

Eco-friendly technology for “Nitrofos” fertilizer obtained from radioactive man-made waste

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Abstract. The article presents the results of research into the process of purification of phosphoric acid from radioactive isotopes after extraction of uranium, thorium, and REE. It is shown that the main purification of acid is achieved in the process of gypsum precipitation with sulfuric acid and barium nitrate. Additional purification of nitrate-phosphate solution is achieved after uranium extraction and sorption-extraction purification of REE. The sorption raffinate with a concentration of P_2O_5 25 g/L, REE 0.5 g/L and NH_4NO_3 300 g/L were used for fertilizer production. Additional purification of NH_4NO_3 solution from isotopes ^{226}Ra , ^{210}Po , ^{227}Ac is achieved in the process of REE extraction purification. The aggregate of all refining processes of purification of nitrate-phosphate solution from radioactive isotopes provided NP-fertilizer “Nitrofos”, which meets the quality standards. Extraction of P_2O_5 from raw materials into NP-fertilizer – 90%; extraction of REE from raw materials into collective chemical concentrate – 95%; direct commercial extraction of REE from raw materials into the product – 85%.

1 Introduction

Global phosphate fertilizer production is steadily increasing, making it possible to feed the growing populations of developing countries. It is impossible to increase the yield of agricultural land without phosphorus, only through nitrogen and potash fertilizers. The main sources of phosphorus are phosphate rock and apatite of different origin and composition [1]. Ukraine has 41 million hectares of arable land and consumes in the best years up to 90 kg of P_2O_5 per hectare, while producing no more than 50% of the required amount of phosphate fertilizers [2, 3]. Phosphorus raw materials of the CIS countries from the Kola Peninsula and the Republic of Kazakhstan in the form of uranium-phosphorus-rare earth concentrate “Melovoye”. Apatite is the most phosphorus-rich (up to 39%) raw material and contains a minimum amount of radionuclides [4]. Earlier it served as the main source of phosphorus fertilizer “Ammophos” with a P_2O_5 content of 52% [5].

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Ammonium sulfate $(\text{HN}_4)_2\text{SO}_4$, a source of sulfur that improves the microcomponent composition of soil, is important for improving soil fertility [6]. This compound should be applied to soil up to 7 kg/ha, which for Ukraine is equal to more than 250 kt/year [7].

To apply fertilizers to the soil, their composition should contain nitrogen, phosphorus and potassium in the ratio of 1:1:1, which is provided by mixing the components in the form of separate salts. The most available are NP-fertilizers such as “Nitrofos” of different compositions, obtained by processing phosphate rock with P_2O_5 content of ~20%. Phosphate-poor phosphate rock (as compared to apatite) contains valuable elements and radioactive impurities, which must be extracted to obtain environmentally friendly fertilizers with reduced production costs [8].

In the processing of phosphate rock, reagents such as nitric and sulfuric acid, ammonia, and chalk are used. They can constitute the nitrogen part of NP-fertilizers, so they should be extracted into separate soluble compounds. Processing of phosphorites of such composition is not only of scientific but also of practical interest.

Earlier the technology of extraction of valuable components (U, Sc, REE) from phosphorus concentrate “Melovoye” and their purification from radionuclides was developed [9 – 11]. This raw material includes calcium, which, using sulfuric acid, forms gypsum, which can serve as a cheap raw material for obtaining ammonium or potassium sulfate. These compounds are required by plants as sulfur-containing fertilizers. The production of the different components of complex NP-fertilizers within the same production process represents a very important factor in their economic efficiency.

Uranium-containing phosphate rock is a non-traditional raw material, but its reserves in the world are quite significant up to 15.5 kt of uranium per year, or 25% of the world’s production [12]. In Ukraine, the analog of such raw materials is the Novopoltavske deposit in the Zaporizhzhia region, processing of which will require similar complexity processing operations.

The present paper presents the results of tests of the process of processing nitrate-phosphate solutions of various compositions to obtain a wide range of mineral fertilizers and associated commercial products.

