

## **URANIUM PRODUCTION FROM IMPORTED RAW MATERIAL AT SILLAMÄE IN 1949–1989**

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*Ores, ore concentrates and chemical concentrates imported mainly from Czechoslovakia and German Democratic Republic were processed at Sillamäe plant in the years 1949–1989. The paper describes the development of uranium extraction technology and the equipment used.*

### **Introduction**

Sillamäe uranium extraction factory (Combine No 7) was founded in 1946 to produce uranium from the local Dictyonema shale [1]. This process proved to be technologically and economically unprofitable, and the local mine was closed (conserved) in 1952. The plant was reconstructed for treating imported ores much richer in uranium and much easier to win the metal. A special complex (Shop No 4) for processing of imported ores with the throughput rate 100 t/day was launched in April 1950.

### **Chlorate-Acid-Soda Scheme 1949–1954 [2–5]**

For uranium production in the former USSR in the 1950s the following schemes were used:

- different versions of the acid-soda treatment;
- acid treatment (acid-lime, phosphate);
- extraction;
- static and dynamic versions of sorption on cation or anion exchangers.

At Sillamäe first the classical leaching with soda or acid-soda was carried out. Sulphuric acid-lime leaching used in some cases for some other kind of ores, as well as phosphate treatment were both a great step forward.

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At the very beginning the ores were treated at Sillamäe with melange and soda. This scheme was soon replaced by chlorate-sulphuric acid-soda leaching with gravity concentration at the process head. Gravity concentration was ended in 1951. The flow sheet of the chlorate-acid-soda scheme in general lines coincides (without burning of ore) with the scheme used for uranium processing from Dictyonema shale at Sillamäe this time [2]. It included the following main operations: grinding, potassium chlorate treatment, acid treatment, leaching with soda. Thickened soda pulp was twice filtrated on vacuum filters, the cake was repulped with soda, then treated with sea water and discharged by hydrotransport to depository. Uranium was precipitated from the filtrate with acid and ammonia, filtrated, dried, separated and packed. The final product was 40% chemical concentrate. By the end of 1951, extraction of uranium into chemical concentrate reached almost 80%.

The process of chemical concentrate repurification by salting out ammonium uranyl tricarbonate (AUTC) crystals with ammonium carbonate was introduced in 1952. The regeneration process of ammonium carbonate was mastered as well as calcination of AUTC crystals in rotary tube electric furnace to obtain a new product – mixed oxide  $U_3O_8$ . The latter operation enabled to produce high-quality  $U_3O_8$  in 1953. In this respect the designed capacity of the shop was not only reached but it even surpassed the next year.

Only 3rd-grade ores (0.12–0.27% U) were processed at Sillamäe in 1950–1951. The ores imported from secret production sites had only code names (Volohov, Maltsev, Yermolayev). The shipments transported in open or closed railway wagons were unloaded on a special concrete platform, weighed and stored in a warehouse in separate piles according to ore grade and supplies. In 1950 21.9 t (0.176% U) and in 1951 39.0 t (0.181% U) were processed, maximum extraction degree being 67.9 and 77%, respectively.

The production line for treating 2nd-grade ores was launched in September 1953, raw material was imported from secret production sites Nilov, Grib, Voloschtschuk and others.

U content of 3rd-grade ores processed in 1952–1954 was 0.139–0.94%, that of 2nd-grade ores – 1.527–1.93%.

Imported raw material consisted of primary, mixed and oxidized ores. The first ones were mainly metamorphized shales with nasturan (pitchblende) prevailing upon the other U-containing minerals. Mixed ores were represented by various noncombustible shales rich in hematite. As for U-containing minerals, beside nasturan plenty of secondary minerals (otenite, torbernite) and some black were present. Oxidized ores were mainly quartzomaceous and dimaceous gneisses, in which U-containing minerals were represented by secondary ones (75–80%), heavily altered tar and black (15–20%).

