ENRICHED URANIUM TECHNOLOGY
AT THE SILLAMÄE OIL SHALE PROCESSING PLANT

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The shale oil factory at Sillamäe, Estonia was founded in 1928 by the "Estonian Oil Consortium", belonging to Swedish capital. It is the only factory that has processed both the brown (kukersite) oil shale and the black (dictyonema) shale that are both abundant in Estonia. The much older black shale contains, besides the oil-bearing organic material, significant amounts of various heavy metals, including uranium, and is therefore radioactive. Uranium-based nuclear technology has dominated the second half of the last century, but now faces potential competition from the emerging hydrogen-based energy technologies. It is little known that the Sillamäe Oil Shale Plant has played a significant role in the development of the gas cooled very high temperature pebble bed reactor for direct production of either hydrogen or electricity. We analyze here the timeline of this development effort.

Introduction

As a logical sequel to dictyonema shale processing, work with enriched uranium ^{235}U power reactor fuel and the thorium-rich loparite from Kola Peninsula [1] followed. Both projects ran concurrently in the eighties and ended in early nineties.

The production of up to 180 tons per annum of the metal in the 2.0%- and 3.6%-enriched $^{235}UO_2$ uranium dioxide nuclear power reactor fuel at the Oil Shale Processing Plant at Sillamäe (then P.O.B. P-6685) was decided on March 24, 1980. The factory had to recondition for high temperature operation and bring to the proper isotopic composition enriched U_3O_8 uranium oxide from the Electrostal factory (A-7340), located some 50 km eastwards from Moscow.

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Table 1. **Production of ^{235}U-enriched UO$_2$ in 1983–1989 at the Sillamäe Oil Shale Processing Plant**

Nominal* ^{235}U enrichment, %	Content of uranium metal in kilograms in ^{235}U-enriched UO$_{2.08}$ dioxide**							1989 retail price, roubles/kg
	1983	1984	1985	1986	1987	1988	1989	
2.0	34 623	79 109	98 606	53 489	103 547	119 173	40 119	337
2.4	–	–	–	–	78 036	58 679	150 569	422
3.0	13 190	25 504	–	–	40 347	73 816	66 082	553
3.3	68 025	52 056	71 492	88 342	22 571	4 252	–	
3.6	–	–	–	19 027	–	–	–	
4.4	–	–	–	–	–	–	–	840
21.0	–	–	–	–	–	–	–	4080
45.0	–	–	–	–	–	–	–	8900
90.0	–	–	–	–	–	–	–	19800
Total	115 838	156 669	170 098	160 858	244 501	255 920	256 770	

* The actual ^{235}U enrichment is slightly larger than nominal due to ^{236}U contamination.
** The dioxide is not fully reduced for better thermal stability in the fuel rod.

Altogether 1 360 654 kilograms of enriched uranium in the dioxide were produced from 1983 to 1990, when all uranium-related activities ceased due to political developments that ended the Soviet system, see *Table* 1. Before that, the factory formed an integral part of the large Soviet nuclear complex, employing more than 100 000 people and serving both military and civilian needs with conjoined fuel cycles. Even electricity was mostly produced in the thermally unstable military-style, originally plutonium-producing light water graphite-moderated RBMK reactors with positive void (vapor bubble) feedback coefficients, well known from Chernobyl, Ignalina and Sosnovy Bor. The main partners in the nuclear fuel fabrication work were the two large fuel fabrication plants at Electrostal (A-7340), at Ust'-Kamenogorsk (B-8857) and the Glazov metallurgical plant M-5057 at Chepetsk that fabricated the zircaloy cladding for fuel rods and assemblies. The two fuel factories received irradiated uranium and chopped scrap from the plutonium and tritium production sites and reactor fuel producers, recovered the uranium as U_3O_8 and fabricated the dioxide UO_2 into both low-enriched (LEU) and highly enriched (HEU) uranium fuel rods and assemblies for military, civilian, naval and special reactors. The RBMK graphite-moderated reactors use 2%-enriched LEU fuel, the pressurized water reactors 2.4%- to 4.4%-enriched LEU, naval reactors, such as the two PWR/VM-A and PWR-VM4 70-MW and 90-MW submarine reactors at the former Paldiski naval base, use 21%-HEU. Very powerful special reactors use anything up to the full bomb quality of >90%.