2 Research methods

2.1 Characterization of raw materials

The phosphorite concentrate of the “Melovoye” deposit and apatite concentrate were used in the study, which had the following composition (Tables 1 and 2).

Table 1. Chemical composition of phosphorite concentrate.

Component	U	P_2O_5	$\Sigma\text{TR}_2\text{O}_3$	CaO	S	F	H_2O	CaO: P_2O_5
Content	0.173	18.5	0.73	30	7.0	1.6	20	1.6

Table 2. Chemical composition of apatite concentrate.

Component	P_2O_5	$\Sigma\text{TR}_2\text{O}_3$	CaO	Fe_2O_3	Al_2O_3	MgO	H_2O	CaO: P_2O_5
Content	39.2	1.0	51.0	0.42	0.48	0.25	7.0	1.3

The coarseness of phosphate concentrate was 95% fraction < 3 mm; moisture content 18 – 21%; density 3 g/cm³; bulk weight 1.45 g/cm³.

The concentrate is mainly represented by francolite-type apatite mineral $(\text{Ca}_{10}(\text{PO}_4)_6[\text{F}_2(\text{OH})_2(\text{CO}_3)_3\text{O}])$, finely dispersed pyrite (FeS_2) and clay minerals of hydrous mica composition. REEs and uranium are impurities in calcium phosphate and do not form

their own minerals. REE replaces calcium in the crystal lattice of francolite due to the proximity of ionic radii ($r(\text{TR}^{3+}) = 0.99 - 1.22 \cdot 10^{-10}$ m; $r(\text{Ca}^{2+}) = 1.06 \cdot 10^{-10}$ m). The presence of sulfur in the form of pyrite complicates the processing of raw materials, as the process of uranium oxidation with nitric acid can cause undesirable oxidation of sulfur, which requires increased consumption of urea (40 kg/t).

In the concentrate in small amounts ($\sim 1 \cdot 10^{-30}\%$) there are daughter products of radioactive decay ^{238}U and ^{232}Th , which should be selectively extracted and safely buried. The presence of up to 20% clay in the concentrate complicates the filtration process. Phosphorus content is lower than in conventional phosphate rock.

2.2 Methodology of nitrate-phosphate solution recycling

Phosphorus-containing concentrate was treated with a mixture of sulfuric and nitric acid in ratios of 100:1, 50:50, 25:75, 1:100. During processing, the yield of phosphorus in phosphoric acid solution and collective chemical concentrate (CCC), conditions of minimum loss of phosphorus with solid phase, the use of sulfuric acid to obtain fertilizers such as ammonium or potassium sulfate, according to the methodology from the previous study [13] were studied. Chemical analysis of solutions and CCC was carried out according to standard methods [14, 15].

Calcium and ^{226}Ra were precipitated from nitrate-phosphate solution (NPS) in the form of radium sulfate RaSO_4 mixed with gypsum by various reagents, gypsum was extracted and subjected to its conversion by gaseous ammonia, carbon dioxide (or K_2CO_3 solution) to obtain ammonium or potassium sulfate fertilizer. The resulting chalk mixture ($\text{CaCO}_3 + \text{RaCO}_3$) was sent to neutralize ore processing discharge cakes. NPS after calcium extraction was analyzed for the content of phosphorus, nitrogen, calcium, iron and subjected to ammoniation with the study of optimal parameters of evaporation, and granulation to obtain complex fertilizer "Nitrofos".

2.3 Methodology of the purification of phosphoric acid solution from uranium and REEs

CCC containing (%): U – 3.97; P_2O_5 – 38.7; REE – 11.73; CaO – 5.2; Fe – 10.1; N – 8.54; F – 2.7; H_2O – 43.5, had been treated with 47% nitric acid to convert phosphate from insoluble to soluble form, the conditions of maximum phosphorus yield in the liquid phase were determined. After filtration, the concentration of valuable elements and radioactive isotopes ^{226}Ra , ^{210}Po , and ^{227}Ac were determined in the solid phase and filtrate.