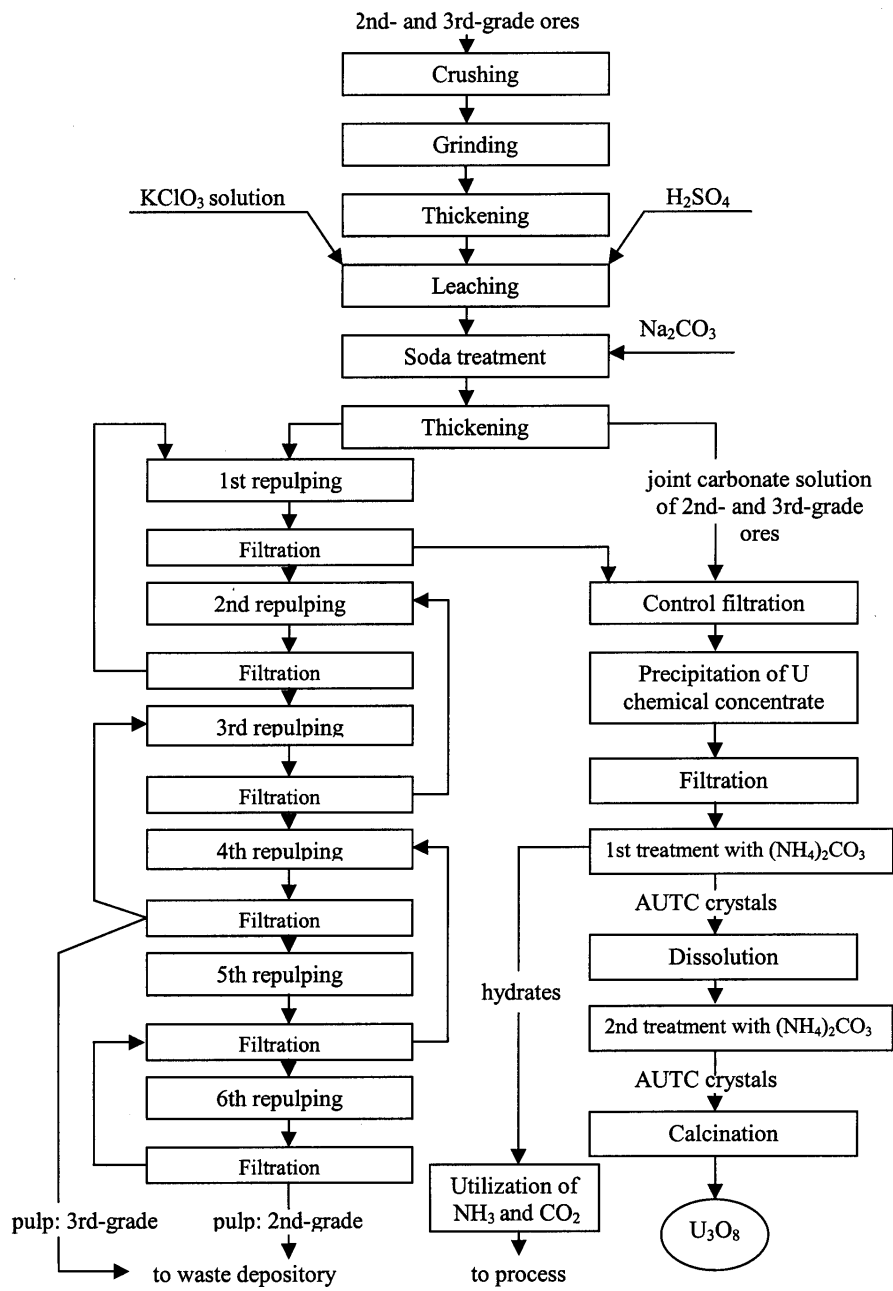


Fig. 1. Technological flow sheet of processing imported ores using the acid-chlorate-soda scheme

The method of processing imported ores based on acid leaching to extract the metal and its purification from main admixtures (Fe and Al) with calcined soda (Fig. 1). Consumption of the latter reached sometimes even 35%, depending on metal and carbonate content of the ore. Soda treatment is effective only when diluted solutions are used. Large amounts of soda pulp had to be thickened and hydrated cakes repeatedly repulped.

As a rule, the concentration of uranium in soda liquors was not high, and for obtaining U chemical concentrate large amounts of soda liquor were treated. Thickening, filtrating and repulping of cakes required enormously large equipment, much steam, electricity and manpower. So, this technology proved to be neither effective, nor economical.

## Acid Sorption Scheme 1955–1985

### The Period 1955-1959 [4, 5]

The changes made at Sillamäe within the period 1955–1959 were as follows.

- Richer ores were imported. 3rd-grade ores contained 0.244–0.433% U, 2nd-grade ones – 1.70–2.58% (in 1955 from secret production sites named Zvezdinsk, Kedrovsk, Sakhanov, Mayevsk, Bogatov).
- The origin of the ores was made public in 1956. The main suppliers were Czechoslovakia, Poland, Hungary, German Democratic Republic.
- Acid sorption scheme was taken into use.

The ministerial decree from October 1954 obliged the Combine to design and mount a full-scale unit for testing the sorption method. In 1954–1955 Sillamäe was one of the first uranium production plants of the all-union hydrometallurgical industry introducing the acid sorption without filtration.

Uranium was extracted from acidic, only partially neutralized pulp using a carboxyl resin SG-1. Sorption department was launched in March 1956. Figure 2 shows two separate lines for processing 2nd- and 3rd-grade ores. Setting up a complementary stage of sorption in lean line – 1st sorption treatment – gave a possibility to combine two pulp flows in sorption unit. Combined processing of the 2nd- and 3rd-grade ores using this new sorption method had satisfactory characteristics and enabled to treat very various raw materials.

The scheme included leaching with acid, but leaching with soda was omitted. Labor-consuming filtrating and repulping of cakes as well as need to set still some more sorption lines were excluded, and uranium losses were less. Less steam, electricity and manpower were needed as well. Working area was half of the old one – i.e. the production required less capital investments.

