

**IFA TECHNICAL SUB-COMMITTEE AND COMMITTEE MEETING
15-17 September 1999, Novgorod, Russia**

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NITRIC ACID AND SULPHURIC ACID PROCESSING OF APATITE
TO FERTILIZERS**

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The Khibini apatite is the best phosphate raw stuff in the world. Its processing to fertilizers is profitable even without the extraction of other valuable components contained in it. However, the introduction of the processes which allow extraction of rare-earth elements (REE) contained in it at concentration of about 1% solves the problem of their raw materials in a new fashion and can form the basic stage in revitalization of the rare-earth industry in Russia. The capacities of the apatite concentrate production are about 20,000,000 t/year. Allowing incidental extraction would amount to about 200,000 t/year of REE, and this exceeds world needs many times.

The relative content of oxides of individual REE in apatite is as follows (% by mass):

Ce - 45.0	Y - 3.0	Eu - 0.55
La - 27.0	Gd - 2.0	Er - 0.2
Nd - 14.5	Sm - 1.5	Tb - 0.15
Pr - 5.0	Dy - 1.1	Yb - 0.1
		Ho - 0.1

Interestingly, the REE mixture contains mainly light elements (La to Nd), and the content of such scarce elements like samarium, yttrium, and in particular europium is large enough for organization of their industrial extraction.

Unlike the majority of the sources of REE, the Khibini apatite practically contains no radio-active elements. This considerably simplifies and cheapens the technology of obtaining the commodity RE products because the REE extracted from apatite are also not radio-active and, hence, do not require decontamination or the question about burying the radio-active wastes.

A lesser part of the apatite not exceeding 10% of the total quantity, is processed by the nitric acid method at enterprises in Novgorod, Kirovo-Chepetsk, Dörögobuzh, and Rossosh. During the decomposition of apatite with nitric acid, up to 90% of REE passes into the nitric/phosphoric acid solution (NPS). On introduction of the REE concentrate extraction unit, which is not implemented at any of the above enterprises for the time being, the process flowsheet does not undergo changes both at the start of operations and at the final stage of finished fertilizer products.

The studies carried out have established that the most effective way of extraction of REE from NPS is precipitation of REE phosphates by neutralization of NPS with ammonia up to pH = 1.5 to 2. Such a method well conforms to the technological operations of ammonization of NPS up to pH = 5.8 which exist at the enterprises, for example, at the Novgorod J.-St.Co. "AKRON". In this case, obtaining the REE phosphates by neutralization up to pH = 1.5 to 2 becomes an intermediate stage of the complete neutralization of NPS up to pH = 5.8.

The process flowsheet of obtaining the phosphate rare-earth concentrate (PREC) from NPS is presented in Figure 1. The designations of the apparatuses meet those adopted at J.-St.Co. "AKRON". The flowsheet includes removal of insoluble sediment from the initial NPS, three-stage neutralization of the clarified NPS with

¹ Paper presented at the IFA Technical Sub-Committee and Committee Meeting, 15-17 September 1999, Novgorod, Russia

ammonia up to pH = 1.7 to 1.8, thickening, filtration, and washing the PREC precipitates. The methods for subsequent processing of PREC chosen are based on the specific conditions present:

- drying and sending to an enterprise for centralized processing into commodity products;
- preliminary conversion to hydroxides, carbonates, sulphates, and other compounds,
- dissolving in nitric acid and purifying of REE from phosphorus, iron, and other impurities.

The two last methods allow the return of the whole phosphorus from PREC to the main process and do not affect the fertilizer output.

Taking J.-St.Co. "AKRON" as an example, one can see how the introduction of operations for extraction of REE will affect the technology of producing fertilizers. The installation of thickeners 1 and 2 and vacuum filters 1 and 2 for clarification of NPS and separation of PREC as well as that of a cascade of two reactors for repulping PREC will cause only some increase in the transition residue of the process media, and the alteration of the neutralization conditions in the ammonization stages while maintaining the total ammonia consumption will cause only alterations in the flowrates for the operation stages. So, instead of the existing ammonia distribution: to DC 038 – 75%, to DC 039 – 22%, to DC 040 – 3%, it will be fed: to the high-rate ammonizer – 40%, to DC 038 – 20%, to DC 039 – 20%, to DC 040 – 20%. As a result, the temperature conditions and the water balance of the ammonization unit remain constant, owing to which there will be no remarkable alterations at the tail gas purification and nitroammophos evaporation areas.