^{235}U enrichment is not the only criterion. The usual U_3O_8 oxide is low-melting and cannot be used as reactor fuel. UO_2 can be thermally stable, but must be prepared as a well-sinterable variety. The oxides are actually groups

of more than 40 [2] ill-defined compounds, phases, allotropic forms and solid solutions around $U_3O_{<8}$ and $UO_{>2}$.

Production of low-enriched $^{235}UO_2$ (LEU)

Enriched uranium is recovered at the A-7340 and B-8857 fuel fabrication factories as U_3O_8 from the sheared and chopped fuel pins. This oxide must be isotopically reconditioned and converted into the proper modification of UO_2 for use in new fuel rods. Chemical procedures allow to remove all unwanted components except ^{236}U, formed in the plutonium production reactor through neutron capture to ^{235}U. This isotope is a non-fissile neutron-absorbing reactor poison that is practically absent in natural uranium ores (relative abundance 10^{-10}), but HEU reprocessed from nuclear weapons production material may contain up to 25% of it. The recovered LEU shipments to Sillamäe were therefore individually marked with the exact percentages of ^{238}U, ^{236}U and ^{235}U and were additionally measured by mass spectrometry. The ^{236}U content in recovered U_3O_8 was highest (up to 0.43%) in shipments from B-8857 at Ust'-Kamenogorsk, but it never even approached the theoretical 25% limit because the concurrent ^{240}Pu formation from ^{239}Pu must be kept below 7% in order to avoid premature chain reaction during weapon implosion. The Electrostal product was mostly clean (0.01 to 0.02% ^{236}U) and that from Glazov M-5057 even pristine.

The ^{236}U percentage in the regenerated UO_2 product was generally held close to 0.1% and the ^{235}U enrichment slightly higher than nominal to compensate for the neutron capture by ^{236}U.

The enriched UO_2 production begins with pulsed mixing dissolution of the recovered U_3O_8 in 30% nitric acid at 60–70°C for 2 hours, followed by selective pulsed column 12-contact extraction of uranium with 25–30% tributylphosphate in aromatics-free kerosene (n-dodecane), re-extraction of uranium with water at pH 1 to 2, 60°C in a 1:1 volume ratio, 8-contact pulsed column, precipitation of ammonium diuranate yellow cake at 60°C pH 6.8 to 8.0, its thermal decomposition to UO_3 and thereafter to U_3O_8 at 350 to 450°C and finally reduction to UO_2 at 650 to 720°C in a 60 to 70 L/min hydrogen flow, using 245 m^3 H_2 for a not quite complete (84 to 91%) reduction of 1 ton of uranium in the dioxide $UO_{2.08}$. The incomplete reduction and even yellow cake decomposition procedure details are critical for good thermal stability of the dioxide.

The enriched uranium yield from raw U_3O_8 to pure UO_2 was fixed in 1981 for Sillamäe to equal the surprisingly low yield practiced for enriched LEU uranium at Electrostal A-7340, see *Table* 2.

In 1987 the official natural unenriched uranium yield from the concentrates was 99.84% at the Sillamäe Oil Shale Processing Plant and the planned share of loss as material unaccounted for (MUF) was just 0.008%. This very high yield was not quite achieved, but the 0.013% unaccounted for

loss is also a very good result. For the [235]U-enriched uranium the situation was very different. Instead of the quite realistic 0.008% MUF, 0.730% was officially planned for the unknown losses, and even more (0.746%) was actually reported. The whole uranium project ended at Sillamäe in December 1989 due to imminent political changes in the Baltic States. All uranium stocks, materials and equipment were immediately removed to Electrostal and the enriched uranium MUF fell immediately to the very reasonable 0.004% level just before final shutdown without any preceding technological improvements. Why the rather large, about 10 tons at Sillamäe alone with possibly much more at Electrostal, where the same excessive losses were enforced, officially nonexistent enriched uranium stocks were created in a very non-transparent manner even at the Top Secret level, is unknown. At any rate, it is not in the waste depository at Sillamäe. The very careful measurements of Ehdwall et al. at the Swedish Radiation Protection Institute [3] show that the average ^{238}U/^{235}U activity ratio is equal to 20.5±3.5 in the waste dump borehole core samples, taken at ≤10 m depth from the upper gray layer that accumulated in the eighties.