The phosphoric acid solution was sequentially purified from radioactive elements (U, Th) by extraction on TBP-DEHPA extractant and sorption on KU-2-8 resin. Ammonium nitrate solution was purified from uranium, radium and thorium isotopes by hydrate cake precipitation at pH 4, uranium rhodanide complex and joint extraction of La and ^{227}Ac .

All technological solutions containing HN_4NO_3 and H_3PO_4 , after purification from radioactive elements, were returned to ore processing to obtain commercial NPS.

Three variants of technological solutions were proposed:

- 1) increasing the concentration of P_2O_5 by reducing the washing solution;
- 2) reduction of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ballast content in "Nitrofos" by replacing part of sulfuric acid with $(\text{NH}_4)_2\text{SO}_4$ solution of 500 g/L;
- 3) increasing the concentration of P_2O_5 by introducing fresh H_3PO_4 obtained during the acid processing of apatite.

3 Research results

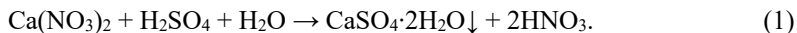
3.1 Extraction of P₂O₅ into nitrate-phosphate solution

Leaching of phosphorite concentrate with 47% nitric acid ensured 99% recovery of P₂O₅ in NPS. Uranium, thorium, REE, calcium, fluorine, and radioactive isotopes ²²⁶Ra, ²³⁰Th, ²²⁷Ac, ²¹⁰Po, and ²¹⁰Pb were transferred to the liquid phase. The addition of sulfuric acid to nitric acid leads to a decrease in P₂O₅ extraction because its word precipitation with gypsum and loss with solid phase after filtration occurs. Calcium in the form of Ca(NO₃)₂ was almost completely transferred to NPS.

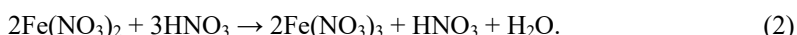
When the NPS is neutralized with ammonia to pH 0.7 and U⁶⁺ is reduced to U⁴⁺ at pH 1.2 – 1.4, most of the uranium in the form of U₃(PO₄)₄ passes into the CCC together with insoluble phosphates Fe, REE, Th, Sc and radioactive isotopes. Thus, the first purification of phosphoric acid from radioactive elements and their decay products occurs. At the same time, 90% of phosphorus passes into the cake, which will have to be extracted in the subsequent operations of purification from radioactive isotopes. During the experiments, it was determined that 91% of P₂O₅ from the raw material was converted to NPS.

3.2 Purification of nitrate-phosphate solution from radioactive impurities and calcium

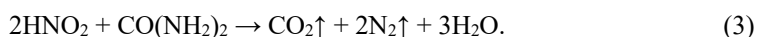
During the experiments, several variants of calcium extraction from NPS were tested. Initially, calcium was precipitated by treating the solution with sulfuric acid until the required ratio between CaO and P₂O₅ (0.40 – 0.45) was reached. In this case, the temperature of the solution was raised to 50– 60 °C due to the formation of nitric acid by reaction (1):



Simultaneously, iron oxidation by reaction (2) occurred:



Under these conditions (60 – 70 °C and an acidity of 40 – 60 g/L HNO₃), the iron precipitated together with gypsum as the acidic phosphate FeH₃(PO₄)₂·2H₂O. Nitric acid was decomposed by urea present in solution by reaction (3):



As a result of precipitation of iron phosphate, up to 10% of P₂O₅ was lost. In this connection, a variant of calcium precipitation with ammonium sulfate solution at a temperature of ~40 °C was tested. This made it possible to reduce phosphorus losses by about 2 times since the process of Fe³⁺ oxidation was sharply practically stopped. However, precipitation of calcium with ammonium sulfate leads to dilution of the solution, which is very undesirable due to the increasing cost of the evaporation process.

To eliminate this disadvantage, a variant of calcium precipitation by sulfuric acid with HNO₃ addition was worked out. In this case, as well as in the first one, iron oxidation occurs, but due to a sharp increase in the concentration of free nitric acid (up to 100 g/L), iron phosphate precipitation does not occur. This variant was taken as a basis for further studies.