The PREC cake being withdrawn from drum-type vacuum filter 2 has the humidity of about 50%. As dry product, it contains in %: REE – 20 to 25; P_2O_5 – 35 to 40, Fe_2O_3 – 1.2 to 1.7; Al_2O_3 – 1.2 to 1.7.

Finally, to remove the impurities from REE, the concentrate is dissolved in nitric acid, thus obtaining the secondary NPS of the following composition, g/l: RE oxides (REO) – 135; P_2O_5 - 185; HNO_3 – 340; NH_4NO_3 – 210. The most effective way of extraction and purification of REE from the solutions of the above composition is a solvent extraction method. As extractant, the most available and cheapest of neutral phosphor-organic compounds, tributyl phosphate (TBP), is used. The selectivity of REE extraction and the increase of the extractant capacity is assured by regulation of the aqueous phase composition in the operation of preparation of the initial solution. It consists of neutralization of excess nitric acid which depresses the REE extraction up to the concentration of about 100 g/l. A greater degree of neutralization of the acid is impossible because of the formation of precipitates. After preparation, the solution undergoes solvent extraction. It seems impossible to achieve the absolute selectivity of REE solvent extraction. The extractant enriched with the components to be extracted also contains other components of the initial solution. To decrease their content to the level required, a washing operation is carried out; i.e. selective re-extraction of accompanying components (impurities) with aqueous solution, which retains possibly a greater part of REE in the extract. The washer extractant undergoes a re-extraction operation. The re-extract is aqueous solution of REE. Carbonate concentrate is precipitated by mixing two solutions, those of re-extract and of precipitant, ammonium carbonate.

The REE solvent extraction is realized in industry in extraction cascades which allow different versions of binding. They are presented on Figure 2.

The cascade consists of three main sections, consecutive extractors (apparatuses) intended for different operations. The cascade is organized on the principle of complete countercurrent operation: countercurrent saturation of extractant with the component to be extracted followed by countercurrent washing of the extractant saturated. The principle of complete countercurrent assures the necessary degree of refining of the desired component, REE.

After preparation, the initial aqueous solution goes into the extraction section. In countercurrent to it, extractant (organic phase) is fed. The aqueous phase – raffinate of extraction – impoverished in the component to be extracted leaves the cascade.

The organic phase saturated upon leaving the extraction section, goes into the washing section. In countercurrent to it, the washing solution is fed in which there are no impurity components. As a washing solution, one may use an aqueous solution that does not contain the component to be extracted or a part of re-extract. The part of re-extract used in washing may be subjected to an additional preparation.

The cascade binding allows, in the limits of the principle of complete countercurrent, different versions of transmission of the aqueous solution, raffinate of washing, leaving the washing section. This solution contains, parallel with impurities, the component to be extracted, or partly re-extracted. The raffinate of washing may be withdrawn from the cascade (Figure 2A). In this case, to decrease the losses of the component to be extracted, it is necessary that the raffinate of washing is delivered to the flowsheet areas preceding the solvent extraction, i.e. into circulation. In particular, it may be withdrawn for preparation of the initial solution (Figure 2B). The version is possible when the refined product of washing does not leave the cascade. In this case, mixing with the initial solution prepared takes place upstream of feeding the aqueous phase into the extraction section (Figure 1C).

The washed extractant leaving the washing section is delivered for re-extraction. In this part, a liquid-phase version is considered in conformity with which an aqueous re-extracting solution is fed into re-extraction section in countercurrent to the organic phase. Re-extract is withdrawn from the cascade. It is the nitric-acid solution of REE purified from non-rare-earth impurities, delivered to precipitation of carbonates. The extractant after re-extraction returns to the cascade, into the extraction section. If necessary, additional sections of extractant preparation are introduced: purification, acidifying.

