ENVIRONMENTAL CONSIDERATIONS ON URANIUM AND RADIUM FROM PHOSPHATE FERTILIZERS

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Abstract

In the process of fertilizer production from natural phosphates of sedimentary origin, most of the existing radioactivity will be found in the final product. The phosphates exploited for fertilizer production at about 150 mill. tons/year are processed by two chemical methods: sulphuric and nitric acid attack. In the process of sulphuric acid attack of the phosphate rock, phosphoric acid and phosphogypsum are produced. The first product is used for fertilizer production, either as triplesuperphosphate (TSP) or diammonium phosphate (DAP). The phosphogypsum waste is deposited on stacks thus becoming a source of concern. In the case of nitric acid attack, the result is a phosphonitric (PN) solution, which is used to produce a complex fertilizer NPK. Uranium and 226Ra (usually in secular equilibrium) are dissolved and distributed between the intermediary products. Thus the average concentration of 100 mg/kg U in the phosphate rock is dissolved in 90–95 % in phosphoric acid while the 226Ra of initial 1000 / 2000 Bq/kg concentration is completely precipitated together with phosphogypsum. Therefore phosphogypsum waste has 1000–1500 Bq/kg 226Ra. The TSP fertilizer being produced by partial neutralization of phosphoric acid with phosphate rock with 100–150 mg/kg U, while 226Ra is only introduced in the neutralization process i.e. 500–800 Bq/kg. In the case of DAP, the uranium content is 140–170 mg/kg without the present of 226Ra. The complex fertilizer obtained through the process of nitric acid attack will have the whole uranium and radium of the phosphate rock (both are dissolved in nitric acid) with uranium and radium contents of 120–160 mg/kg, 1000–1500 Bq/kg respectively. The radio-activities of fertilizers produced may be a source of concern since both uranium and radium are exceeding the present accepted limits for their disposal in the environment. About 10,000–15,000 tons/yr. of uranium is spread every year on the agricultural lands worldwide by the use of phosphate fertilizers. In the case of phosphogypsum, there are regulations prohibiting its use in agriculture, construction industry etc., due to its 226Ra content. However, there is no such a rule in the case of fertilizers. There are several recovery plants for uranium from phosphoric acid based on solvent extraction, but as a consequence of unfavourable uranium market some of them were have been closed. However, the profitable consideration that should be taken into account in connection with the uranium recovery, should be the production of a non-radioactive fertilizer. We have developed a simple uranium recovery process in Romania based on a one cycle extraction-stripping principle. This process was successfully demonstrated in a big pilot plant of 7 m^3/h phosphoric acid capacity. The process was extended to industrial scale and three plants were built in Romania. This process was extended to the nitric acid attack that resulted in the elimination of 226Ra. Thus in both cases, either in sulphuric acid or in nitric acid attack, the final product is a non-radioactive fertilizer. The two flowsheets of the process are given is this paper.

1. INTRODUCTION

The natural phosphates of sedimentary origin which represent about 85% of those exploited for fertilizer production were found to be radioactive [1]. Uranium and its decay products

were the source of this radioactivity. Radium is the main radioactive member of the series, which is in equilibrium with ^{222}Rn [2].

A special attention was given to uranium from sedimentary phosphates starting in 1950 [3]. At that time all new sources of uranium were screened for the fast developing nuclear programmes.

Phosphate fertilizer industry has also much extended requiring about 150 mil.tons/year natural phosphates [3]. Since average uranium content of phosphate rock was 100 mg/kg [4, 5] it is easy to estimate a non negligible 10–15,000 t/yr. uranium wasted at the same time with the fertilizer spread on agricultural lands. It is an important energy source lost and also a health hazard [6, 7].

In order to obtain a phosphate fertilizer, the phosphate rock undergoes an acid attack resulting an intermediate product phosphoric acid containing more than 90% of uranium in the liquid phase which is easy do be recovered. Since the mining costs are supported by the fertilizer plant, uranium eventually recovered is a by product obtained at lower costs.

For this reason in the booming era of nuclear programmes, uranium price soared to USD 100/kg or even more being a serious incentive to build several recovery plants in USA and elsewhere attaining a recovery capacity of 4,000 tons/yr. uranium in the phosphate fertilizer industry. However this booming era reached its peak in 1978–1982 then followed an interval of decreasing trend which in 1989 had much affected the uranium industry with its market marginal in profits [8].