Simultaneously with the acid mixture, barium nitrate solution was introduced for purification from radioactive radium. The operation is carried out in the following mode:

- precipitant – a mixture of nitric and sulfuric acids with the content of H₂SO₄ – 1130 g/L; HNO₃ – 487 g/L;
- final CaO content in the solution – 11–12 g/L;
- duration of operation – 3.5 h;
- temperature – 55 °C.

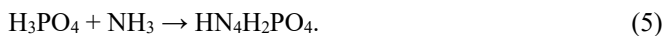
As a result, a solution of the following composition was obtained (g/L): N – 36; P₂O₅ – 50.6; REE – 0.26; CaO – 11.9; Fe – 7 – 9; HNO₃ – 100–120; SO₄²⁻ – 28.2; U – 0.005; ²²⁸Ra – 225.7– 281.2 Bq/L; ²¹⁰Po – 1.78 Bq/L. The content of radioactive impurities in NPS was within the limits allowed by sanitary norms, and the ratio of nitrate nitrogen to P₂O₅ was ~0.7.

3.3 Ammoniation of nitrate-phosphate solution

It was found that during long-term storage from NPS, precipitates fall out, which consist mainly of acidic iron phosphates – NH₄H₂Fe(PO₄)₂ and FeH₃(PO₄)₂·2.5H₂O, which have a fine crystalline structure. The kinetics of phosphate precipitation depends significantly on the amount of free nitric acid, so to prevent the precipitation of iron phosphates from the solution, the nitric acid content of the solution should be at least 100 g/L. Therefore, long-term storage of NPS is not recommended.

It is known that divalent iron phosphates have much higher solubility than trivalent iron phosphates. The results of studies have shown that precipitation from the solution containing mainly divalent iron begins only on the third day of storage. These precipitates contain Fe³⁺ compounds, i.e. during storage there is a partial oxidation of iron, which precipitates. The oxidation rate and sedimentation kinetics depend on the temperature of the solution. The higher the temperature, the faster the oxidation and hence the precipitation of iron phosphate. The solution after calcium release can be stored at 40 °C and pH 1.2 – 1.5 for three days without phosphate precipitation.

NPS containing ammonium, calcium, magnesium nitrates, free nitric and phosphoric acids, as well as fluorine compounds, is a complex multicomponent system. The following reactions can take place during ammoniation of the solution:



In case of excess HNO₃:



Iron ions with phosphoric acid form a series of complex compounds in which H₃[Fe(PO₄)₂] and H₆[Fe(PO₄)₃] are treated as mono-basic acids to form multi-substituted salts, e.g. NH₄H₂[Fe(PO₄)₂].

The NPS was treated with gaseous ammonia in three steps maintaining the following pH values: step I – pH 1.2 – 2.5; step II – pH 3.4 – 4.5; step III – pH 4.4 – 5.0. The duration of the process at a temperature of 85 – 95 °C was 1.5 h. The resulting pulp has the following composition (%): NH₄NO₃ – 19.3; HN₄H₂PO₄ – 5.56; (HN₄)₂SO₄ – 0.35; CaHPO₄ – 0.41; MgHPO₄ – 0.57; FePO₄ – 1.38; AlPO₄ – 0.51; CO(NH₂)₂ – 0.21; CaF₂ – 1.37; H₂O – 69.64; impurities – 0.7.

It was found that decreasing pH < 0.4 decreased the content of the water-soluble form of phosphorus, and pH > 5.5 decreased the total amount of assimilable phosphorus due to the formation of Ca₃(PO₄)₂. The pH range from 1.2 to 5.0 was selected as optimal.