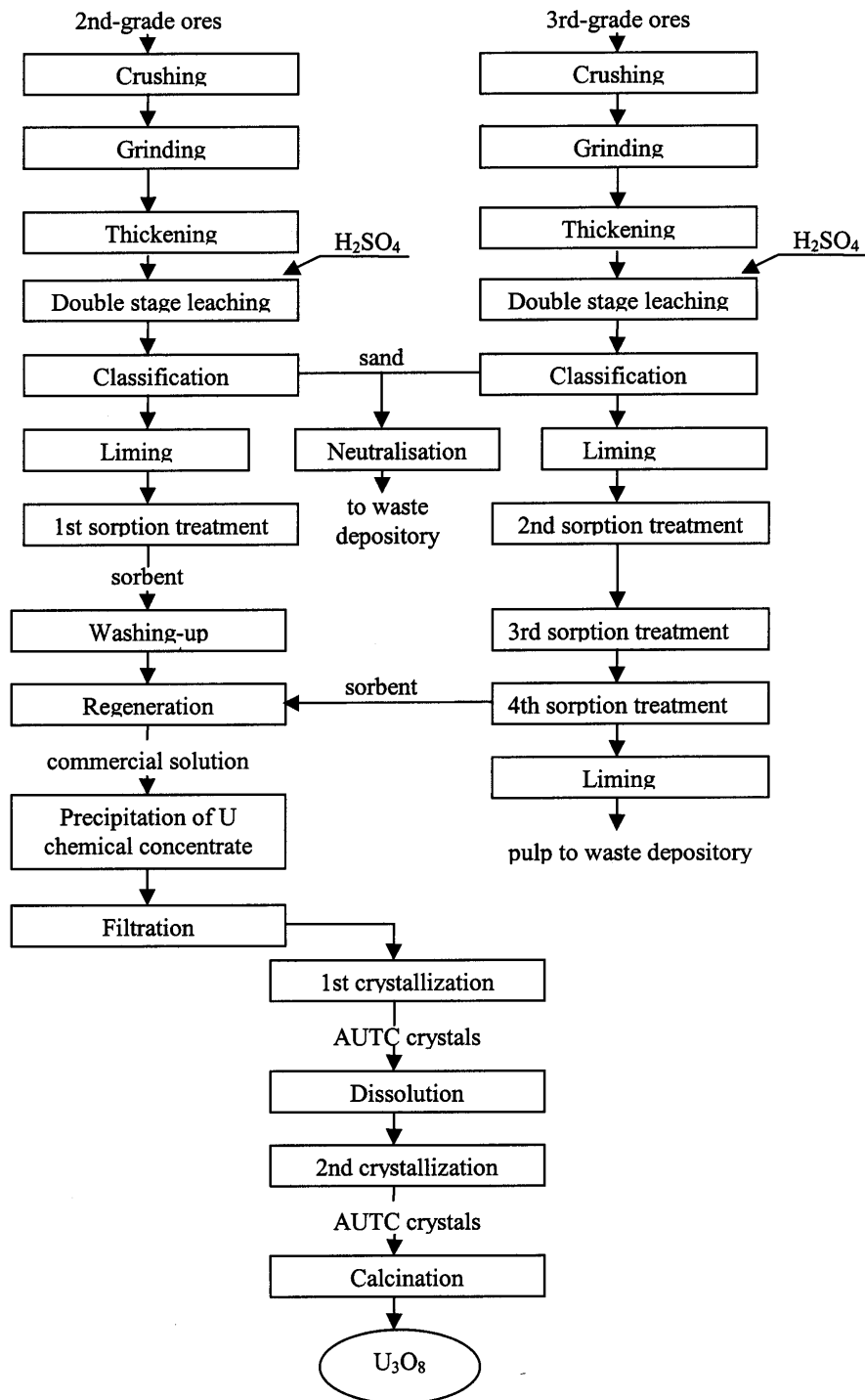
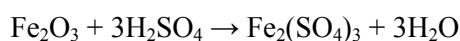
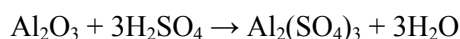
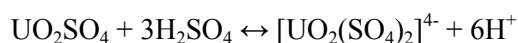
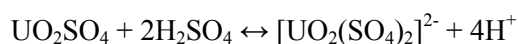
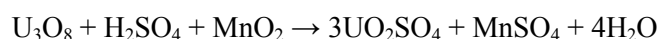


Fig. 2. Technological flow sheet of processing imported ores using the acid-sorption scheme

During the trials from Nov. 1955 to 1958 many steps of the flow sheet were elaborated, and both the technology and equipment were considerably improved. Desorption was carried out using a more economic and less labor-consuming flow scheme of wash water. Six plate-and-frame filters were excluded, 31 employers liberated from hard physical labor. This novel route in uranium hydrometallurgy enabled to enhance the productivity while markedly reducing reagent consumption and the cost price of processing.

Acid leachment of uranium and some accompanying admixtures includes the following reactions:



Selectivity, the most important factor at metal extraction, is strongly effected by both salt composition of the liquor after acid leaching and presence of adsorbable admixtures.