Table 1 gives the process variables of the area of REE solvent extraction, which are necessary to compare different versions.

Table 1 – Main Process Variables of Binding Versions of Purifying Extraction Cascade

Variable Characteristics	Version							
	A-1	A-2	B-1	B-2	C-1(1)	C-1(2)	C-2(1)	C-2(2)
Using raffinate of washing	Withdrawal to process head	Withdrawal to process head	Delivery to preparation of initial solution to extraction	Delivery to preparation of initial solution to extraction	Delivery to extraction	Delivery to extraction	Delivery to extraction	Delivery to extraction
Acidifying section	Yes	No	Yes	No	Yes	Yes	No	No
Productivity by REE in initial solution, kg/h	112.22	112.22	100.00	100.00	100.00	100.00	100.00	100.00
REE withdrawal to re-extract: - % of initial - kg/hour	87.08 97.72	87.10 97.75	97.97 97.97	97.99 97.99	97.97 97.97	97.96 97.96	97.99 97.99	97.99 97.99
Quantity of cascade stages: - of extraction and washing - of cascade	20 36	20 33	20 36	20 33	20 36	20 36	20 33	20 33
Load to extraction section by sum of phases	3.62	3.62	6.88	6.88	6.96	6.96	6.96	6.96
HNO ₃ concentration in aqueous phases, g/l: - initial to cascade - initial to extraction - raffinate of washing	- 100 64	- 100 64	- 100 64	- 100 64	100 80 61	100 90 80	100 80 61	100 90 80
Re-extract composition: - REE, g/l - HNO ₃ , g/l - P ₂ O ₅ , % mass to REE	125.4 165.0 0.5	125.5 159.0 0.5	65.7 183.0 0.5	65.7 160.0 0.5	64.9 166.0 0.5	64.9 252.0 0.5	64.9 139.0 0.5	64.9 252.0 0.5
Consumption of reagents: NH ₃ (gas), kg/h HNO ₃ (100%), kg/h NH ₄ NO ₃ , kg/h (NH ₄) ₂ CO ₃ , kg/h H ₂ O techn., m ³ /h, TBP, kg/h	53 216 159 46 1.41 1.4	53 226 159 97 1.71 1.4	39 427 305 82 2.61 2.3	39 433 305 185 3.27 2.4	47 435 308 81 2.62 2.3	47 774 308 95 2.87 3.0	47 438 308 187 3.31 2.4	47 719 30 256 3.62 2.8
Waste solutions. Nitric/phosphoric-acid, m ³ /h REE, g/l P ₂ O ₅ , g/l NH ₄ NO ₃ , g/l HNO ₃ , g/l Nitric acid, m ³ /h NHO ₃ , g/l	1.35 1.7 62.2 373 51 0.20 93	1.86 1.2 45.2 316 19 - -	2.47 0.8 55.6 317 52 0.37 75	3.51 0.6 39.2 272 17 - -	2.49 0.8 55.3 331 53 0.37 71	2.62 0.8 52.5 323 72 0.93 174	3.55 0.6 38.8 282 17 - -	4.23 0.5 32.5 263 20 - -

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From the data of Table 1, it follows that the binding with withdrawal of the raffinate of washing to the preceding operations (version A-1) has obvious advantages. It is characterized with less volume loads to the cascade, less consumption of reagents, and less volume of waste solutions. Its only disadvantage is the necessity of avoiding REE losses in the preceding operations. Exclusion of the extragent acidifying section (version A-2) is not presented as justified because it brings to an increase of consumption of nitric acid, ammonium carbonate and of the volume of waste solutions. Besides, the acidifying section is in essence the control section of re-extraction.

It should be noticed that when the raffinate of washing is delivered to solvent extraction (versions C-1 and C-2), within the cascade the acidity of the aqueous phase decreases, which can cause precipitation. An increase of the acidity of the extragent going to extraction partly removes this effect, but requires a considerable consumption of nitric acid (versions C-1-(2) and C-2(2)).

