

EXTRACTION OF URANIUM FROM LOCAL DICTYONEMA SHALE AT SILLAMÄE IN 1948–1952

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The paper gives a detailed flow sheet of uranium production from Estonian Dictyonema shale used at Sillamäe uranium factory in 1948–1952 and comparison with other methods (Swedish, Estonian).

Introduction

This paper, compiled basing on the Archives of the Sillamäe Metallurgical Plant [1], is a direct sequel to the article [2] dealing with the foundation and operation of the Sillamäe uranium factory (Combine No. 7) and some of its subunits in 1946–1952. The technology applied at this factory for uranium extraction from the local black Dictyonema shale is discussed here in more detail.

Construction of the Combine No. 7 was started at the end of 1946 and its most important unit – chemical factory for uranium production, Plant No. 1 – was completed in June 1948. The first output, 99 kg uranium that made 6.6 % of the planned production, was obtained at the end of this year. The year 1949 is considered to be the start of actual operation. However, the yield of uranium did not reach the designed production level in 1949 either – barely 25 % of the planned 15 tons were produced.

Technological Units of the Combine

In Figure 1 the administrative structure of the Combine is presented. The Plant No. 1, the actual place of uranium extraction, was subordinated directly to the chief engineer. The Plant had three departments: No. 1 – Crushing and Percolation, No. 2 – Combustion, and No. 3 – Hydrometallurgy. The departments Nos 4 and 5 were subject to the Complex No. 4 erected for treating imported ores (beginning from 1950), and their operation is not discussed in this paper.