At Sillamäe double-stage leaching with intermediary hydrocycling was applied to process both lean and rich ores. It enabled to improve extraction selectivity considerably, decrease acid consumption to some extent and, as a result, to diminish the capacity of SG-1 towards admixtures, especially Al. Besides, it became possible to process carbonate-rich ores.

After 2nd leaching the sands were repulped once more to catch more uranium. In 1956 discharged sands contained 0.04% U in average, in 1959 – only 0.025%. In the ratio of 2nd- to 3rd-grade ones 1:4, the share of the latter was increased to 1:5. Leaner mixtures were processed preserving the same extraction level – i.e. commercial recovery was higher and uranium losses with sludge pulp were less.

### The Period 1960–1969 [5–7]

The mixtures of ores processed in 1961–1962 contained 0.51–0.52% U on average. 2nd- and 3rd-grade ores were imported from

Poland – 0.22% (3rd), 2.34% (2nd)

Czechoslovakia – 0.39% (3rd), 0.81% (3rd), 1.95% (2nd)

Romania – 0.41% (3rd)

Hungary – 0.21% (3rd)

East Germany – 1.58% (2nd), 3.50% (2nd)

Bulgaria – 2.32% (2nd)

In the end of the 1960s the share of the 1st-grade ores began to grow; the raw material was imported mainly from East Germany and Czechoslovakia.

In 1960 the sorption process equipment was modernized again – eleven novel ion-exchange column-reactors (pachuks) for sorption leaching and five desorption columns were installed. Pachuks worked on counter-current principle – pulp flow from pachuk to pachuk met the flow of AMP resin fed by air lifts. Dosage of sulphuric acid as the leaching agent into pachuks was effected automatically. The pulp from the 11th pachuk was neutralized with ash pulp in the 12th pachuk, the resin from the 1st pachuk was channelled to desorption. In 1961 the pachuks were put into full-scale operation. Flow sheet of the process became shorter owing to omitting precipitation of the 1st chemical concentrate of uranium and filtration on plate-and-frame filters.

In 1961 when old static or reactor-variant was operated, the end product contained 93.1–93.2% U; in 1962 in new pachuk-variant this percentage was already 93.5–93.6%. Maximum content of U in the residual cake fell from 0.034 to 0.021–0.023%, and U losses with leaching tails from 3.3 to 2.1–2.2%.

In 1965–1966 a new original version of the sorption method – sorption leaching – was introduced (Fig. 3). Sorption leaching was carried out in pachuks. Other processes developed were AMP regeneration using the method of chloride conversion, sorption repurification of chloride solutions on SG-1, neutralization of spent pulp with oil shale ash from thermal power plant (TPP). Regeneration of ammonium carbonate after salting out AUTC crystals was mastered. The end product  $U_3O_8$  met more strict requirements concerning admixtures. This new scheme fully replaced the previous one in 1967–1968.

Realization of the combined process in acid medium enhanced the extraction degree and enabled to avoid the labor-intensive treatment of ore sand fraction in a separate unit. Upon that the use of AMP enabled to use the same equipment for ore leaching and uranium sorption on AMP (i.e. to create the so-called “sorption leaching”) and to introduce its large-scale use for the first time in the world practice.

Less  $H_2SO_4$  was needed at leaching carbonate-rich (12–18%) ores as a part of carbonate minerals remained decomposable. Also less lime for pulp neutralization was needed. Limitations caused by diffusion processes were eliminated as the same equipment was used for leaching and sorption.

Uranium production at Sillamäe in 1967–1970 can be characterized by the following data:

	1967	1968	1969	1970
Uranium output, t	1.320	1.357	1.409	1.465
U content of ore, %	0.703	1.085	1.480	1.828
Extraction, %	97.12	97.74	98.02	98.07
$H_2SO_4$ consumption, t/t of U	36.05	28.84	25.22	23.87
Manpower	529	482	301	266

