

HISTORICA

THE BEGINNINGS OF URANIUM PRODUCTION IN ESTONIA

E. LIPPMAA, E. MAREMÄE

National Institute of Chemical Physics and Biophysics
10 Rävåla Blvd., 10143 Tallinn, Estonia

Large amounts of uranium available in the Estonian black alum (Dictyonema) shale created intense interest towards this low-grade ore in the very beginning of the atomic era. Various selective leaching and concentration technologies were tried with both roasted and native shale, at first at the Narva Pilot Plant and thereafter at the Sillamäe factory. Even though most of the USSR leading R&D centers participated in this effort, industrial uranium production turned out to be both technologically possible, but at the same time economically untenable at this time, just as it was the case in Sweden.

Black alum (Dictyonema) shale is abundant in Estonia. This Ordovician deposit formed long ago when oceans were rich in heavy elements and the Baltoscandian plate was located halfway between Equator and the South pole. Estonian black shale contains only about 250 ppm of uranium, but the seams are up to 8 meters thick and the total amount of uranium is significant, more than a million tons. It is thus not surprising that the first demonstration batch of Estonian uranium was produced in great hurry during the 1944/45 winter and active uranium prospecting by the Estonian Central Institute of Industrial Research began.

Two top-secret decrees were issued by the USSR Council of Ministers. The decree No. 0282 cc of August 6, 1946 established a mining-industrial complex at Sillamäe for processing the Estonian alum shale, and a small uranium production research and pilot plant was set up in Narva, codenamed "Dyeing Factory", which had a broader reach, including experiments with other ores as these became available. For this the decree of July 27, 1946 ordered twelve well-known research institutions of the Soviet Union to carry out research on shale in the following areas:

- Chemical composition:
 - All-Union Institute of Mineral Raw Materials (*ВИМС*)
 - W.G. Hlopin Radium Institute of the USSR Acad. Sci. (*РИАН*)
 - Leningrad Mining Institute (*ЛМИ*)
 - Scientific Research Institute of Processing Mineral Resources (*Механообр*)

- Beneficiation:
 - Scientific Research Institute No. 9 (*НИИ-9*)
 - State Scientific Research Institute of Nonferrous Metals (*Гинцветмет*)
 - All-Union Institute of Mineral Raw Materials (*ВИМС*)
 - Scientific Research Institute of Processing Mineral Resources (*Механобр*)
- Hydrometallurgical extraction of uranium:
 - Scientific Research Institute No. 9 (*НИИ-9*)
 - All-Union Scientific Research Institute of Halurgy (Hydrometallurgy) (*ВНИИГ*)
 - All-Union Institute of Mineral Raw Materials (*ВИМС*)
 - N.S. Kurnakov Institute of General and Inorganic Chemistry of the USSR Acad. Sci. (*ИОХХ АН*)
 - All-Union Scientific Research Institute of Geology (*ВЦЕГЕИ*)
- Uses of shale organic matter:
 - Institute of Combustible Mineral Resources of the USSR Acad. Sci. (*ИГМ АН*), Moscow Division of the Mendeleev Chemistry Association
 - Institute of Industrial Research of the Estonian Acad. Sci.

All research was classified to the highest degree (cc meaning top secret) and the codename for uranium varied. In 1946/47 it was “A-9”, a designation introduced by the Research Institute No. 9, which led to rather transparent formulas like (A-9)₃O₈. In 1948/49 the designations used by the same Institute No. 9 were also “silicon” and “carbon”, which then supposedly formed mixed oxides. In 1950 uranium was codenamed “pitch” which led to reports about Estonian argillite shales with 0.029 and 0.034 % pitch content, respectively.

Most of this secret research was carried out before 1950 by the Scientific Research Institute No. 9 at the Narva Pilot Plant. This small facility consisted of four sections – ore beneficiation, ore roasting, hydrometallurgical extraction, and analytical laboratory with sample preparation and dosimetry.

The ore processing involved crushing, milling, mechanical classification, flotation, centrifuging and filtering. Hydrometallurgy started with ore concentrate roasting in a rotary kiln and involved two approaches – acid leaching with sulfuric acid and alkaline soda-based leaching, both with percolation.

First laboratory experiments with Estonian black shale and another low-grade ore from Ranolovo (Russia) carried out by Institute No. 9 in December 1946/January 1947 showed that after roasting at 450 to 650 °C up to 78 % of the uranium can be hot-leached with 5 % soda solution, but up to 82 % with 10 % pyrite added to the ore before roasting. In the last case up to 85 % of the uranium could be leached from Ranolovo ore.