The analysis of the versions of binding of the REE solvent extraction purification cascades carried out allowed to recommend J.-St.Co. "AKRON" the elementary process flowsheet of the units for REE solvent extraction purification from impurities and for obtaining REE carbonates represented on Figure 3. As solvent extraction equipment, centrifugal extractors are recommended since they have a substantially large productivity compared to traditional mixer-settlers.

The majority of Khibini apatite is processed by the sulphuric acid method in three different modes: dihydrate, hemihydrate, and mixed ones. Phosphogypsum obtained by the mixed mode is the mixture of about 30% of calcium sulphate hemihydrate (CSHH) and about 70% of calcium sulphate dihydrate (CSDH). We have studied the REE distribution between the products of sulphuric acid decomposition of Khibini apatite concentrate taking as an example J.-St.Co. "Voskresensk Mineral Fertilizers". The data in Table 2 characterize the REE distribution between extraction phosphoric acid (EPA) and phosphogypsum (PG). It is seen that while transition from the dihydrate mode to the hemihydrate one the degree of REE co-crystallization increases up to 90%.

Table 2 – Distribution of REE between EPA and PG while sulphuric acid decomposition of apatite

Mode	Product	Yield from 1 t of apatite, t	REE content of products	REE distribution	
				kg	%
	apatite	-	1%	10	100
Dihydrate	EPA	1.35	1.36 g/l	1.84	18.4
	PG	1.60	0.51%	8.16	81.6
Mixed	EPA	1.2	0.83 g/l	1.0	10.0
	PG	1.52	0.59%	8.97	90.0
Hemihydrate	EPA	1.05	0.78 g/l	0.82	8.2
	PG	1.35	0.68%	9.18	91.8

The studies of the mechanism of co-crystallization of REE with PG in different modes and their subsequent extraction from the PG phase into solution have shown that PG formed in the hemihydrate mode of apatite decomposition is expedient to be used as initial raw stuff for obtaining REE concentrate.

The development of the technology for obtaining REE concentrate from PG was carried out in the directions as follows:

- determination of the optimum conditions of REE extraction from PG phase into solution;
- processing the solutions obtained with the aim of REE concentration and obtaining pure concentrate;
- possibility of utilization of the wastes formed in the main production.

While processing CSHH with solutions of mineral acids, its recrystallization to CSDH takes place accompanied by transition of the main part of REE into solution. To optimize the conditions of PG recrystallization, the influence of different factors on the degree of REE extraction into solution has been determined.

It is established that the maximum degree of REE extraction makes up 80 to 85% and 55 to 60% in case of PG recrystallization in solutions of nitric and sulphuric acids with the concentrations of 75 to 80 g/l and 100 to 110 g/l, respectively. Additives of nitrates of metals and ammonium favour an increase of the degree of REE extraction into solution and a decrease of the nitric acid consumption while recrystallization. So, while PG recrystallization in nitric acid solutions with concentrations of HNO_3 – 60 g/l and additives – 100 g/l, the degree of REE extraction into solution made up: while using additive of $\text{Ca}(\text{NO}_3)_2$ – 85%, NaNO_3 – 22%, NH_4NO_3 – 52%. The decrease of the degree of REE extraction in the presence of NaNO_3 is obviously connected with formation of double sulphates of REE which have a limited solubility. The increase of the concentration of $\text{Ca}(\text{NO}_3)_2$ higher than 70 g/l causes a negligible increase of the degree of REE extraction into solution.

While increasing the temperature from 20 to 80°C, the degree of REE extraction increases negligibly. The subsequent increase of the temperature brings to a decrease of the degree of REE extraction into solution, which is obviously connected with a displacement of the CSHH $\leftarrow \rightarrow$ CSDH equilibrium to the zone of existence of CSHH.

In the PG recrystallization process, it is expedient to carry out at the S:L ratio of 1:2 to 3 because the increase of this ratio higher than the above value negatively influences the degree of REE extraction into solution, but causes a decrease of the REE concentration, which negatively affects its subsequent processing.

The maximum REE extraction into solution is achieved while agitation of the pulp for 1 hour; in this case sufficiently big CSDH crystals are formed, which favourably affects the filtration productivity.