In the last 10 years uranium price dropped to 20–25 USD/kg and immediate consequence was the closure of many mines and uranium industry suffered an important setback, uranium from phosphate being not excepted of these phenomena even if some plants survived.

Uranium recovery for nuclear purposes is one aspect of the problem. However there is another aspect related to environmental contamination by uranium and its decay products mostly ^{226}Ra. Since some existing regulations impose a limit on uranium disposal at about 0.2 mg/kg and for radium at 50–80 Bq/kg, for various other sources no such rules are given. It is known that most of phosphate fertilizer have 100 mg/kg Uranium content which are spread annually on agricultural lands and the same time also 700–800 or 1400–1500 Bq/kg ^{226}Ra. Some consider these values are not relevant in the case of fertilizer on the ground that only small radio-activities are involved, but in other cases it is relevant.

2. RADIOACTIVITY OF NATURAL PHOSPHATES

Sedimentary phosphates are radioactive, uranium being in equilibrium (exception are also possible) with ^{226}Ra (and ^{222}Rn) while some volcanic phosphates like those of Kola have traces radioactivity (slight trace of thorium). In this paper uranium and radium were determined in various phosphate [9, 10] feeding the four Romanian fertilizer plants (sulphuric acid attack) and other four fertilizer plants by nitric acid attack, each plant having 330,000 tons/yr. phosphate capacity. The results are given in Table I.

Most of sedimentary phosphates are radioactive. As long as the phosphate deposits are not disturbed (exploited), the natural environmental radioactivity is given by surface layers, the

rest is contained in the mass of the rock. Rain waters may disturb this equilibrium and some radioactivity is carried by surface waters contaminating the surrounding agricultural lands. Phosphate exploitation zones may also be a source of concern like those of Florida contaminating large areas [11] due to beneficiation processes. As a result of beneficiation processes, sand and clay are separated of phosphate mineral and are disposed of in ponds. The phosphate clays resulted in the washing process and slimes are pumped to large settling areas. The clay is allowed to settle and water is recirculated. It was believed that settling areas would become waste lands due to radioactive contaminants. However using modern machines the drain of clay surface is feasible and the land reclamation is a process much speeded. Various plants as alfalfa were used to speed the drying process. The land reclamation is a process carried out in 3–5 years. Problems related of working the clay areas were minimized. The phosphatic clay is a fertile soil unique to Florida. Special steps were taken to grow agricultural crops on reclaimed lands. A project was developed but the problem were the uranium and radium distribution in the crops. Thus ^{226}Ra content is of the order of 500–600 Bq/kg compared with common soils of 30 Bq/kg. Therefore plants grown on phosphatic soils accumulate higher radioactivity and the pickup is dependent on the type of crop, and for the same plant they are differently distributed between roots, stem and leaves. Therefore the milk had higher ^{226}Ra content when cows were fed with alfalfa grown on phosphatic clays.

We have insisted on this subject since a similar behaviour might be extrapolated on agricultural lands fertilized every year with phosphate fertilizer.

TABLE I. URANIUM AND RADIUM IN COMMERCIAL NATURAL PHOSPHATES

Phosphate deposit from	Type	U content mg/kg	^{226}Ra content Bq/kg
Florida	Sedimentary	100–150	750–1500
Florida	11	80–100	600–800
Carolina	11	80–120	600–1000
Morocco	11	100–160	800–1600
Tunis	11	30–50	250–350
Algeria	11	100–120	700–850
Israel	11	80–140	800–1200
Jordan	11	80–110	800–900
Togo	11	100–110	950–1000
Senegal	11	100–120	950–1100
Curacao	11	20	--
Kola	Volcanic	20	70

3. RADIOACTIVE DISTRIBUTION IN THE PROCESS OF FERTILIZER PRODUCTION

There are two main processes for fertilizer production starting with natural phosphates: sulphuric and nitric acid attack.

i) Sulphuric acid attack (dehydrate process)

This is by far the most important process discussed here and is based on the chemical reaction:

$$Ca_{10}(PO_4)_6F_2 + 10\ H_2SO_4 + 20\ H_2O \rightarrow 6\ H_3PO_4 + 10\ CaSO_4{*}2H_2O + 2HF$$

From this process, two product resulted:

(a) phosphoric acid (liquid phase) where more than 90% of uranium of the rock is found. No radium is present.
(b) gypsum, usually named phosphogypsum, is the solid phase which carries the whole amount of ^{226}Ra that initial found in the phosphate rock. Phosphogypsum may also carry 5–10% of uranium of the rock.