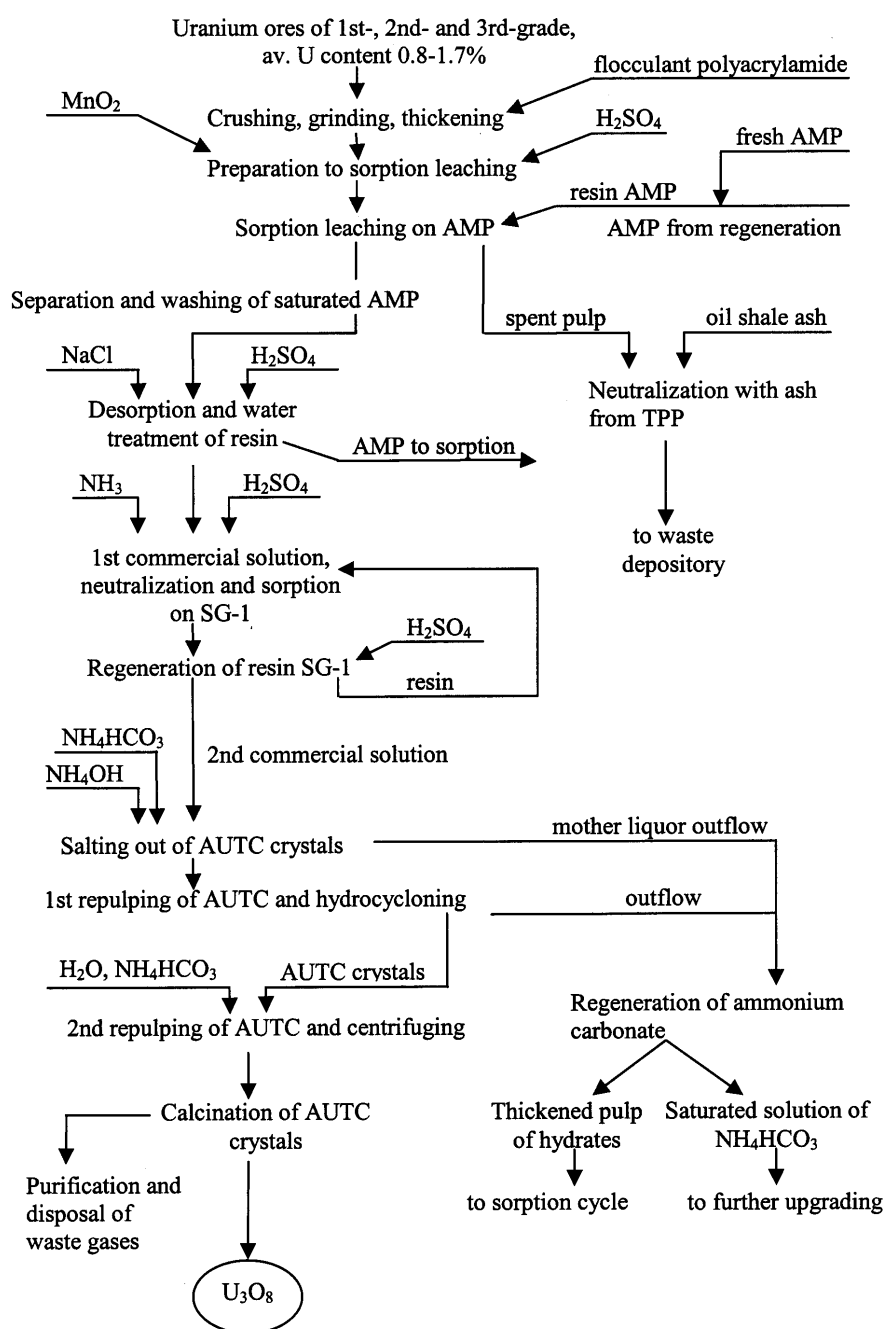


Fig. 3. Flow sheet of combined processing of 1st-, 2nd- and 3rd-grade ores using sorption leaching on AMP (1967-1970)



### The Period 1970–1979 [7, 8]

In 1970 it was decided to decrease ore import in 1971–1975, simultaneously starting to import a 50% chemical concentrate from East Germany. This time two types of uranium containing raw material were processed at Sillamäe:

1. 1st- and 2nd-grade ore concentrates (gravity concentration products, uranium percentage 1.6–7%, supplier – USSR-GDR joint-stock company “Wismut”), and 2nd-grade ore concentrates (1.5–2%) from Czechoslovakia,
2. chemical concentrates (45–55%) provided by “Wismut”.

Ore concentrates were transported in railway wagons in bulk, chemical ones – in special wooden containers which were stored on a special platform on the factory's territory.

Ore concentrates imported from Czechoslovakia were represented by nonoxidized, semioxidized and oxidized U-containing minerals. Nonoxidized (primary) ones consisted mainly of nasturan (80–90%) with black, gummite and uranium mica. Semioxidized and oxidized concentrates contained 40–60 and 10–20% nasturan, respectively, and the same minor components.

2nd-grade ore concentrates from Czechoslovakia were easily leachable with acid as the rock of their origin was mainly of carbonate and aluminosilicate type. Sulphides were also present. At Sillamäe they were commonly known as “shales” with the following chemical composition (wt.%):

U	1.5–2.5	CuO	0.03–0.05
SiO <sub>2</sub>	40–45	CO <sub>2</sub>	9–13
CaO	11–15	S <sub>total</sub>	0.07–1.0
Al <sub>2</sub> O <sub>3</sub>	8–11	P	0.04–0.1
Fe <sub>2</sub> O <sub>3</sub>	5–7	V	0.018–0.030
MgO	1–4	Mo	0.005–0.008
MnO <sub>2</sub>	0.5–0.7		

Gravity concentrates from East-Germany contained the same chemical components but the minerals containing uranium were more mineralized. Their rock-forming minerals – quartz, amphibolite, sericite, feldspars, muscovite – were hard to leach and therefore figuring as “stone” at Sillamäe. These “stones” required preliminary leaching under more severe conditions.