In summary, the optimum conditions of PG recrystallization are as follows:

Nitric acid solution:

HNO_3 – 60 g/l
 $\text{Ca}(\text{NO}_3)_2$ – 70 g/l
S:L = 1:2 to 3
t = 20 to 25°C
agitation time – 1 hour

Sulphuric acid solution:

H_2SO_4 – 75 to 100 g/l
S:L = 1:2 to 3
t = 20 to 25°C
Agitation time – 1 hour

Table 3 gives the distribution of the main components in the PG recrystallization process. The maximum degree of REE extraction into solution is achieved in case of the PG recrystallization in nitric acid solutions with addition of calcium nitrate.

In spite of the fact that the degree of REE extraction in sulphuric acid solutions is lower than that in nitric acid and yielding only 50 to 60%, using sulphuric acid for PG recrystallization is economically and ecologically justified at the enterprises where there are no purification works able to render harmless the liquid effluents containing nitrate ions.

It is substantial that the PG recrystallization is accompanied by transition of phosphorus and fluorine into solution: the degree of their extraction is more than 90 and 80%, respectively. The additional purification of PG from phosphorus and fluorine compounds assures a high quality of CSDH as a raw stuff for obtaining a gypsum binder.

Withdrawal of REE from the solutions obtained after PG recrystallization is implemented by a solvent extraction method. This method allows considerable decrease in the consumption of reagents and the volumes of the

process solutions in a closed cycle, while obtaining a minimum quantity of waste solutions which may be utilized in the process lines of the main production plant in operation.

In case of using the nitric acid solutions, it is most effective to apply neutral phosphor-organic extragents - phosphine oxides with different radicals (PODR) and di-isooctylmethyl phosphonate (DIOMP). For the sulphuric acid solutions, it is expedient to use acidic phosphor-organic extragents, for example, polyalkylphosphonitrylic acid (PAPNA).

The organization of the extraction cascade for REE solvent extraction in the whole is similar to that examined before the cascade of REE extraction from APS. A substantial difference is in the way of carrying out the re-extraction.

Traditionally, it is implemented by a liquid-phase method with obtaining, as re-extract, aqueous solution for the component to be extracted.

For REE solvent extraction with such extragents as PODR, DIOMP, and PAPNA, requires solutions of mineral acids with a high concentration to assure the completeness of re-extraction. The hydrolysis of extragents taking place under these conditions causes their destruction. The hydrolysis products promote formation of emulsions, which worsens by dividing the phases into layers.

We have developed a process of solid phase re-extraction which combines re-extraction and precipitation of REE carbonate concentrate. Essentially, it involves contact of the extragent containing REE with aqueous solution of ammonium carbonate resulting in the REE carbonate precipitate. After dividing the layers, three phases are formed: extragent, aqueous part of re-extract, and precipitate of REE carbonates.

The result of the complex studies was the flowsheet of production of RE concentrate from PG presented on Figure 4.

The cake being withdrawn from the process is CSDH and has the composition as follows: %: H₂O – 49 to 50; P₂O₅ (total) – 0.2 to 0.3; P₂O₅ (aqueous) – 0.04; F – 0.04. The coefficient of washing from P₂O₅ – 99.8%, the specific surface area is 0.29 to 0.37 m²/g. The CSDH obtained may be used as a raw stuff to produce a gypsum binder. Laboratory studies have shown that using this gypsum allows a binder to be obtained with the mark of T-5 to T-9.

As an extragent, one may use: for nitric acid solutions 0.5 M PODR or 2 M DIOMP in hydrocarbon raw stuff, for sulphuric acid solutions 10% PAPNA in hydrocarbon raw stuff. Table 4 gives the working variables of an extraction cascade.