Since they are dependent on the phosphate rocks used in the process, the following uranium and radium contents are given in the resulted phosphoric acid of 1.25–1.27 density (24–28% P_2O_5). The measurements were based on gamma spectrometry, NAA, X ray fluorescence.

TABLE II. URANIUM AND RADIUM CONCENTRATION IN PHOSPHORIC ACID

Phosphate rock used	Uranium mg/L	^{226}Ra Bq/L
Florida	120–140	40–70
Jordan	80–100	30–50
Morocco	120–160	30–60
Israel	90–110	40–50
Togo	100–110	60
Senegal	100–100	70
Kola	5–10	--
Syria	70–90	60
Egypt	80–100	50
Tunis	40–60	40
Algeria	80–100	60

Therefore most of the uranium in the rock was dissolved and the ^{226}Ra was virtually absent being precipitated in the phosphogypsum. The phosphogypsum analysis is given below:

TABLE III. URANIUM AND RADIUM CARRIED BY PHOSPHOGYPSUM

Phosphate rock used	Uranium mg/kg	^{226}Ra Bq/kg
Florida	10–20	500–1200
Jordan	5–10	500–1000
Morocco	10–15	600–1300
Israel	10–20	600–1200
Tunis	5–8	300–400
Kola	--	60–100
Togo	10	700–1100

Table III confirms the data of Table II.

Phosphoric acid, the intermediate product, is separated from the phosphogypsum and is used for the production of fertilizer. The phosphoric acid is concentrated to 45–50% P_2O_5 and then reacted with phosphate to produce triplesuperphosphate (TSP) according to reaction:

$$14H_3PO_4 + Ca_{10}(PO_4)_6F_2 + 10H_2O \rightarrow 10Ca(H_2PO_4)_2H_2O + 2HF$$

Such a fertilizer includes all uranium in the phosphoric acid and also those in the phosphate rock used in the neutralization process as well as the whole ^{226}Ra of the rock. Therefore the TSP fertilizer from sedimentary rock has an average 80–140 mg/kgU and 300–700 Bq/kg ^{226}Ra. If Kola phosphate rock was used in the phosphoric acid neutralization then no radium was carried by TSP.

The alternative, where phosphoric acid is neutralised with ammonia, the fertilizer produced is usually DAP (diammoniumphosphate). In the alternative of DAP the radioactivity involved is that of the phosphoric acid and therefore no radium is present.

Uranium and radium contents for various TSP and DAP fertilizer are given in Table IV.

TABLE IV. URANIUM AND RADIUM IN VARIOUS FERTILIZERS (SULPHURIC ATTACK)

Phosphate rock used	TSP		DAP	
	U mg/kg	^{226}RaBq/kg	U mg/kg	^{226}RaBq/kg
Morocco	120	400	140	40
Jordan	90	300	100	30
Florida	130	450	140	40
Israel	120	400	120	50
Tunis	60	150	70	30
Kola	--	30	--	30

If uranium is eliminated and recovered by solvent extraction then the TSP uranium content is minimized and in the case of DAP no radioactivity is present. However there are also natural phosphates of much higher radioactivity resulting from uranium phosphates content which may be 20–30 times higher than that met in commercial phosphates. In this case radium follows a similar trend and its high radioactivity in phosphogypsum is of a great problem. Some literature data [2, 4, 6] on uranium content in the phosphate rock is given in Table V.

TABLE V. PHOSPHATE DEPOSITS OF HIGH URANIUM CONTENT

Phosphate rock used	Uranium mg/kg
Brazil	1200
Central African Republic	1600–5600
Siberia (depressions)	up to 4000
Utah	up to 3000
India	up to 300

The high uranium content of phosphate rock is a health hazard and the radioactivity must be removed from phosphoric acid before producing a fertilizer. The alternative, the production of TSP must be avoided and replaced by DAP.

ii) Nitric acid attack of phosphate rock

In this process the rock is completely dissolved including uranium and radium which are found 100% in the liquid phosphonitric (PN) solution [12]. The advantage of the process is that nothing like phosphogypsum was produced. In the process of fertilizer (complex)

production of this type the calcium nitrate $Ca(NO_3)_24H_2O$ is usually separated by strong cooling as a solid crystallized product which is later converted to NH_4NO_3 and $CaCO_3$ by $(NH_4)_2CO_3$. Our determinations have shown that no radioactivity was present in the separated $Ca(NO_3)_24H_2O$ and therefore no radioactivity was carried in the solid $CaCO_3$. Thus the whole uranium and radium from the initial rock are present in liquid PN solution, after the separation of $Ca(NO_3)_24H_2O$.