It turned out to be very difficult to introduce any improvements into this process. Beneficiation allowed getting concentrates of the organic matter or pyrite of the shale, but it led to no concentration of uranium. Separation of uranium by chlorination of the Estonian shale in pulp and in the solid phase was tried in 1946–47 by the Institute of General and Inorganic Chemistry and by the Scientific Research Institute No. 10 (*HIII-10*), but not with much success. Likewise, soda leaching experiments carried out during 1947 with oxidizers (nitrates, hypochlorite) or combined soda-acid leaching did not significantly increase uranium yields. In the last case the over 20 mesh fraction was acid-leached in percolators with dilute $\text{H}_2\text{SO}_4 + \text{HNO}_3$. All in all, in the first industrial experiments carried out during 1949 only 60 % leaching and 40 % product yield were achieved.

Other approaches were tried too. The Leningrad Mining Institute achieved in 1947/48 fairly good results with acid uranium leaching of the Estonian shale, 79 % with 8 % H_2SO_4 and 91 % with 8 % $\text{H}_2\text{SO}_4 + 2$ % HF. Weaker acids fared worse, 40 % with acetic acid and 70 % with HNO_3 or HCl, all at 50 °C. The Leningrad institute explained the surprisingly uniform distribution of element A-9 between the separable components of the Estonian black shale by the possible presence of A-9 in the form of extremely small particles of a heavy oxide mineral, such as uraninite!

Several attempts to increase uranium extraction yield by oxidative leaching of both the native shale and the roasted oxidized ore were carried out during 1948/49. The Leningrad division of the State Union Project Institute No. 12 used both acid and alkaline leaching regimens with added nitric acid, or in case of alkaline leaching, potassium chlorate, sodium hypochlorite or potassium dichromate as oxidizers. Later even pyrolusite MnO_2 was tried. In nearly all cases the use of oxidizers increased the uranium (codenamed “silicon”) yield by 15 to 30 %. The best results (up to 70 %) were achieved with chlorates.

Since oxidative roasting is perhaps the cheapest form of oxidation and also creates acid from the burning pyrite, it was also tried. The All-Union Scientific Research Institute of Geology was in some cases in 1949 able to leach up to 70–80 % of the uranium with just plain pure water. For consistent results at the 55–65 % yield level, roasting was carried out at 550 °C without local overheating and hot spots, and instead of pure water a 7.5 % solution of ammonium carbonate was used. The leached roast was in this case not dumped, but used as fertilizer by the Leningrad Agricultural Institute (*JICXII*). In a closely related study carried out in 1949 by the All-Union Scientific Research Institute of Halurgy, ferric sulphate was used as the oxidizing additive to 4 % soda. 70 to 77 % uranium (A-9) leaching from shale roasted at 525 to 600 °C was achieved. The effect of ferric sulphate was thus marginal at least.

The various leaching processes all achieved significant uranium yields in the laboratory even under the mildest conditions, but these results turned out to be not very well reproducible and difficult to apply industrially. As can be

seen from the directive dated 04.06.1948 by the First Chief Directorate of the USSR Council of Ministers titled “The results of the scientific research on the Dictyonema shale”, the results of the institutes differed widely and did not meet expectations at all. The most important objective, extraction of uranium from the shale into the final product was, instead of the expected 70–80 % extraction, as follows: All-Union Institute of Mineral Raw Material – 20 %, Scientific Research Institute No. 9 – 44 %, Institute of Halurgy – 57 %. The amount of chemicals used for extracting one ton of uranium into the final product differed from 1155 to 2026 t.

In order to find schemes with the best extraction and lowest use of reagents, five institutes were instructed to continue their research at the Narva Pilot Plant and, from the middle of 1948, in the Factory No. 1 at Sillamäe. A year later, a second directive of the First Chief Directorate was issued on May 7, 1949. It stressed the importance of developing new technology for efficient uranium extraction from the black Estonian shale and announced unheard of bonuses, up to one million roubles (more than 1000 average wages) for the task. The best USSR equipment and new highly qualified staff were to be provided.

However, just in case, establishment of a new temporary plant in Factory No. 1 for processing higher grade imported ores by the end on 1949 was also decreed.

In the first large scale experimental runs at Sillamäe in 1949/50 only 41.4 % average uranium (codenamed “pitch”) industrial leaching yield could be achieved, which was insufficient for any premiums to be paid. The Estonian black alum shale turned out to be a rather non-uniform ore with unpredictable properties.