This gravity concentrate contained 45–55% uranium, mainly in the form of sodium diuranate. Fallow powder (specific gravity 4–5 g/cm<sup>3</sup>, bulk – 0.9–1.1 g/cm<sup>3</sup>) of the concentrate had the following average chemical composition (wt.%):

U	45–55	MnO <sub>2</sub>	0.5–1.2
Fe <sub>2</sub> O <sub>3</sub>	9–13	CuO	0.1–1.0
P <sub>2</sub> O <sub>5</sub>	2–4	SO <sub>4</sub> <sup>2-</sup>	8–16
SiO <sub>2</sub>	1.0–3.0	Na	1.0–3.0
Al <sub>2</sub> O <sub>3</sub>	0.1–0.2	K	0.1–0.2
CaO	0.3–3.0	As	0.05–0.5
MgO	0.3–0.8		

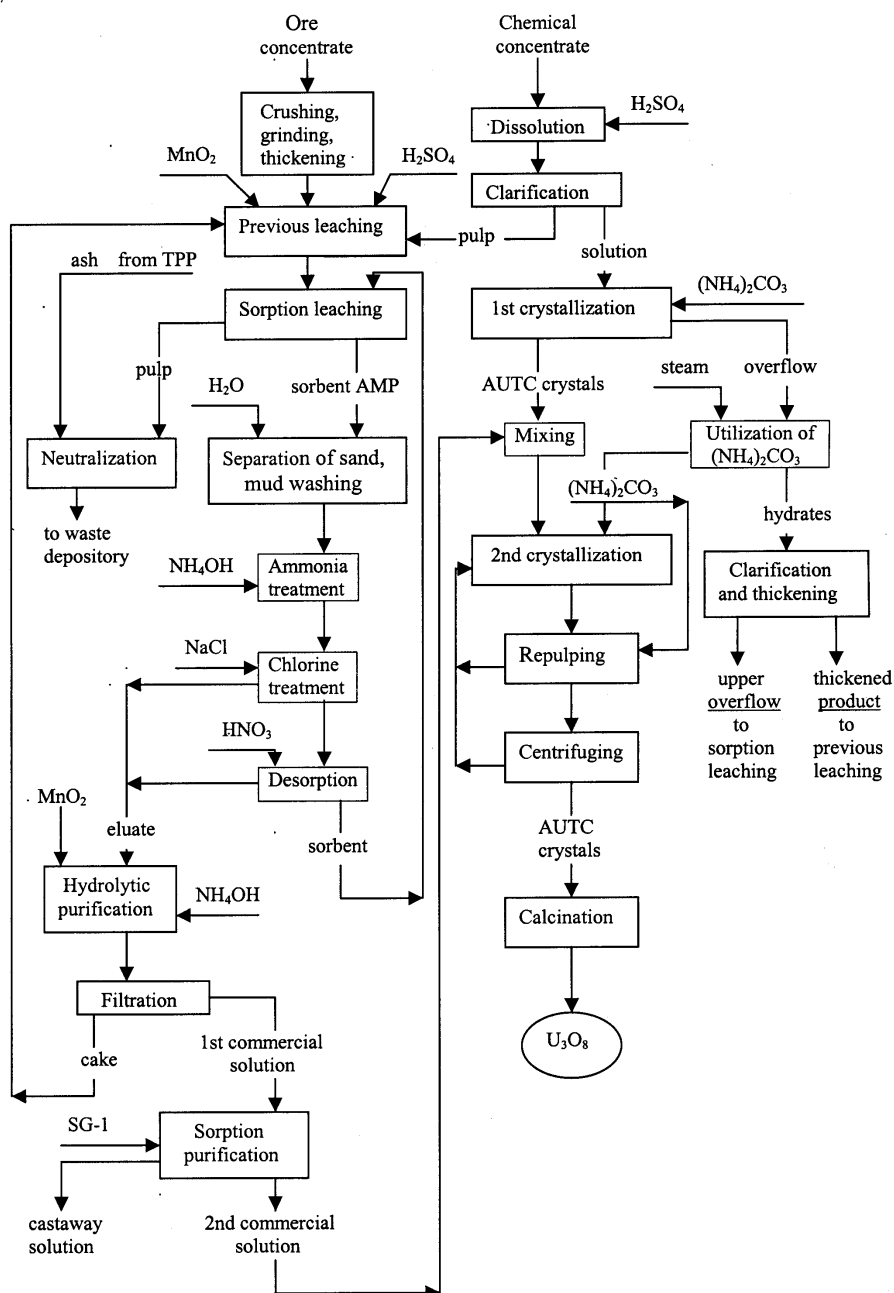


Fig. 4. Technological flow sheet of processing ore concentrate and chemical concentrate using acid-sorption scheme

Sulphuric acid sorption leaching was used to win  $U_3O_8$  from both ore and chemical concentrates (Fig. 4). Sorption leaching was followed by purification and concentration using sorption and carbon-ammonium technology, respectively.

Sorption leaching of fine-grained ore concentrate was carried out in eleven pachuks, using anion exchanger AMP. Sorbent saturated with uranium underwent four stages of regeneration:

- washing with water to remove silt and sludge;
- washing with ammonia to disrupt polymers of silicic acid;
- treatment with NaCl to obtain chloride fraction of the 1st commercial solution and to remove silicon partially;
- desorption with water to obtain water fraction of the 1st commercial solution and to remove silicon completely.