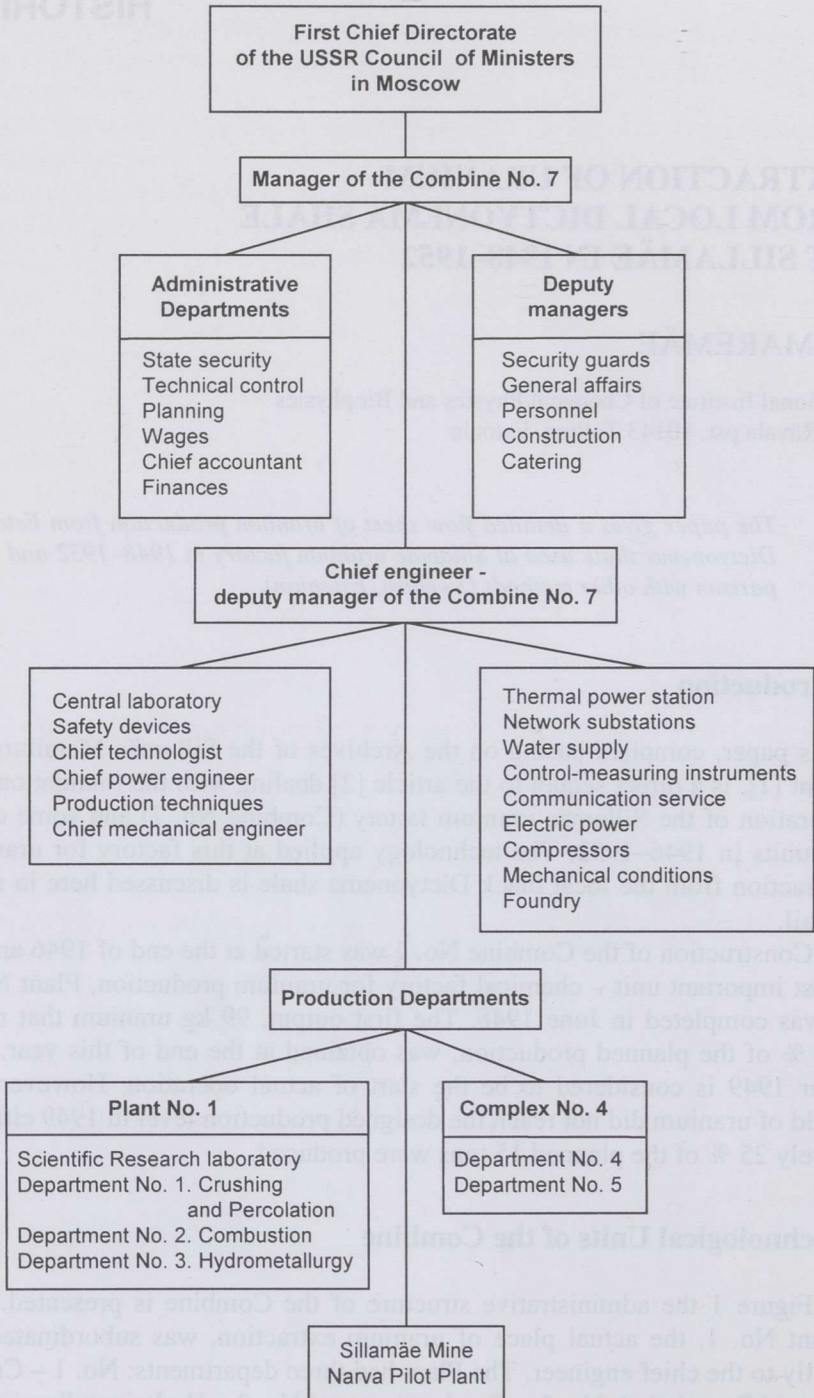


Fig. 1. Administrative structure of the Sillamäe uranium factory Combine No. 7 in 1949–1953

Department No. 1 (Crushing and Percolation)

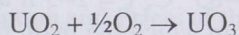
By August 1949 Department No. 1 consisted of two sections: crushing and percolation. The first one included ore storage, equipment for coarse, middle and fine crushing, and bins for crushed ore. Dictyonema shale from the local mine (< 300 mm, chemical composition is presented in Table 1) was grinded into pieces (< 100 mm) and sieved. The fraction < 6 mm was directed into Department No. 2 for combustion. The fraction > 6 mm was directed for re-grinding.

The percolation section served for carrying out the experiments of uranium extraction from the initial unburned shale.

The staff: 68 civilian, 82 soldiers*, 21 prisoners (daily relief only) – 171 persons altogether.

Department No. 2 (Combustion)

At this department shale was burnt to oxidize its four-valency uranium to more soluble six-valency one:



The main equipment consisted of ten-bottom Gerreshof kilns (G-kilns), scrubbers for dust catching, wet ash-handling system and fuel oil handling system. Dictyonema shale particles (< 6 mm) were burnt in G-kilns at 550–580 °C. Mother liquor (8–10 % of shale weight) was added to shale in the lower bottoms of the kilns to moisten the ore. Moistening promoted extraction of uranium from shale and its transfer into solution by 3–4 % and also decreased the losses with dust.

Serious troubles caused by inexperienced design and installation caused many difficulties at operation. The mistakes resulted mostly from the want of knowledge as no previous research was made to find the optimum conditions of combustion process. As for catching combustion gases, in the wooden-grate scrubbers almost no solution circulation took place, and 10–15 % of the dust were thrown into the sea (the Gulf of Finland). Later new multicyclones were built, and the conditions improved. Combustion gases, after passing the system of cyclones and scrubbers, were thrown into the at-

Table 1. Data on Chemical Composition of Dictyonema Shale from the Sillamäe Deposit

Component	wt %
SiO ₂	49.54–54.68
Al ₂ O ₃	7.98–9.10
Fe ₂ O ₃	7.82–10.77
K ₂ O	4.74–4.97
CaO	3.30–5.82
Na ₂ O	0.37–1.47
MgO	0.91–1.07
NiO	0.02–0.03
CuO	< 0.017
P ₂ O ₅	0.87–0.93
V ₂ O ₅	0.11–0.30
MoO ₃	0.03–0.080
CO ₂	< 1.72
SO ₃	0.33–1.80
Sulfides	< 4.38
Uranium	0.01–0.09, av. 0.025
Others	0.5–1.20

* Men of forced labor unit consisting mainly of Baltic conscripts who had served in the German army.

mosphere. The dust caught in cyclons was recycled into kilns using a spiral conveyer, and the dust caught in scrubbers was directed into hydraulic ash-handling system and stored in a dump.