The research carried out in the forties had showed that natural weathering leads to significant, up to 45 % leaching of uranium from the oxidized shale. USSR Ministry of Geology therefore proposed in 1950 to use this natural process for uranium production through natural leaching (M.N. Althausen, Dec. 1950).

Directives issued in 1951 by the Second Chief Directorate of the USSR Council of Ministers show dissatisfaction with the work of Combine No. 7. The two main processes – combustion and filtering – were still not operating satisfactorily and scientific research was constantly lagging behind schedule. Additional problems were pointed out: 1) long shutdowns in the combine due to cold weather between December 1950 and February 1951 as there was not enough electric power and technological steam and 2) preference by the combine for higher grades of imported uraniferous ore and lack of interest towards the problems of processing the local shale.

To remove the last mentioned shortcoming the chief of the Second Chief Directorate S.P. Aleksandrov ordered: 1) stepping up the work for studying the technology of the Dictyonema shale and sending a corresponding report to Moscow by March 10, 1951, and 2) changing the structure of the combine

to achieve better results in developing technology for Dictyonema shale processing.

It took all of 1951 to fulfill the directives of S.P. Aleksandrov. Deputy director G.J. Salman summed up the work at the end of the year, on Dec. 17. Until that time two processing schemes had been developed at the Narva Pilot Plant: acid-chlorate-soda and sulphuric acid. Neither of these schemes could be considered effective or economical due to low uranium extraction (up to 50 %) and the large amounts of reagents that were required which resulted in a high factory price of the uranium concentrates.

The results proved that despite some progress in the improvement of Estonian Dictyonema shale technology (for the first time the uranium extraction exceeded 50 % by the end of 1952), uranium extraction from this shale was too expensive and uneconomic when compared to the imported ores. The imported ores were ten- and hundredfold richer in grade and easier to process than the Dictyonema shale. For these reasons processing of the Dictyonema shale was stopped.

A directive issued on April 15, 1952 by the Second Chief Directorate of the USSR Council of Ministers ordered to stop the processing of the Dictyonema shale for uranium in Factory No. 1 in 1952 and to restructure the factory for processing imported ores. The mine was to be shut down by Aug. 1, 1952 while retaining the possibility to mine local shale for scientific research. Development of roasting technology for local shale was to continue at the Narva Pilot Plant and the construction of a new 26 m long rotary kiln was to be finished by Aug. 1, 1952.

These orders were soon followed by a number of directives issued by the management of the Combine No. 7. The mining shutdown deadline was determined as July 10, 1952 and preparations for receiving imported ores were started with the objective of producing 80 % oxide concentrate in Combine No. 7 beginning January 1, 1953.

The experiments carried out at the Narva Pilot Plant in 1947–1953 showed that as mined fresh shale leaching by column percolation with dilute sulfuric acid gives a reasonably good 60 % uranium yield. Partially oxidized weathered, but unroasted shale leached much better, providing a more than 20 % uranium yield even with plain water. Scientific Research Institute No. 10 (B.N. Laskorin) had stated developments of percolation-based acid leaching with following ion-exchange-based concentration of the heavy metals already in 1952. This approach was used in various forms with ores from Pervomaisk, Zheltorechensk, Kurdai, and in 1954 at the Narva Pilot Plant for uranium extraction from the black Estonian shale. It proved to be superior to alkaline soda leaching and was later widely used at Combine No. 7 in Sillamäe for processing imported ores.

The Sillamäe factory was ordered on October 16, 1954 by the ministry to convert fully to this new technology. This conversion was completed in 1955 while the Narva Pilot Plant was developing it further. During 1955–56 this continuous countercurrent percolation acid leaching scheme with uranium

sorption at AN-2F anionite was fully developed and applied at Sillamäe. Using <6 mm crushed shale provided a 50 to 65 % uranium yield in the final 450 mg U/l leachate that was processed into the ammonium salt form with 30 % uranium content. Direct uranium precipitation from raw leachate with phosphates was also considered, but not used.

Ten years of research and development at the Narva Pilot Plant has thus shown that up to 2/3 of the uranium present in the Estonian black shales can in some cases be leached and concentrated fairly easily even with rather primitive technology and without any pretreatment like burning or roasting. However, these shales are very inhomogeneous and large scale production yields are much lower.

Imported ores started to gain importance and the Pilot Plant got new tasks. It was ordered by the Ministry of Medium Machinebuilding (MCM) to start processing lithium and beryllium ores in addition to the current uranium production efforts (order No. 417 from July 11, 1955). This work was carried out at the Narva Pilot Plant in collaboration with the Scientific Research Institute No. 10 and consisted mostly of Zavitinsk spodumene ore processing. This process involved ore roasting in a fluidized bed with the following acid leaching of lithium and beryllium with dilute sulfuric acid.