Table 4 - Extraction Cascade Operational Variables

Stage	Org.: aq. Ratio	Quantity of Stages	Residence time	
			Mixing	Settling
Extraction	1:3	6	3	20
Washing	3:1	5	3	20
Re-extraction	2:1	2	3	40
Acidifying	1:1	5	3	20

The REE carbonates filtered and washed are dried at 100 to 120°C. The carbonates dried are the finished product, REE carbonate concentrate. After calcination at 900°C, the concentrate contains 96% of RE oxides (REO) and 4% of impurities (Fe, P₂O₅, F, Ca, Si, etc.). In case of intensification of the process of washing the organic phase saturated with REE, the content of non rare earth impurities in the finished product can be decreased.

Based on the process flowsheet proposed, at J.-St.Co. "Voskresenks Mineral Fertilizers" and J.-St.Co. "Sviatogor", Krasnouralsk, pilot plants were created for mastering the process variables and turning out pilot batches of concentrate, respectively, according to the nitric acid and sulphuric acid methods of PG recrystallization.

As a result of the tests, the data have been obtained as follows:

	J.-St.Co. "VMF"	J.-St.Co. "Sviatogor"
Degree of REE extraction into solution while recrystallization	51.0%	80.0%
REE extraction in the extraction stage	98.4%	98.0%
Degree of extraction in the re-extraction stage	99.0%	99.0%
Purity of the carbonates obtained (calcinated to oxides)	94.8%	96.1%

The REE concentrate obtained according to this technology may be used an initial raw stuff for processing to individual REE.

The samples of rare earth oxides obtained on calcination of REE carbonate concentrate have been transmitted to SPA "Optika" for evaluation of its polishing properties.

The preliminary results have shown that this product has polishing properties, that is an analogue of polirite produced by the Russian industry, and has the following technical data: REO – 96% including CeO₂ – 44 to 45%, particle size – 2.5 to 3.0 µm, polishing ability – 30 to 45 mg/30 min.

This product may be used to polish technical and optical glass of the III and IV classes.

Based on semi-industrial tests, the technical and economic offers for organization of production at J.-St.Co. "VMF" and the process regulations for J.-St.Co. "Sviatogor" have been issued.

The organization of production of collective RE concentrate at the enterprises producing mineral fertilizers will allow it:

- to manufacture additional commodity products in form of REE concentrate and gypsum binder;
- to increase the P₂O₅ yield into fertilizers owing to after extraction from phosphogypsum;
- to create additional employment;
- to improve the ecological situation in the region.

Finally, as a result of many years of work at ARRICT, the process flowsheets for the separation of rare earth concentrate using nitric acid and sulphuric acid processing of Khibini apatite have been developed and tested.

