel in which the substance is slurried in leaching liquid at a temperature of 120–180° C and leached at a partial pressure of oxygen of 0.1–0.6 MPa.

EP 0 005 420 A1

A METHOD OF PURIFYING A SUBSTANCE BY THE SELECTIVE ALKALINE
CARBONATE LEACHING OF SAID SUBSTANCE TO REMOVE URANIUM THEREFROM

The present invention relates to a novel purifying process for separation uranium from a uranium-containing substance, by subjecting said substance to a selective, alkaline leaching process. By substances is herein meant primarily phosphorous - containing, carbon-
5 containing and/or sulphur-containing substances having compounds of one or more of the metals aluminium, magnesium, calcium and iron. Purification of the substance is effected by leaching a finely-divided slurry thereof in a leaching liquid containing 0.3-1.5 mole of carbonate ions per litre and having an oxidation potential of 0.3-1 V,
10 said leaching process being effected so that the leaching liquid, subsequent to said leaching process, has a pH of 8.5 to 10.5. The leaching process is carried out at a pressure of 0.2-2.0 MPa.

It has been discovered in recent times that radioactive material is
15 abundantly present in a highly undesirable manner in industrial products. Thus, uranium has been found in building materials and radioactive substances have been found in fertilizers such as phosphates, phosphorites and apatites. When mining slates or shales containing kerogen, it would also seem necessary to separate the uranium present
20 therein. Granite also contains uranium. Moreover, uranium is a valuable crude product for the manufacture of energy.

Thus, the removal of radioactive components from a long list of materials is highly desirable, it being of particular interest to remove
25 uranium, which is one of the most abundant radioactive materials in nature. It has now been found that such purification can be effected to advantage without removing aluminium, magnesium, calcium and iron from the substances at the same time. This enables the method to be used on a commercial scale, for purifying substances containing
30 said metals in large quantities. The method can also be used to advantage on those substances which contain phosphorus, carbon and sulphur, and particularly kerogen-containing substances such as slates and shales.

Uranium is present in the form of an impurity in many substances. Thus, crude phosphate normally contains from 200 - 400 grams of uranium per ton; phosphorite normally contains from 100 - 1000 grams of uranium per ton; apatite normally contains 50 - 200 grams of uranium per ton; granite normally contains 0 - 100 grams of uranium per ton; and slates and shales normally contain 50 - 1500 grams of uranium per ton.

The pressure leaching of uranium ores for removing uranium therefrom with carbonate solutions is generally known. It has now been found possible to use this technique for the purpose of removing uranium from other materials, a surprisingly good and selective purifying result being obtained.

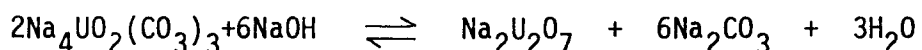
It has also surprisingly been found possible to effect the purifying of such substances by carbonate leaching processes with a considerably higher yield than that obtained when using acid leaching processes, which was not previously supposed. Purification of substances in accordance with the invention has been found to give a substantially better result during a 24 hours leaching time than a seven day leaching time using conventional sulphuric acid leaching processes. A sulphuric acid leaching process at the same temperature and pressure as with the present invention, provides a much poorer result.

It has previously been presumed that when leaching with an alkaline solution, the materials must be ground to a much higher degree of fineness, which would render the process much more expensive than an acid leaching process (Erzmetall 30 (1977) page 147). It has been found, however, that extremely good results are obtained with materials which are ground to a lesser degree of fineness than that previously considered necessary.

As a result of the selectivity of the method when leaching uranium from uranium-containing substances, important advantages are gained in the form of low reagent consumption and a lowering in the percentage of metals lost. An acid leaching process is not selective in this respect.

The method according to the invention is suitably effected by wet grinding the substance, optionally whilst adding an oxidant to the leaching liquid, in a mill, such as a ball or rod mill. The suspension obtained is then transferred to an autoclave, suitably a tube reactor vessel, by means of a pump. The suspension is treated in the autoclave for a sufficient period of time in the presence of an oxidant, normally from 0.25 to 24 hours, at a pressure of 0.2-2.0 MPa, whereafter the leaching liquid is separated from the leaching residues. The leaching residues can then be used as a purified crude material for different processes, such as the manufacture of fertilizers and the recovery of valuable products present in the substances. When using a tube reactor vessel, the reactor is suitably cooled by lowering the pressure stepwise whilst, at the same time, utilizing the heat content of the suspension to heat the input material to the reactor.

The suspension is conveniently thickened by sedimentation or separation, and is finally filtered through a suitable filter, such as a drum filter, a disc filter or band filter. The leached uranium is then removed from the leaching liquid, for example by precipitating with an alkali in accordance with the formula:



Another method is to utilize the ion exchange reaction of, for example, a cation exchanger. Hexavalent uranium, UO_3 , forms in a carbonate ion environment the complex ions $\text{UO}_2(\text{CO}_3)_3^{4-}$. The uranium precipitated out can then be used in a known manner.

Further, it is necessary to maintain an oxidation potential of 0.3-1 V, which as previously mentioned is conveniently effected by supplying oxygen under pressure so as to obtain a partial pressure of oxygen of 0.1-0.6 MPa. It is also possible to add other oxidants, such as peroxides and the like.

In order to obtain a satisfactory leaching yield in respect of

uranium, the temperature should be between 120-180°C. This temperature is obtained by supplying heat to the reactor vessel, and the temperature is suitably regulated by maintaining a total pressure of 0.3-2.0 MPa in the autoclave. It is necessary that the pH of the suspension upon termination of the leaching process is in excess of 8.5, in order to obtain the necessary selective, and beneath about 10.5, to prevent the precipitation of uranates.