In the process of complex fertilizer production of NP(K) type the PN solution is neutralized by ammonia. Therefore the end product contains the entire uranium and radium. This is shown in the following table VI.

TABLE VI. URANIUM AND RADIUM CONTENT IN THE NP FERTILIZER PRODUCED

Phosphate rock used	Uranium mg/kg	^{226}Ra Bq/kg
Florida	100–120	1000–1200
Morocco	100–130	1200–1300
Algeria	90–100	1000–1100
Israel	90–100	900–1100
Jordan	80–90	800–900

In this table, it is noted that uranium and radium of the phosphate rock are present in the produced fertilizer. Even in this case where ^{226}Ra concentration is similar or higher than in the case of phosphogypsum no regulations are given for complex fertilizers, but the use of phosphogypsum is forbidden. Uranium in phosphogypsum is negligible but in the case of complex fertilizer the uranium is added to the existing radium. However the Regulating Authority is not issuing limits in this case.

Radium removal from complex fertilizer is a simple matter. In our determination based on classical coprecipitation of Ra by $BaSO_4$ it was possible to eliminate at one stage about 80% of ^{226}Ra from PN solution after $Ca(NO_3)_24H_2O$ separation. A better elimination is feasible at higher yield if Ba^{++} and SO_4^{-}ions are introduced with a flocculant at the clarification stage of PN solution destined for uranium and rare earth recovery by solvent extraction. Solids involved in this process are 5% and usually are recirculated in the fertilizer process. Therefore we have introduced Ba^{++} and SO_4^{-}ions just before neutralization of PN solution by ammonia. In this condition $Ba(Ra)SO_4$ has precipitated and was separated by filtering. About 80% of radium was removed while Habashi mentioned [3] 90% yield, in different conditions. In Table VII the radioactivity of ^{226}Ra in the PN solution is given before and after precipitation process.

After this treatment a complex fertilizer produced will maintain its uranium content but radium is now 150–250 Bq/kg. A further treatment on $BaSO_4$ in another stage may reduce it still further to 100Bq/kg. However, the uranium is left in the fertilizer.

In the next stage Uranium and Rare Earths are recovered by solvent extraction and the end product (fertilizer) has 10 mg/kg Uranium.

TABLE VII. RADIUM ELIMINATION AS BA(RA)SO4 IN PN SOLUTION

^{226}Ra in PN solution Bq/l	% ^{226}Ra removed
1500	83
1200	80
1100	81
1000	78

4. RADIOACTIVITY REMOVAL FROM PHOSPHATE FERTILIZERS

A simple process for uranium recovery from phosphoric acid and a slightly modified version for uranium and radium removal, including rare earth recovery, from PN solution are given in this paper. Based of these versions, two ways of eliminating uranium and radium from phosphate fertilizer are suggested. In the case of sulphuric acid attack the process experimented at pilot scale of 7 m^3/h phosphoric acid capacity, led to the construction of three uranium recovery plants in Romania. At the same time that uranium is obtained for nuclear purposes, as UF_4xH_2O, the produced fertilizer had a low radioactivity. Since the purpose of this work is for the production of fertilizer with very low radioactivity, the processes used are given below for the two cases: sulphuric and nitric acid attack of the phosphate rock.

In the case that no treatment is involved, uranium and radium from the phosphate rock are found in the final fertilizer at various contents. If the alternative of phosphoric acid (sulphuric attack) treated by solvent extraction to remove uranium is selected, the end product, TSP, has only the radioactivity contributed from the phosphate rock in the reaction with phosphoric acid. If Kola volcanic rock is used for this purpose, the resulted TSP has no radioactivity (Fig. 1).

In the case of DAP, no radioactivity is involved, but the uranium has previously been removed by solvent extraction. Starting with PN solutions, first ^{226}Ra has to be removed as $Ba(Ra)SO_4$ then uranium (and rare earth) is extracted and eliminated. The final complex fertilizer (NP type) has a very small radioactivity (Fig. 2).

However phosphogypsum is still a problem due to its ^{226}Ra content and the large amounts stacked near the fertilizer plants. In Romania there are millions tons of phosphogypsum near the 4 existent fertilizer plants, which is a source of concern due to fine particles spread by the wind and ^{222}Rn continuos evolution. No rehabilitation works were involved to cover these stacks with soil and vegetation to stop the environmental pollution. Most of the countries have introduced regulation and have drastically reduced phosphogypsum use in agriculture and construction industry.