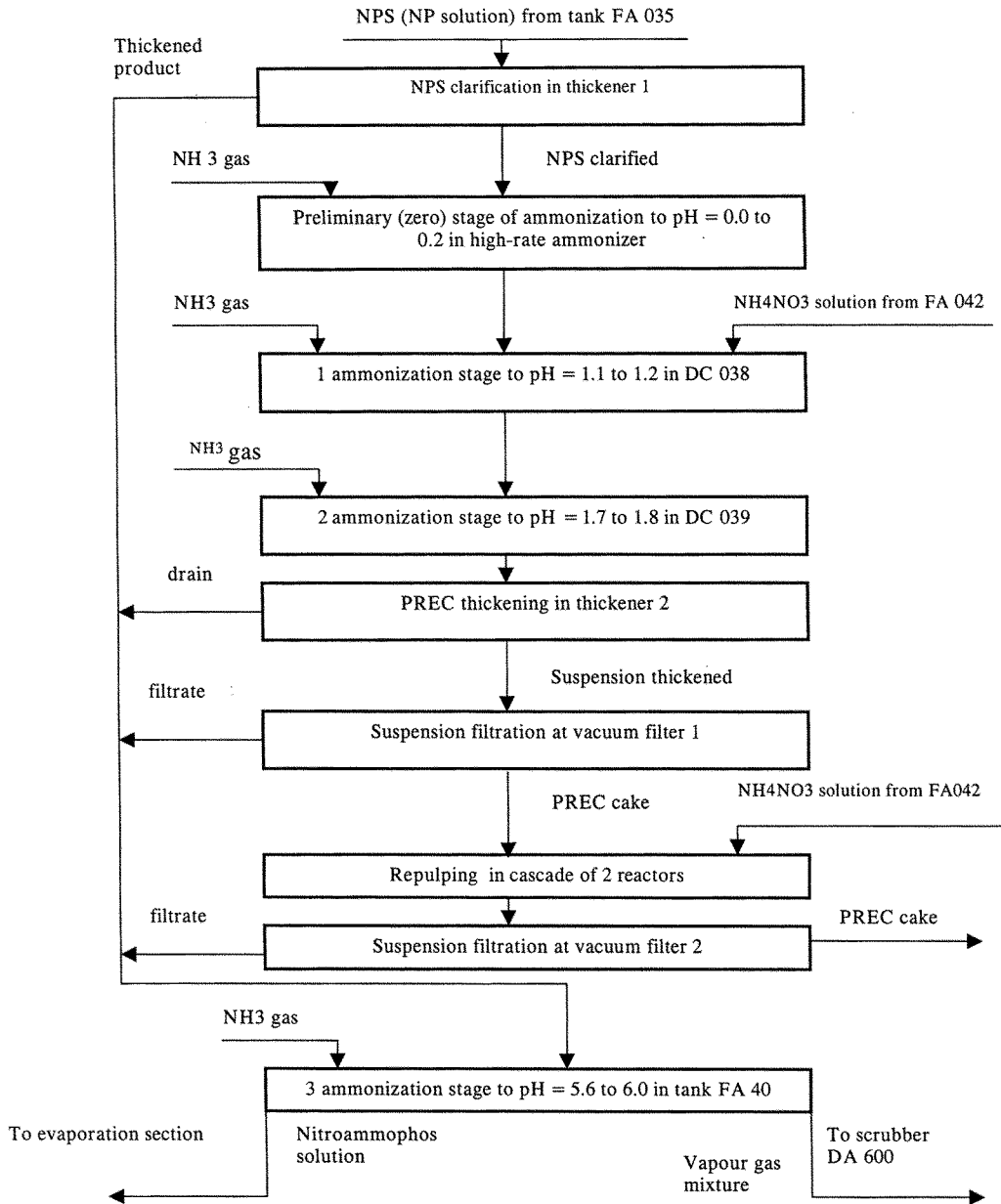
References

1. A.I. Mikhailichenko, E.B. Mikhlin, Yu.B. Patrikeev. Rare-Earth Metals. M., "Metallurgiya", 1987 (in Russian).
2. V.V. Babkin, A.A. Brodsky. Phosphate Fertilizers of Russia. Moscow, "Margus", 1995 (in Russian).
3. A.L. Goldinov, S.D. Moiseev, et al. "Khimicheskaya Promyshlennost", 1980, N° 4, p. 225 (in Russian).
4. S.D. Moiseev, V.A. Semenov, G.L. Shelekhova, "Khimicheskaya Promyshlennost", 1981, N° 8, p. 472 (in Russian)
5. V.S. Ulyanov, S.V. Kudriavtsev, N.A. Tarasova. The IX All-Union Conference on Solvent Extraction. Adler. Theses of Reports. M., 1991, p. 434 (in Russian)
6. V.S. Ulyanov, S.V. Kudriavtsev, N.A. Tarasova, A.M. Shatokhin. Questions of Atomic Science and Technics. Ser. "Chemical Problems of Nuclear Energetics". Issue 1, 19912, p. 12 (in Russian)
7. V.D. Kosynkin, S.D. Moiseev, C.X. Peterson, B.V. Nikipelov. Rare Earth Materials of the 21st Century. Extended Rate Earth '92 in Kyoto. The Rare Earth Society of Japan, 1992, p. 108.

8. J.I. Skorovarov, V.D. Kosynkin, S.D. Moiseev, N.N. Rura. *Journal of Alloys and Compounds*, 180 (1992), p.71)
9. V.D.Kosynkin, S.D. Moiseev, C.X. Peterson, B.V. Nikipelov. *Journal of Alloys and Compounds*, 192 (1993), p. 118.

Figure 1

Scheme of separation of rare-earth concentrate (PREC) while ammonization of NPS



Versions of Binding Schemes of Extraction Cascade Operating by the Principle of Complete Countercurrent. Designation of streams.