Since 1950 shale burnt at 550–580 °C was directed through coolers from G-kilns into agitators and mixed there with 1 % solution of potassium chlorate at the ratio solid : liquid (S : L) = 1 : 0.8. The chlorate pulp was regrinded and then pumped into classifiers from which the overflow (<0.3 mm) was directed into Department No. 3.

The staff: 125 workers, 14 engineers and technicians, 1 office cleaner and 1 watchman – 141 persons altogether.

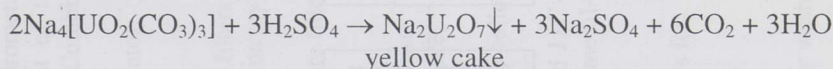
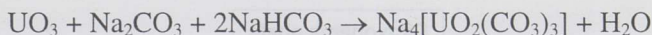
Department No. 3 (Hydrometallurgy)

This department served as the actual place for extraction of uranium from the chlorate pulp. This procedure included the following stages: leaching, filtration, uranium precipitation, alkali washing, and treatment of the final product – drying, grinding and packing of the concentrate obtained.

Till November 1949 the burnt shale was treated with soda, thereafter till July 1950 with chlorate and soda, then with soda again. Finally the chlorate-soda scheme (Fig. 2) was chosen as it guaranteed a better extraction of uranium. The flow sheet of this procedure with a list of the equipment of the hydrometallurgical department is schematically presented in Fig. 3.

Chlorate pulp was treated with sulfur acid in 33 m³ acid agitators (1) at $t = 60\text{--}75$ °C, $\tau = 1$ h and S : L = 1 : 0.8 to sulfur acid residual content 3–5 g per litre. Acid pulp was then neutralized with soda in a neutralizer (2) to carbonate residual content 1.8–2.2 %, and after this step the main process – leaching with 20 % Na₂CO₃ solution – was carried out in 33 m³ alkali agitators (3 – iron containers equipped with special stirrers and inlets for water, steam and air) where $t = 70\text{--}85$ °C, $\tau = 2\text{--}3$ h and S : L = 1 : 2.5. The pulp flew onto drum filters (4) from which the main filtrate was sent through collectors (9, 10) to plate-and-frame filters (11, 11A) for clarification, the solid residue – by a belt conveyer (5) through agitator (6) to repulping. This process was carried out in a 33 m³ agitator (7) at 85 °C using 2 % Na₂CO₃ solution. Repulping was also filtered (4A), added to the main filtrate and sent to clarification. Solid residue was sent by a belt conveyer (5A) to an agitator (8). Here it was mixed with seawater and mother liquors at S : L = 1 : 6–8, and pumped into sandbox from which it flew directly into the Gulf of Finland.

Filtrate clarified on plate-and-frame filters (11, 11A) was directed into 33 m³ (or 60 m³) precipitators (13) where it was neutralized with sulfur acid to pH = 5–5.5 enabling to precipitate the first uranium concentrate (U-I). The end product – sodium diuranate (yellow cake) – is formed as a result of the following main reactions:



The 1st concentrate was filtered on plate-and-frame filters (11B). The mother liquor was sent through carbon filters (14) into a drainpipe (finally into dump). A part of it was pumped into G-kilns to moisten shale before burning. The 1st concentrate from filters (11B) was washed with NaOH to get rid of admixtures. For this purpose the concentrate was loaded by hand into small (2 m³) agitators (15) to leach it with 20 % NaOH solution ($t = 80\text{--}85^\circ\text{C}$, $\tau = 1\text{ h}$, $S : L = 1 : 2$). After that it was refiltered (11C). The washing solution was gathered in collectors (16) and pumped into Department No. 2 to be used there for moistening the ore.

The washed solid end product – the 2nd uranium concentrate (U-II) – was taken from filters (11C) also by hand, then repulped with water and dried in electric ovens. Dry concentrate was crushed in a special ball mill. The product was assorted and packed according to established standards and consumer needs.

Over 1.8 t of chemicals with their total price of about 800 roubles was needed for production of the end product containing 1 kg of pure uranium. The prices and consumption of chemicals are given in Table 2. As seen from the Table, calcined soda was the main chemical used making 53 % of total costs.