Already in 1949 beneficiation of Bala-Sauskandyk ore had been studied. In 1956–57 quite an interesting ore containing 0.15 % U, 1.2 % Zr and 23 % P₂O₅ in concentrate from Tastykol was investigated in collaboration with the Scientific Research Institute No. 10. The Utch-Kuduk ore with 0.13 % U content was countercurrent-extracted with dilute sulfuric acid and AN-2F anionite was used for uranium concentration from leachate. Imported ores from Metchek, Chudonovichy, Prschibram and others were also processed.

Since much richer imported ores had become available, on April 15, 1957 the Narva Pilot Plant (Dyeing Factory, or Enterprise P.O.B.2) was transferred by ministerial order No. 162 from March 30, 1957 from the Sillamäe factory (Combine No. 7, or Enterprise P.O.B. P-6685) to the State Union Project Institute No. 12 (*ГЦИИ-12*). The new owner continued the acid leaching experiments and could in 1959 show that year-long weathering of the black shale does not significantly increase the uranium yields, which remained between 67 and 70 %. In these experiments the EDE-10P anionite was used for uranium concentration from the leachate.

The Sillamäe factory continued experiments with acid leaching after shale pretreatment through low temperature burning in a fluidized bed at 500 to 550 °C. Column percolation and uranium concentration on AN-2F, EDE-10P and AMP anionites were used. The uranium yield remained between 65–69 % as it was with untreated raw shale, but only about 5 w/w% of sulfuric acid had to be used for leaching instead of 10 % in the case of raw shale. Acid use was diminished by sulphates formation from burning pyrite FeS₂.

Of course, some oxidation of pyrite always accompanies shale weathering. Based on this, the Leningrad Technological Institute in collaboration with Combine No. 7 made numerous draft proposals to process 10,000 t of

black shale per day in the Combine No. 7 according to four versions given in the Table. Of these schemes, version 1 (considered the best) describes planning of pilot operation in 1959 and allotment of capital resources to build the installation in Combine No. 7 in 1960. It is difficult to imagine what could have happened if the second, or even the third version, would have been considered best. These versions would have produced huge waste heaps of Dictyonema shale with extraction of only 30–40 % of the uranium. The crushed and oxidizing shale tailings would have been subject to unavoidable self-ignition as well as leaching of deleterious pollutants by surface and ground waters, and would have been left, according to version 3, even underground.

**Proposals of the Leningrad Technological Institute
for Processing Estonian Black Shale in Combine No. 7**

Version No.	Proposal	Uranium extraction yield %	Calculated factory cost of 1 t of uranium (K roubles)
1	Leaching of black shale using the percolation method	49	724
2	Leaching of black shale in heaps on special stands or in a quarry	42	900
3	Underground leaching of shale for uranium	34	1010
4	Combined scheme, where 70 % of the shale goes to direct percolation and 30 % for leaching after roasting	59	665

The proposed open-air leaching experiments with Estonian black shale were carried out in 1960–63 by the Sillamäe Factory No. 7. A 50 % uranium yield was achieved in a large 20,000 ton open-air concrete percolator with up to 25 mm crushed shale. In a two-year run (23 months) in open-air heaps, and the wooden percolators with shelves and added bacterial cultures, a 55 % uranium yield was achieved with up to 25 mm crushed shale, but only 33 % with larger up to 50 mm material and only 1 % with 100 to 200 mm lumps (18 months run). These results proved to be unsatisfactory and further studies of this extremely polluting process were discontinued.

Some other approaches to achieve better uranium extraction yields from the Estonian shale were also tried, such as extraction under pressure. The 30 m³ stainless steel autoclave was installed at Sillamäe in 1965 and experiments with acid leaching under oxygen pressure at 120 °C were carried out during 1966. Under these conditions pyrite and U^{IV} are nearly fully (90 %) oxidized into soluble UO₂SO₄. Since the pyrite content in a 35 % black shale pulp was high (10 %), the reaction was thermally self-sustaining without external heating. However, results were not good enough for such an expensive process. Only up to 73 to 76 % uranium leaching yield was achieved. The financing of the Pilot Plant at Sillamäe was terminated in 1973 and work

with the Estonian black alum (Dictyonema) shale ceased at about the same time.

All attempts to achieve reasonably good uranium (and possibly also molybdenum and vanadium) yields by native or roasted/burned shale leaching have thus failed. At the same time, the very large reserves of the easily accessible ore (in places just surface overlay over rich phosphate deposits) remain both untouched and tempting.

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