For sorbent regeneration processes several types of equipment were used: columns with mobile layer of sorbent; continuously working sorption columns with pulsating discharge of sorbent; cascade of agitators.

Iron, aluminium and other admixtures were precipitated from the eluate (mixture of chloride and water fractions) at the neutralization stage of the hydrolytic purification process. 1st commercial solution was, after control filtration on plate-and-frame filters, additionally purified in columns packed with cation exchanger SG-1, 2nd commercial solution obtained was directed to carbon-ammonium purification.

Sorption purification was carried out in columns packed with sorbent SG-1 in static state. From eighteen columns a part was included into sorption, the other into regeneration cycle.

Chemical concentrates supplied to the plant were dissolved in 2–4%  $H_2SO_4$ . AUTC crystals salted out were mixed with 2nd commercial solution to get complex compounds of the ammonia uranyl carbonate type. From the pulps obtained by this procedure AUTC crystals were salted out once more.

Both crystallization stages were carried out in columns of continuous crystallization. Pure AUTC crystals were pulped with ammonium carbonate, after hydrocycling centrifuged and thereafter calcined in horizontal tube furnace in air-free conditions up to get  $U_3O_8$ .

The color of the end product  $U_3O_8$ , a fine-dispersed heavy powder, varied from gray-black to fallow-brown. It contained 84% U and the admixtures (in wt.%) Fe <0.03, P <0.03, Al <0.01, Si <0.008, Mn <0.006, Cu <0.0006, Na + K <0.02.

$U_3O_8$  was packed into 330L metal containers, the latter washed outside and transported to storage by motor transport.

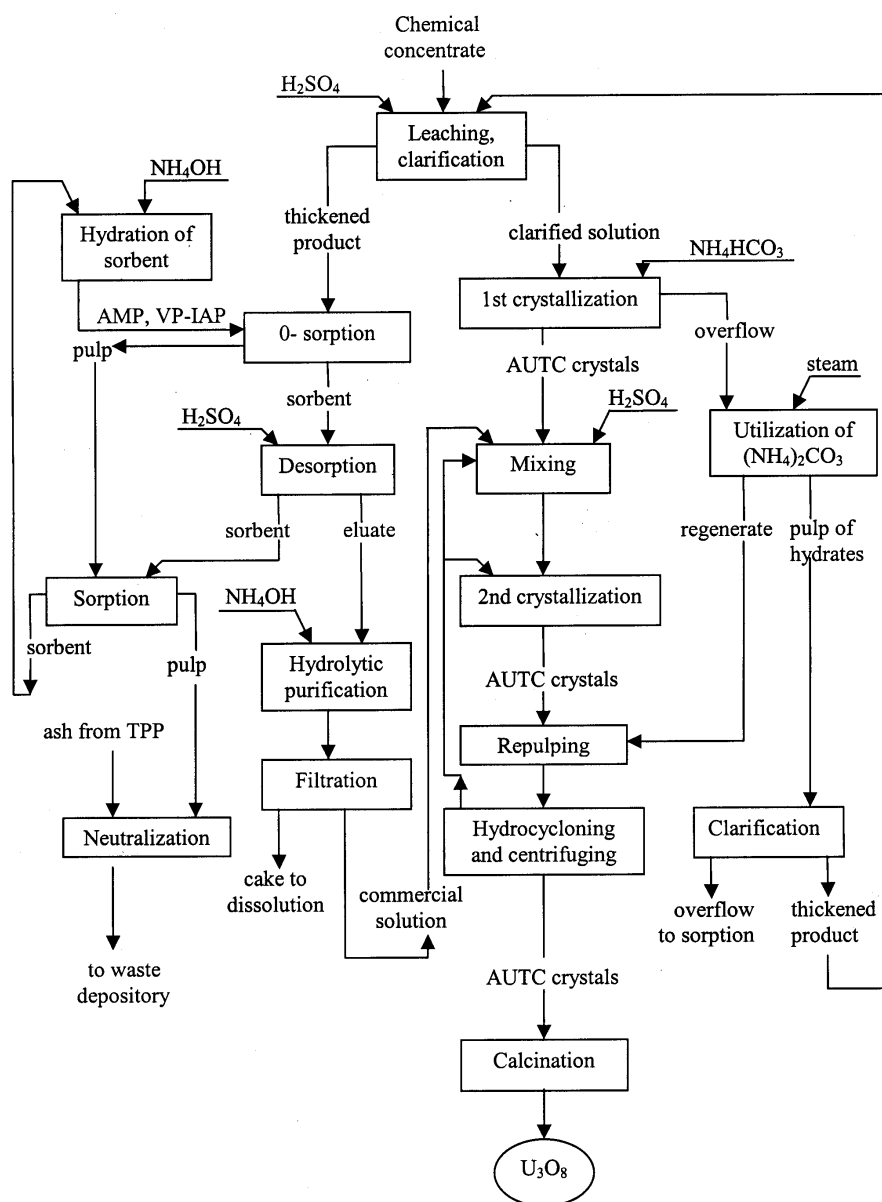


Fig. 5. Technological flow sheet of processing chemical concentrate using acid sorption scheme

### The Period 1980–1985 [8, 9]

In this period mainly chemical concentrates were processed at Sillamäe. The concentrates represented intermediate products, which were obtained by processing of uranium containing ores in hydrometallurgical plants in Czechoslovakia and USSR-GDR joint-stock company “Wismut” in East Germany.