The factory price of 1 kg pure uranium present in the concentrate designed to be 7,100 in 1950 was actually 8,230 roubles.

The staff: 275 workers, 25 engineers and technicians, and 8 office workers, altogether 308 persons. Additionally, also 17 prisoners were employed for transportation of uranium 1st concentrate as well as at chars.

Table 2. Average Consumption and Prices of the Main Chemicals for Uranium Production from Dictyonema Shale in Plant No. 1 of the Combine No. 7 at Sillamäe in 1949–1950

Chemical	Price, roubles per ton	Consumption, kg		Cost, roubles	
		per 1 ton of dry ore	per 1 kg of uranium in the final product	per 1 ton of dry ore	per 1 kg of uranium in the final product
Calcined soda	380	96.0	1113.60	36.48	422.16
Sulfuric acid	295	56.0	649.60	16.52	191.62
Potassium chlorate	2500	4.6	53.36	11.50	133.40
Sodium hydroxide	2150	2.0	23.20	4.30	50.52
Total	–	158.6	1839.76	68.80	797.70

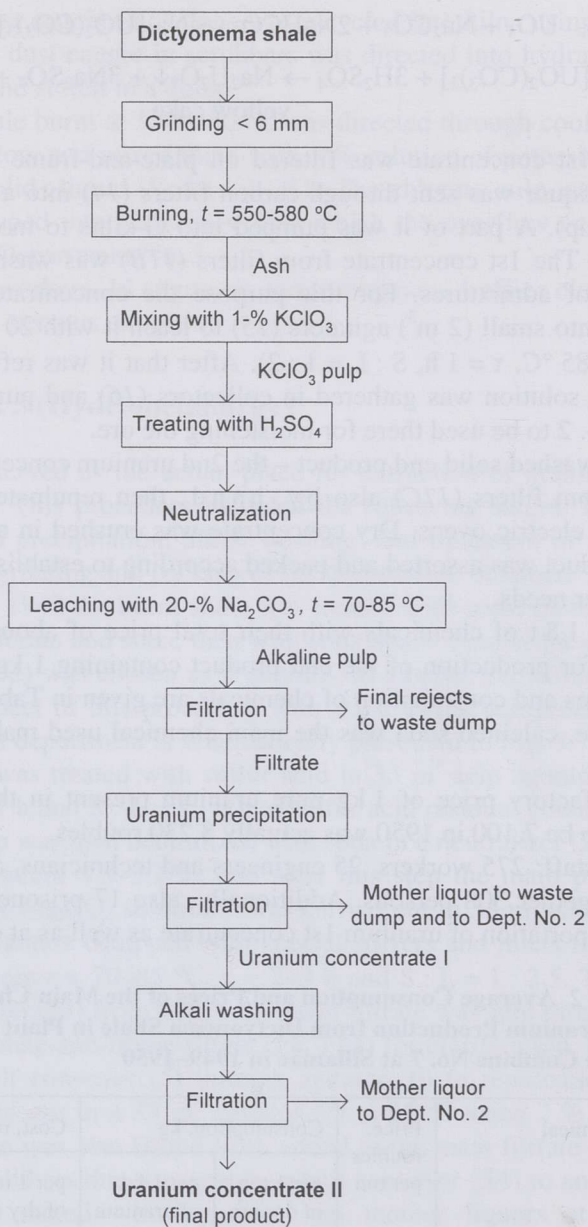


Fig. 2. Flow sheet of uranium processing from local Dictyonema shale in Plant No. 1 of the Combine No. 7 in 1950

Fig. 3. Equipment scheme of the hydrometallurgy department of the Plant No. 1 at Combine No. 7 in 1950.