3.4 Evaporation of ammoniated slurry

The ammoniated slurry contains up to 70% water, therefore granulation of such diluted slurry is not practical. In order to reduce the amount of retort, the slurry should be evaporated to the lowest possible moisture content at which it retains mobility. It has been shown that at a moisture content of ~20% in the evaporated pulp, mobility is retained and the amount of water- and citrate-soluble phosphorus does not change. The tests have shown that for evaporation of ammoniated slurry to 18 – 20% moisture content, to avoid clogging of heating tubes, it is necessary to circulate the slurry in the apparatus at a speed ≥ 2 m/sec.

In order to reduce steam consumption, research was carried out on the development of countercurrent multihull evaporation. The steam consumption was significantly lower than in the single-vessel system. As a result, a variant of 4-compartment countercurrent evaporation of nitrate-phosphate slurry was developed, in which initial heating steam (6 at) is supplied to the first compartment (where the sum of salts is 80%), and in the following compartments juice steam from the previous compartment is used. Evaporation of the ammoniated slurry was carried out to the content of the sum of salts 80 – 82%.

The results of deep evaporation of nitrate-phosphate slurry with different nitrogen-phosphorus ratios and constant ratio of water- and citrate-soluble phosphorus (1:1) showed that slurry with higher nitrogen content can be evaporated to higher concentration. The degree of evaporation and the value of the heat transfer coefficient are determined by the N:P₂O₅ ratio. An increase in the nitrogen content of the slurry leads to an increase in the degree of evaporation as well as an increase in the heat transfer coefficients. Sharp fluctuations of heat transfer coefficients and evaporation depth at the change of N:P₂O₅ ratio are explained by the different content of the solid phase in pulp. The lower the solid phase concentration in the slurry, the deeper it can be evaporated. Thus, it is preferable to have a slurry with a lower solid phase concentration for efficient evaporation.

Analysis of the evaporated slurry showed that at boiling point < 135 °C and total salt content < 95%, there was no retrogradation of phosphorus. Based on the experiments, conclusions were drawn:

- a) The N:P₂O₅ ratio in ammoniated slurry should be ≥ 1.5;
- b) The amount of citrate-soluble phosphorus in the pulp should not exceed half of its total amount;
- c) At the boiling point of the pulp < 135 °C retrogradation of phosphorus was not observed.

The obtained fertilizer “Nitrofos” had the following characteristics (Table 3).

Table 3. Main constituents of “Nitrofos” fertilizer.

Component	P ₂ O ₅	N	²²⁸ Ra (Bq/g)	²¹⁰ Po (Bq/g)
Content	16	24	0.41	4.44

It can be seen that the quality of the fertilizer fully meets the requirements of GOST 11365. “Nitrofos” granules have a pelletized shape with a glossy shine. The advantage of the produced fertilizer is its insignificant caking during storage. Rolled smooth surface and low residual moisture content allowed to exclude from the technology of oiling and powdering operations.

The proposed method of calcium precipitation together with barium nitrate effectively reduces the content of ²²⁶Ra to the sanitary level. In the process of experiments was developed technological scheme for extraction of P₂O₅ from concentrate enrichment with the utilization of nitric acid and ammonia is shown in Fig. 1.

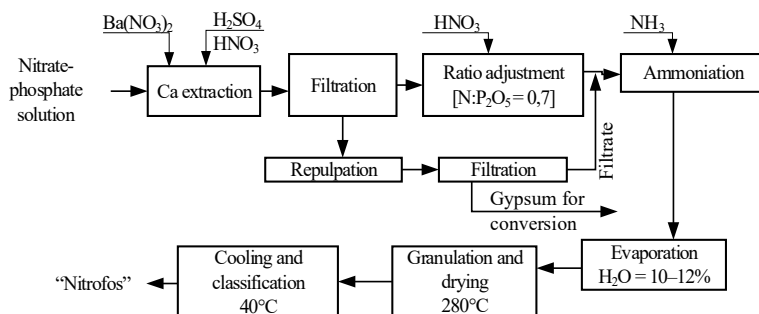


Fig. 1. Technological scheme of “Nitrofos” production from NPS.