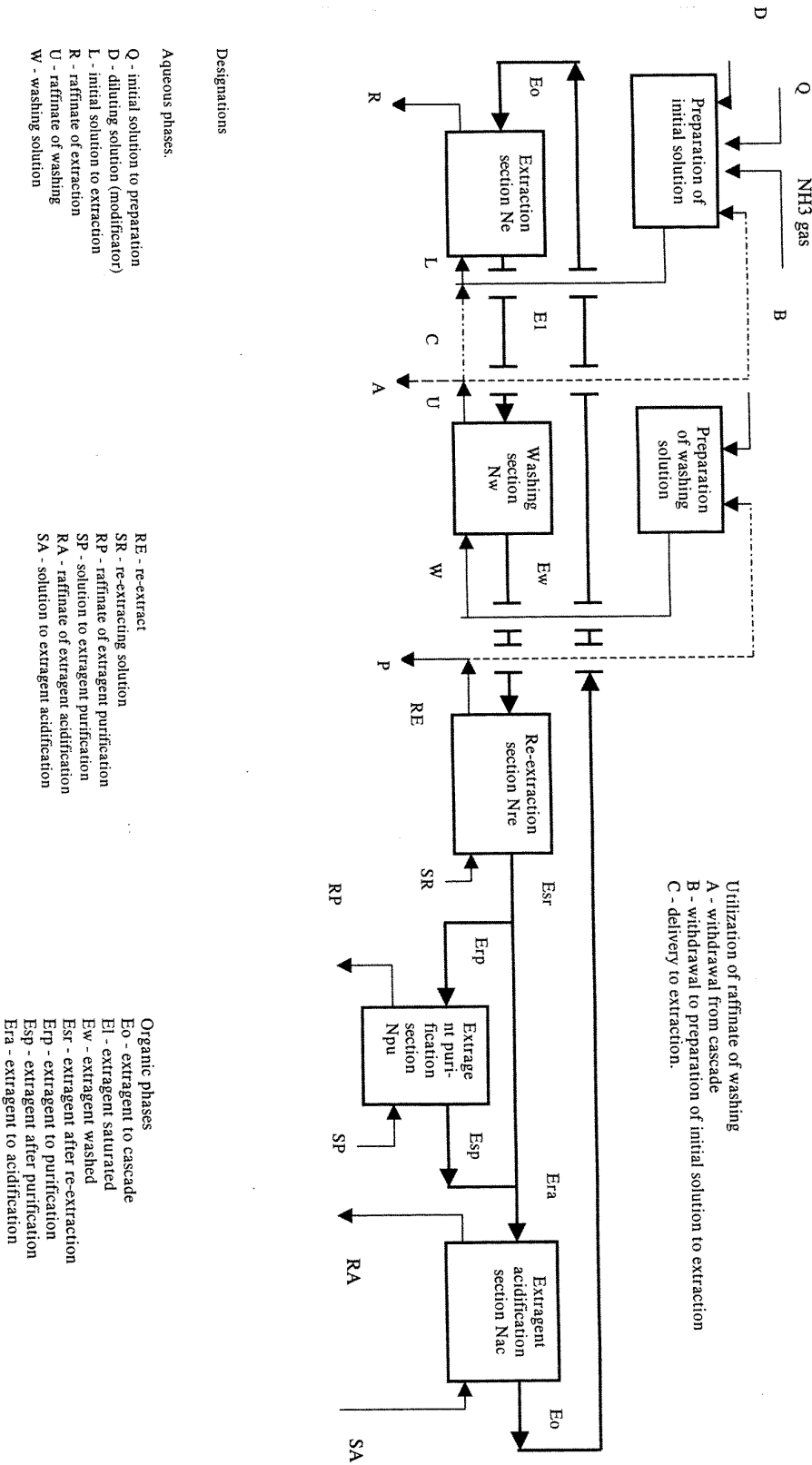


Figure 2

Figure 4

Elementary Process Flowsheet of Production of RE Concentrate from Phosphogypsum