Legend: 1 – agitator;

2 – neutralizer;

3 – agitator;

4 and 4A – drum filters; 5 and 5A – belt conveyers;

6 – agitator for ore filter cake;

7 – agitator;

8 – agitator for waste dump filter cake;

9 – receiver;

10 – intermediate collector for filtrate;

11, 11A, 11B and 11C – plate-and-frame filters;

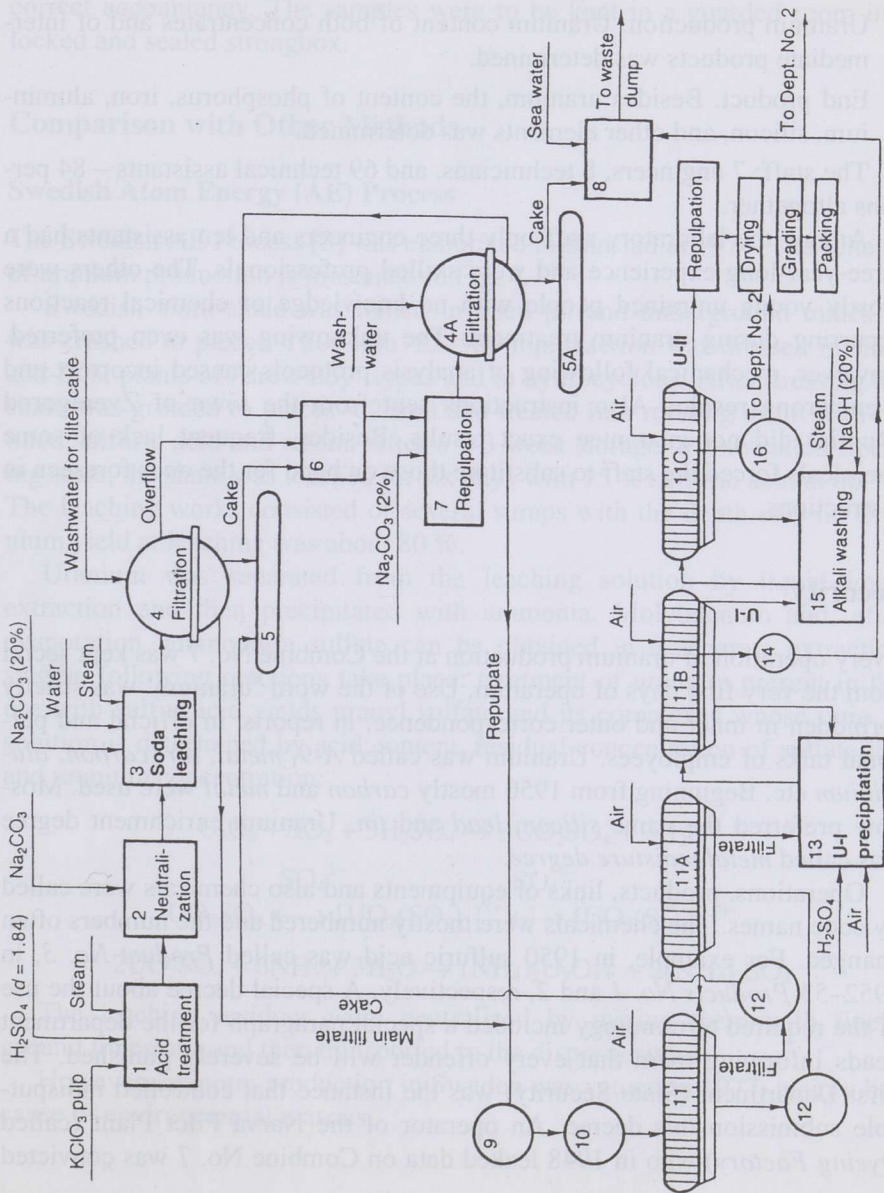
12 – collectors;

13 – precipitators for U-I;

14 – coal filter;

15 – agitator;

16 – collector for washing solution



Central Laboratory

In 1949 there were four groups in the central chemistry laboratory for analyzing the following materials:

- Initial raw material. Uranium content before and after combustion, sulfur content and loss of ignition (on organic matter basis) were determined.
- Solutions. Uranium content was determined in all kinds of samples (pulps, overflows, wash water, etc.) taken in the hydrometallurgy department.
- Uranium production. Uranium content of both concentrates and of intermediate products was determined.
- End product. Besides uranium, the content of phosphorus, iron, aluminium, silicon, and other elements was determined.

The staff: 7 engineers, 8 technicians, and 69 technical assistants – 84 persons altogether.