3.5 Conversion of gypsum by ammonia and carbon dioxide

The gypsum released in the filtration process can be used to produce chalk and ammonium sulfate, a fertilizer needed to restore soil fertility. Industrial production of ammonium sulfate is based on the interaction of sulfuric acid with gaseous ammonia and carbon dioxide. The application of sulfuric acid for extraction of calcium from NPS allows to removal of a part of the expenses for chalk formation necessary for neutralization of radioactive tailings from ore concentrate processing and their burial in the form of insoluble carbonates. The conversion scheme is standard and is realized in the process of phosphogypsum processing [13]. For 1000 kg of concentrate 329.2 kg of CaO is introduced from which 952 kg of CaSO₄ is formed. Up to 10% of gypsum in dissolved form at an acidity of 100 g/L HNO₃ passes into solution and is ballast for fertilizer. Flue gases containing up to 10% CO₂ can be used for gypsum conversion, which improves the environment. Calculations show that up to 0.85 t of ammonium sulfate is produced per 1 t of “Nitrofos”, which reduces the overall cost of production.

3.6 Phosphorus utilization during the processing of collective chemical concentrate

When analyzing the chemical composition of CCC it was shown that it contains 39% P₂O₅. This represents 9% of its weight in the raw material. Phosphorus plays an important role in the formation of water-insoluble phosphates of uranium, thorium, iron and radioactive isotopes, which allows them to concentrate in the solid phase and separate them from the main volume of NPS.

Additional processing of the process solution of complex salt composition, after the dissolution of CCC in nitric acid, by extraction method allowed to purification of phosphoric acid from radioactive isotopes and to obtain a pure nitrogen-phosphoric solution for its return to ore concentrate leaching. Uranium extraction allows to reduction of its content in phosphoric acid from 10 g/L to 6.5 mg/L, while thorium content increases to 0.3 g/L due to its concentration in the form of thorium phosphate.

REE sorption on KU-2-8 allows effective purification of phosphoric acid from uranium, thorium and radioactive isotopes due to their selective sorption and complete desorption by 3M NH₄NO₃ and 3M HNO₃ solution. After the neutralization of nitric acid with ammonium carbonate, the NH₄NO₃ solution is used to produce phosphate fertilizer.

3.7 Brief economic considerations

At complex extraction of all valuable components of raw materials and utilization of spent reagents, five types of commercial products are obtained during purification from radioactive isotopes:

- 1) Commercial U₃O₈, recovery – 93%;
- 2) REE concentrate enriched with yttrium and europium, recovery rate – 85%;
- 3) “Nitrofos” – double granulated fertilizer, commercial recovery of P₂O₅ – 82%, nitrogen utilization rate – 89%;
- 4) Ammonium sulfate – double granular fertilizer containing 24% of sulfur and 10% of nitrogen;
- 5) Scandium oxide Sc₂O₃ with 99.9% purity.

From the analysis of the actual cost of uranium production, it appears that 58.7% of the total costs are for raw materials. The cost of the processing of phosphorus concentrate is fully recouped by by-products. Thus, by-product production of REE, calcium, sulfur and “Nitrofos” makes it possible to reduce the cost of 1 kg of uranium by 60%; of this amount,

38% is a reduction from the production of REE and ammonium sulfate, 22% – from the production of “Nitrofos”.

By-product recovery of REE radically improves the economic indicators of uranium production. When REE recovery increases from 50 to 85%, the total profit of the production complex increases by 30%. Increasing the REE recovery rate through the use of HNO_3 leads to a 60% increase in the total profit of the production complex. Profit by increasing the volume of production increases by 10%.

Thus, the scheme of complex extraction of valuable components of raw materials and utilization of chemicals allows for profit, which provides profitability of production. An increase of REE extraction ratio up to 85% and phosphorus up to 90% will reduce the production cost to a competitive level, while uranium production becomes profitable. By-product recovery of uranium, REE, Ca, S, and Sc significantly increases the profitability of integrated production for processing uranium-phosphorus-rare earth concentrate with a phosphorus content of less than 22%. Selective extraction of radioactive isotopes allows obtaining environmentally friendly and safe products and fertilizers (Fig. 2).