In the case of fertilizers like those produced by nitric acid attack, the radioactivity is even higher than that of phosphogypsum since in addition to ^{226}Ra of the same concentration uranium is also present at 140–180mg/kg. No regulation is involved and no Regulating Authority imposes any restrictions on fertilizer use, and the radioactivity being completely neglected. It must be noted that 10,000–15,000 tons/yr. uranium is spread on agricultural lands every year worldwide attended by corresponding radium. At the same time uranium is a heavy metal (the heaviest) and also toxic [13, 14] chemically. There are regulations imposing drastic limits on heavy elements in fertilizers but uranium is neglected. It was already shown

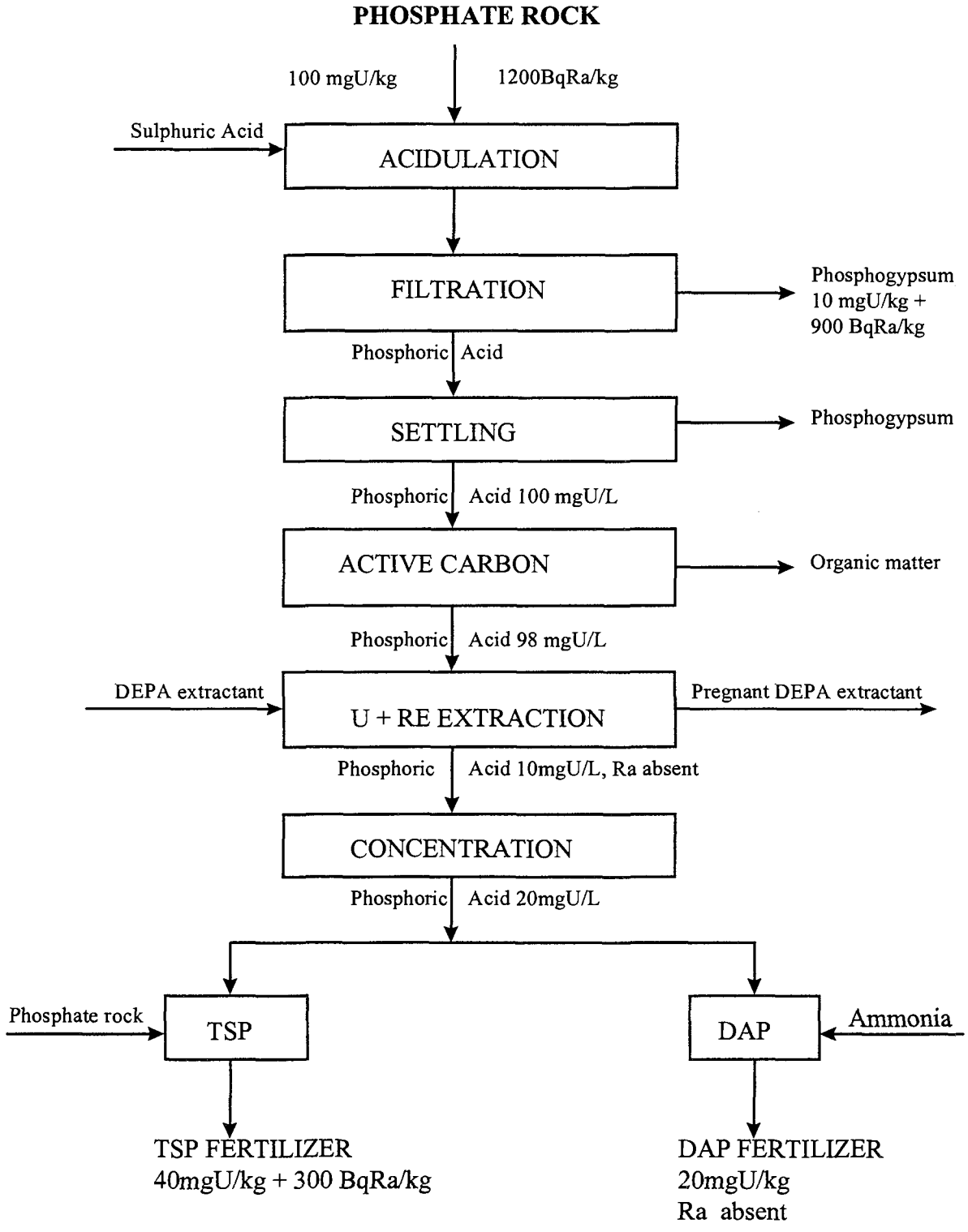

FIG.1. Uranium and radium removal in the process of sulphuric acid attack of phosphate rock for fertilizer production.

that various crops accumulate radioactivity and that ^{226}Ra might be found in milk, but until now no steps were taken to curb the radioactivity in the fertilizers used.