Among the laboratory staff only three engineers and ten assistants had a three-year-long experience and were skilled professionals. The others were mostly young untrained people with no knowledge of chemical reactions occurring during uranium treatment. The unknowing was even preferred. However, mechanical following of analysis protocols caused incorrect and even wrong results. Also instructions sent from the town of Zvenigorod (Russia) did not guarantee exact results. Besides, frequent lack of some chemicals forced the staff to substitute those on hand for the ones foreseen in instructions.

Security

Every operation of uranium production at the Combine No. 7 was kept secret from the very first days of operation. Use of the word 'uranium' was strictly forbidden in inner and outer correspondence, in reports, in official and personal talks of employees. Uranium was called *A-9, metal, tar, carbon, aluminium* etc. Beginning from 1950 mostly *carbon* and *metal* were used. Moscow preferred the name *silicon, lead* and *tin*. Uranium enrichment degree was called *metal moisture degree*.

Operations, products, links of equipments and also chemicals were called by code names. The chemicals were mostly numbered and the numbers often changed. For example, in 1950 sulfuric acid was called *Product No. 3*, in 1952–53 *Products No. 1* and *2*, respectively. A special decree about the use of the required terminology included a special paragraph for the department heads informing them that every offender will be severely punished. The First Department (State Security) was the instance that controlled indisputable submission this decree. An operator of the Narva Pilot Plant (called *Dyeing Factory*) who in 1948 leaked data on Combine No. 7 was convicted

by the Supreme Soviet Presidium of the Soviet Union and sentenced to eight years' imprisonment.

Strict requirements were established for storing the concentrates. However, a control raid made in October 1950 on the Central Laboratory found there precious samples of uranium concentrate to lay in an open wooden locker in an unlocked basement room where employees of another department were working. Neither the head of the laboratory nor anyone else had any idea about the number of the samples. After this inspection a correct booking was introduced, and a special person appointed to be responsible for correct accountancy. The samples were to be kept in a guarded room in a locked and sealed strongbox.

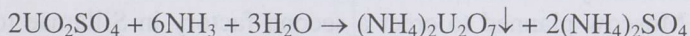
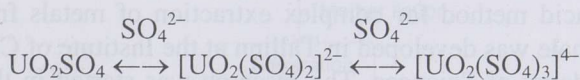
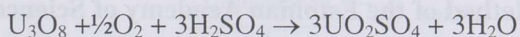
Comparison with Other Methods

Swedish Atom Energy (AE) Process

The Swedish AE Process [3] was elaborated in Ranstad in 1974. The scheme of uranium production is presented in Fig. 4.

Swedish alum shale was mined in open pit and underground mines. It was crushed to pieces < 500 mm. 25–500 mm fraction was dressed in sink-and-float plants of "drew-boy" types and in hydrocyclons. After dressing the shale was grinded to pieces < 2 mm and treated in a rotating drum with diluted sulfuric acid and steam. After a 2–3 week storage in a so-called ripening store, the shale was leached for six days with 15 % sulfuric acid at 60 °C. The leaching works consisted of several sumps with the depth of 6 m. Uranium yield at leaching was about 80 %.

Uranium was separated from the leaching solution by liquid-liquid extraction and then precipitated with ammonia. Molybdenum and, after evaporation, ammonium sulfate can be obtained in a separate extraction stage. The following reactions take place: treatment of uranium present in the ore with sulfur acid yields uranyl sulfate and its complexes whose ratio in solution is determined by acid content, residual concentration of sulfate ion and uranium concentration:



The leaching residues were neutralized by mixing them with finely ground limestone and then transported to the disposal site.

However, uranium production in Sweden was vetoed in 1977, mainly because of environmental reasons.