Processing of chemical concentrates from Czechoslovakia was mastered in 1980. The concentrates were relatively poor in uranium (<50%) but rich in admixtures (K, Na, Fe, Al). In spite of poor quality of the initial matter the production characteristics met the heightened requirements designed for the year 1982.

In 1981 and 1982 chemical concentrates imported from Czechoslovakia and East Germany were processed using the sorption technology (Fig. 5). These concentrates contained beside sodium diuranate also potassium and ammonium diuranates. The reaction between sulphuric acid and uranium salt yields uranyl component:



Iron, aluminium, potassium, sodium, phosphorus, silicium and other admixtures can be dissolved in acid too. Solubility of Fe and Al is less at pH = 2.0–3.5, and under these conditions more clear solutions were obtained. However, selective leaching increased the mass of remained solid residue and so also the load on the sorption system.

As seen in Fig. 5, sulphate solutions were treated in two ways:

- sorption extraction of uranium, sulphuric acid desorption and one-stage carbon-ammonium purification of the commercial solution;
- two-stage carbon-ammonium purification.

Treatment with carbon-ammonium was carried out in crystallization columns. Sorption extraction with AMP and also with new highly efficient sorbent VP-IAP was carried out in pachuks, since 1985 – in pulsating columns packed with KRIMZ. For washing and desorption processes various columns were used: columns with mobile layer of sorbent; continuously working sorption columns with pulsating discharge of sorbent; counter-current ion-exchange columns.

In 1980–1985 attention was paid also to diminishing the amount of harmful waste and reutilization of expensive reagents ammonium carbonate and ammonia. Successful large-scale experiments were made to test a new device ARTKM for thermal decomposition of ammonium carbonate in mother liquor from the crystallization unit. Ammonium carbonate regeneration based on the mentioned ARTKM was considerable as the new node enabled significantly to enhance the utilization coefficient of ammonium carbonate as one of the biggest tonnage reagent needed in uranium industry. At the same time in 1984 the process to reach complete re-

extraction of ammonia from still bottom after crystallization of AUTC was introduced.

The present report does not reflect the period 1986–1989 about sorption process at Sillamäe plant, as the corresponding data were not available.

### **Liquidation of Uranium Processing at Sillamäe [10–12]**

Uranium processing at Sillamäe was liquidated according to the Decree No. 077 of 7 June 1989 of the Ministry of Medium Machine Building of the USSR. The decree “Reprofiling of the specialized production of the Sillamäe Chemical-Metallurgical Production Association (PA) for civil production” ordered the following:

1. To stop processing of the chemical concentrates and rejected enriched uranium at the Sillamäe Chemical-Metallurgical PA from 1 January 1990.
2. To transfer the processing of imported chemical concentrates planned for the 3rd Main Technological Directorate to Pridneprovsk Chemical Plant (in Dneprodzerzhinsk) from 1 January 1990.
3. The Head of the 3rd Main Technological Directorate is obliged to:
  - a) Reduce the supplies of chemical concentrate and rejected enriched uranium arriving to Sillamäe Chemical-Metallurgical PA to the level needed for fulfillment of the production plan of 1989 only.
  - b) Redirect the supplies of recycled enriched uranium and guarantee their processing at Machine Building Plant (Elektrostal, Moscow) and Ulbinsky Metallurgical Plant (Ust-Kamenogorsk, Kazakhstan).
4. As the changes in the production profile will free manpower, the Head of the 3rd Main Technological Directorate and the Deputy Head of the Main Economical Directorate have to reconsider economic specifications of the Sillamäe Chemical-Metallurgical PA to be engaged in development of machine building and production of consumer goods, and to guarantee the processing of loparite concentrate as well as to solve ecological problems.

To obey the above-mentioned decree, the Decree No. 8 from 3 April 1990 “About changing the production profile” was issued by the administration of the Sillamäe plant. For the period till 1 July 1990 the decree foresaw to remove the technological solutions and middling from the equipment, to deactivate the equipment and to dismantle the equipment not needed in the future. The decree included a complete reorganization of the works at Sillamäe, as well as the workforce retraining and reduction.

The decree No. 077 provided that the Sillamäe Chemical-Metallurgical PA was exempted from production funds taxation in 1990–1995 because of low lucrativeness and sharp decrease in profits.

The plant made corresponding preparations to rearrange its work and to proceed with new production. However, the changing political situation and new economic development did not allow to effect these future plans in the Estonian Republic reborn in 1991.

The archive of the present AS Silmet (Sillamäe, Estonia) was the main information source to give an overview about the uranium production activities in Estonia in 1946–1990. In the following Literature the original archival documents (in Russian) are listed, here in English, and the relevant records numbers are given (Archive, file, No).

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