The advantages afforded by the method of the present invention will now be illustrated with reference to two examples.

Example 1

Tests were carried out to remove uranium from scales by selective, alkaline carbonate leaching.

The crushed scale was comminuted to $K_{80} = 30 \mu\text{m}$ in a wet grinding rod mill with 50% solids. An autoclave was charged with the dewatered material with a dry weight of 400 g. 1200 ml hot water and reagents were added. During heating of the charge from 0°C up to 150°C, oxygen with a partial pressure of 0.5 MPa was added.

The test results and the metal yields obtained are shown in tables 1 and 2.

Table 1

Leaching of comminuted scale.

Test	Treatment solvent etc.	Temp °C	pH		Pressure MPa
			Start	Stop	
A	Water	150	7.9	7.1	0.7-1.0
B	Water + O ₂ (P _{O₂} appr. 0.5 MPa)	150	8.3	1.6	1.2-1.3
C	Water + K ₂ CO ₃ (65 g/l) + O ₂	150	11.5	9.0	1.2
D	Water + H ₂ SO ₄ (200 g/l)	100	0.6	0.5	0.7 (-1.1)
E	Water + H ₂ SO ₄ + O ₂	100	0.5	0.7	0.7
F	Water + H ₂ SO ₄ + O ₂	120	0.4	0.7	0.8

Table 2

Metal yield when maximum uranium yield.

Test	% U start	Yield %				Content in solution mg/l		Reached after h
		U	Al	Mg	Fe	P	V	
A	0.016	1.5	0.1	0.1	0	0.02	0.7	0.5
B	0.016	36	0.6	4.4	38	0.11	14	24
C	0.012	87	0	0	0	-	-	24
D	0.014	37	32	80	24	0.26	143	24
E	0.015	76	21	81	-	0.25	119	2
F	0.013	61	23	80	54	0.31	149	24

It appears from the tables that it is possible to recover uranium from scales with a high yield (87%) and without any substantial dissolution of other metals. Compared to other leach treatments (A, B, D, E, F) the alkaline carbonate leaching (C) is extremely selective.

5 Example 2

Tests were carried out to remove uranium from phosphate rock by selective alkaline carbonate leaching.

10 The phosphate rock was crushed and comminuted to a grain size ≤ 1.0 mm and charged into a Parr Mini reactor together with an alkali solution. Oxygen was added, during heating up to 150°C , with a total pressure of 1.2 MPa.

15 The test results and the metal yields obtained are shown in tables 1 and 2.

Table 1

Test	Phosphate rock g	Temp $^{\circ}\text{C}$	$\text{P}_{\text{H}_2\text{O}}$	P_{tot} MPa	P_{O_2}	pH_{start}	pH_{stop}
1	90.0	150	0.5	1.2	0.7	11.7	11.0
2	90.0	150	0.5	1.2	0.7		

Table 2

Test	Material	U $\mu\text{g/g}$	P %	F %	Si %	Na %
1	Rock	124	14.0	4.4	2.0	0.68
	Residue	97	14.2	4.0	1.7	1.0
2	"	100	14.0	4.1	1.7	1.0

It appears from the tables that the method makes it possible to dissolve uranium from phosphate rock with only minor dissolution of other elements.

- 5 The uranium yield was not sufficient, at least not for industrial application, but it can readily be improved by further comminuting of the rock and by optimizing the physical and chemical conditions of the method, e.g. by prolonging of the leaching time.

CLAIMS:

1. A method of purifying uranium-containing substances containing compounds of one or more of the metals aluminium, magnesium, calcium and iron by removing the uranium from said substances, said purification being effected by selective, alkaline carbonate leaching
5 of the uranium, wherein the substance is finely divided and slurried in an aqueous solution containing 0.3-1.5 mole/l of carbonate ions and having an oxidation potential of 0.3-1 V, and wherein, subsequent to the leaching process the leaching liquid has a pH of between 8.5 and 10.5 at a pressure of 0.2 to 2.0 MPa.
10
2. A method according to claim 1, wherein the substance is finely divided by wet-grinding, and wherein the leaching solution is used as the grinding liquid.
- 15 3. A method according to claim 1, wherein leaching is effected in a tube reactor vessel in which the substance is slurried in leaching liquid at a temperature of 120-180°C.
4. A method according to claim 1, wherein leaching is effected at
20 a partial pressure of oxygen of 0.1-0.6 MPa.
5. A method according to claim 3, wherein the pressure in the tube reactor vessel is lowered stepwise during a heat exchange between the outgoing suspension and the suspension incoming to the tube re-
25 actor vessel.



DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ²)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<u>GB - A - 716 597</u> (NATIONAL RESEARCH COUNCIL) * page 5 *	1	C 22 B 60/02 C 22 B 3/00
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	<u>US - A - 3 175 878</u> (PHILLIPS PETROLEUM) * column 2 *	1	
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	<u>FR - A - 1 092 946</u> ((ÉTAT FRANÇAIS)		
--			TECHNICAL FIELDS SEARCHED (Int.Cl. ²)
A	<u>DE - A - 2 523 933</u> (H. CRONJÄGER)		C 01 G 43/00 C 22 B 3/00 C 22 B 60/02
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A	<u>DE - C - 1 058 489</u> (EISENWERK-GESELLSCHAFT MAXIMILIANSHÜTTE et al.)		
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A	<u>DE - C - 1 192 633</u> (COMMISSARIAT À L'ÉNERGIE ATOMIQUE)		
----			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
X	The present search report has been drawn up for all claims		&: member of the same patent family, corresponding document
Place of search Berlin		Date of completion of the search 09-08-1979	Examiner SUTOR