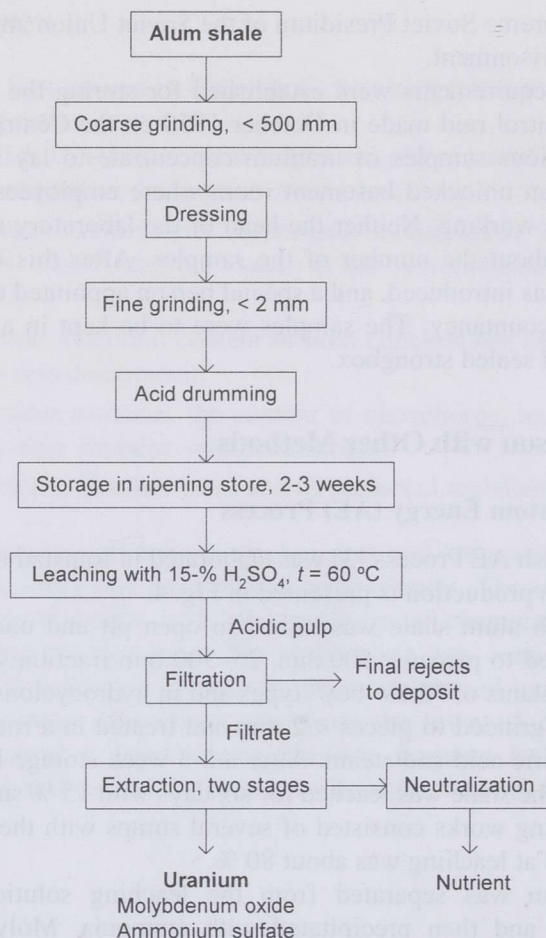


Fig. 4. Flow sheet of uranium processing from Swedish alum shale by AE Process in Ranstad, Sweden, in 1974

Sulfuric Acid Method of the Estonian Academy of Science

The sulfuric acid method for complex extraction of metals from Estonian Dictyonema shale was developed in Tallinn at the Institute of Chemistry, the Estonian Academy of Sciences. The research was started in the 1960s. At this time Moscow planned to erect a second factory in Sillamäe to extract uranium from the local shale. As all actions in Sillamäe were kept secret, the research of Estonian scientists had to start from zero. The scheme of metal extraction they worked out [4] is presented in Fig. 5.

The shale of Toolse deposit was crushed and grinded to pieces < 5 mm which were burnt in fluidized bed at 800–810 °C. The ash formed was mixed with 75 % sulfuric acid to get a uniform paste. The paste was heated at 250–300 °C and thereafter leached with water according to a multistage percola-

tive leaching scheme. The metals were leached out in the following percentage: uranium and vanadium – 80 to 90, molybdenum – 65 to 70, aluminum – 40 to 50.

At first potassium-aluminum alum was separated from the acid leachate by crystallization. After that uranium, molybdenum and vanadium were separated from the acid solution using the methods of ion exchange or liquid-liquid extraction. For precipitation of metals ammonia was used. The oxides U_3O_8 , MoO_3 and V_2O_5 were obtained by thermal treatment of salts $(NH_4)_2U_2O_7$, $(NH_4)_2MoO_4 \cdot 2H_2O$ and $(NH_4)_2VO_3$, respectively. The remaining residue of processed ore was meant to be processed to ceramics.