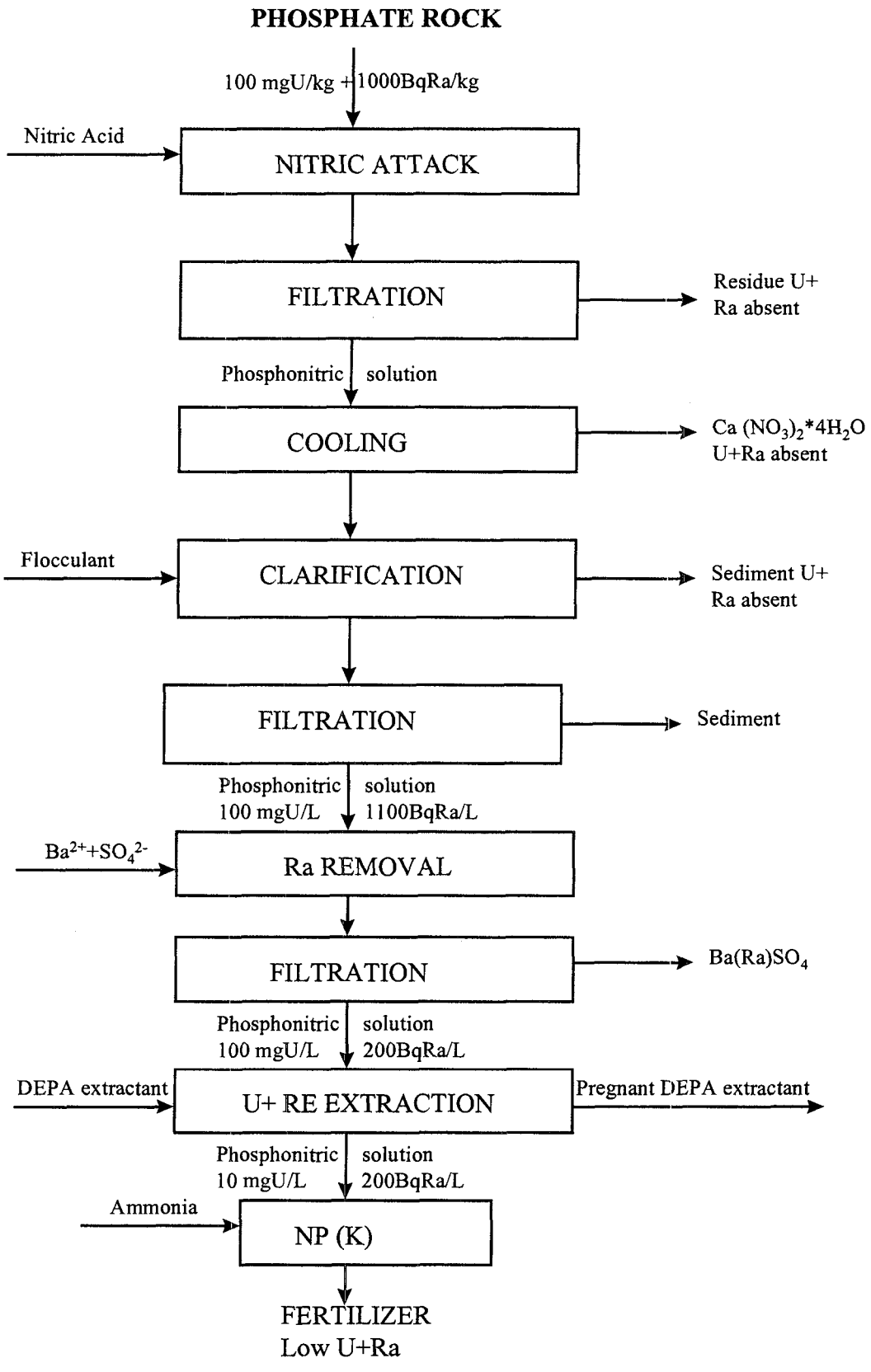

FIG. 2. Uranium and radium removal in the process of nitric acid attack of phosphate rock for fertilizer production.

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