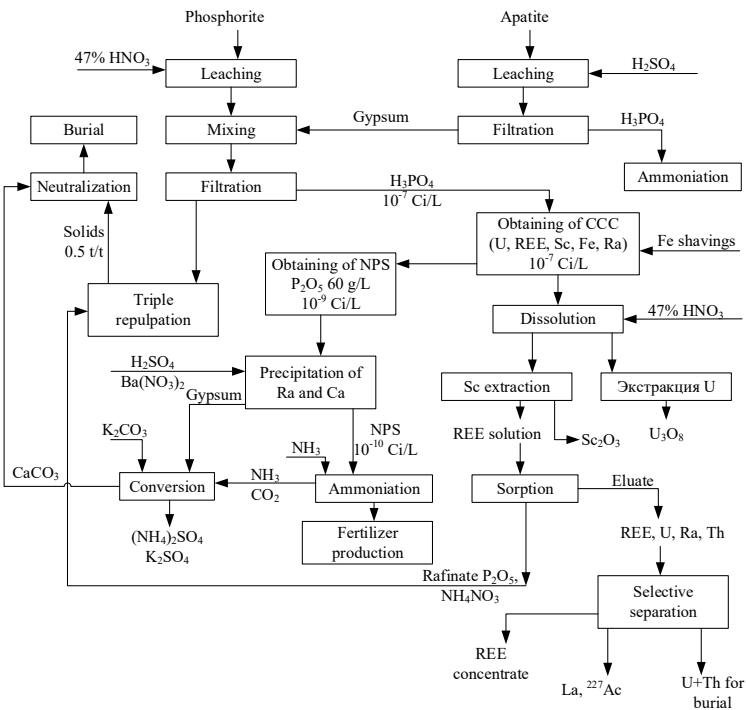


Fig. 2. The influence of the value of the curvature radius on the increasing the well length.

4 Conclusions

The nitric-sulfuric acid scheme for processing poor uranium-phosphorus-rare earth concentrates with a phosphorus content of less than 22% allows, along with uranium and phosphorus, to extract rare earth elements, Ca, S, Sc and utilize the spent reagents in the form of mineral fertilizers, allowing to reduce the cost of production to the world level prices.

A highly economical technological scheme for obtaining REE concentrates ($\Sigma\text{TR}_2\text{O}_3$ not lower than 90%) from nitric acid solutions after uranium extraction by the method of sorption

on the KU-2-8 cation exchanger makes it possible to organize the production of individual REEs.

In the process of researching a comprehensive technological scheme for processing uranium-phosphorus-rare earth concentrates, the following technical indicators were achieved:

- extraction of P₂O₅ from raw materials into NP-fertilizer – 90%;
- extraction of rare earth elements from raw materials in the CCC – 95%;
- direct commercial extraction of rare earth elements from raw materials into finished products – 85%.

The proposed technical solutions for the purification of phosphoric acid from radioactive isotopes have shown their effectiveness and can be recommended for phosphorites of various chemical compositions.

Purification of phosphoric acid from U, Th and their decomposition products by methods of precipitation, sorption and extraction made it possible to obtain environmentally friendly fertilizers.

Associated processing of poor phosphorite and rich apatite concentrate in a ratio of 1:4 made it possible to obtain crystalline gypsum and use it instead of sulfuric acid to ensure filtration of nitrate pulp.

Phosphoric acid obtained from apatite concentrate with a P₂O₅ content of ~24% made it possible to increase the P₂O₅ content in “Nitrofos” to 16%.

The use of nitric acid for leaching phosphorus made it possible to almost completely convert radioactive isotopes into the liquid phase and, using selective processes of precipitation, extraction and sorption, to effectively isolate them into separate products. This made it possible to develop a sustainable technology for processing radioactive phosphorus-containing raw materials.

L.S. Ivanova, L.F. Ryadnenko, and P.YA. Krizhanovskiy, the employees of the “Pridneprovsky Chemical Plant” (PChP) took part in the trials.

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