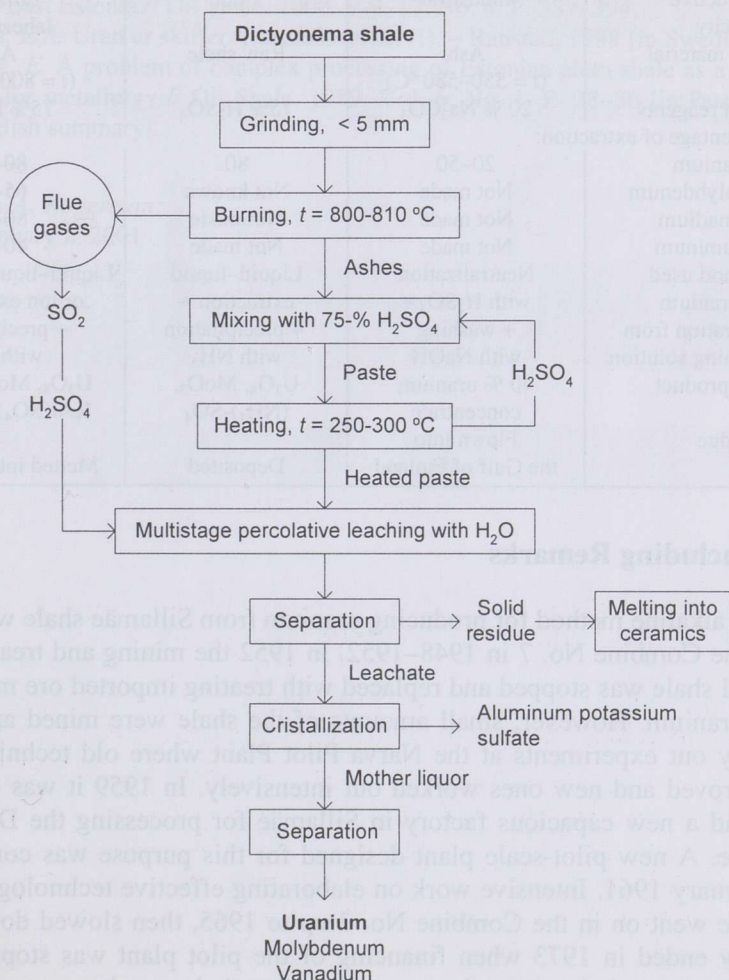


Fig. 5. Flow sheet of uranium processing from local Dictyonema shale according to the scheme of the Institute of Chemistry, Tallinn, in 1975

The scheme was tested at an enlarged laboratory scale unit using 76.2 kg ashes obtained from Toolse shale which was burned in fluidized bed at 800 °C. The high level of sulfuric acid consumption (388 kg of 100 % acid per 1 t ashes) is the main disadvantage of the method.

The methods used for uranium extraction in Estonia and in Sweden are compared in Table 3.

Table 3. Comparison of Estonian and Swedish Schemes

	Sillamäe, 1946–1952	Ranstad (Sweden), 1974–1977	Tallinn, 1970–1975
Productive capacity	Industrial	Pilot	Enlarged laboratorial
Raw material	Ash ($t = 550\text{--}580\text{ }^{\circ}\text{C}$)	Raw shale	Ash ($t = 800\text{--}810\text{ }^{\circ}\text{C}$)
Main reagents	20 % Na_2CO_3	15% H_2SO_4	75% H_2SO_4
Percentage of extraction:			
Uranium	20–50	80	80–90
Molybdenum	Not made	Not known	65–75
Vanadium	Not made	Not made	80–90
Aluminum	Not made	Not made	40–50
Method used for uranium separation from leaching solution	Neutralization with H_2SO_4 + + washing with NaOH	Liquid–liquid extraction + + precipitation with NH_3	Liquid–liquid extraction or ion exchange + + precipitation with NH_3
End product	40 % uranium concentrate	U_3O_8 , MoO_3 , (NH_4) $_2\text{SO}_4$	U_3O_8 , MoO_3 , V_2O_5 , $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
Residue	Flown into the Gulf of Finland	Deposited	Melted into ceramics

Concluding Remarks

The alkaline method for producing uranium from Sillamäe shale was applied in the Combine No. 7 in 1948–1952. In 1952 the mining and treating of the local shale was stopped and replaced with treating imported ore much richer in uranium. However, small amounts of the shale were mined and used to carry out experiments at the Narva Pilot Plant where old techniques were improved and new ones worked out intensively. In 1959 it was decided to found a new capacious factory in Sillamäe for processing the Dictyonema shale. A new pilot-scale plant designed for this purpose was completed in February 1961. Intensive work on elaborating effective technologies for the shale went on in the Combine No. 7 up to 1965, then slowed down and finally ended in 1973 when financing of the pilot plant was stopped as the Dictyonema shale processing was not economical enough.

The same fate struck the shale processing in Sweden and the other Estonian project using a complex scheme different from that applied in Sillamäe both trying to extract besides uranium also other useful elements.

* It will be treated in more detail in the next paper.

Today there is no economically and environmentally acceptable technology for extracting metals from the Dictyonema shale. The shale should be regarded as mineral wealth of the future.

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A member of the Editorial Board of the journal *OIL SHALE*, member of the Estonian Academy of Sciences Arvo Ots celebrated his 70th birthday on the 20th of June 2001.

We congratulate our good colleague on his jubilee, thank him and his co-workers for interesting publications and wait for new papers on oil shale power engineering.

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