The ratio expected for natural uranium is 21.5, but the amount of ^{235}U in MUF, if present, would have nearly halved this number. No ^{236}U or actinides were found, which is also relevant.

Table 2. **Total planned and actual LEU reconditioning losses in 1983–1989 at the Sillamäe Oil Shale Processing Plant according to the formerly classified Top Secret monthly production reports**

Year	Natural uranium in U_3O_8				Enriched LEU uranium in UO_2			
	Total loss % with MUF		Material unaccounted for (MUF), %		Total loss % with MUF		Material unaccounted for (MUF), %	
	Planned	Actual	Planned	Actual	Planned	Actual	Planned	Actual
1981	0.28	0.28			0.85*	–		
1982	0.26	0.25	0.06	0.08	0.85	–		
1983	0.23	0.23		0.06	0.88	0.88		0.44
1984	0.21	0.21		0.04	0.86	0.86		0.54
1985	0.20	0.20	0.10	0.04	0.838	0.835		0.60
1986	0.175	0.174		0.059	0.79	0.79		0.54
1987	0.16	0.16	0.008	0.013	0.750	0.750	0.730	0.746
01. 1988	0.15	0.15			0.74	0.74		
07. 1988	0.15	0.15			0.68	0.68		
12. 1988	0.15	0.15			0.655	0.655		
01. 1989	0.11				0.655	0.655		
07. 1989	0.11				0.600	0.030		
12. 1989	0.11	0.06			0.600	0.004		<0.004

* The total planned LEU reconditioning loss at the Electrostal A-7340 reactor fuel factory

Pebble bed reactor fuel technology at Sillamäe

The centerpiece of any truly modern nuclear power plant is some modification of the high temperature pebble bed modular reactor (PBMR) that uses helium gas as coolant, graphite as moderator and no water in the core. It is completely fail-safe and cannot explode or melt. The very high operating temperature (1000 °C) allows electricity generation by Brayton cycle gas turbines or hydrogen production through direct catalytic (sulfur-iodine cycle) water decomposition for hydrogen-based economy [4]. It uses 60 mm diameter graphite spheres filled with thousands of tiny, less than 1mm diameter HEU particles coated with a layer of porous pyrolytic carbon providing space for fuel expansion and fission gas formation, isotropic pyrolytic carbon layers for mechanical stability, a dense silicon carbide shell as diffusion barrier for the fission-formed Cs, Sr and Ba, and finally a dense strong pyrocarbon layer that compresses and fixes the carbide shell. The coated particles are compacted with pyrocarbon-bonded or coke-generated graphite into 60 mm diameter fuel spheres that are covered with dense graphite and polished into near-perfect tough black spheres that can roll and fall some hundreds of kilometers without any significant dust formation in the reactor hopper. The modular design separates the reactor hopper from the turbines and/or hydrogen production and is designed to withstand rockets and direct hits by large aircraft.

The production of 0.7 mm diameter 21%-enriched HEU microspheres began in 1982 using agglomeration with 17 to 20% hydrocarbon binder (paraffin 65%, petrolatum 30%, oleic acid 5%). The mechanically formed raw microspheres were sorted for perfect sphericity on a 2D-vibrating sorting plate, interspersed at first with Al_2O_3 [5] which introduced unwanted aluminum, and thereafter with NH_4Cl that sublimes at 337.6 °C after driving off all the organics, and heated for several hours in a 10^{-1} to 10^{-3} mm Hg vacuum at first at 90 °C, then 300 °C and finally 950 °C to remove all organic matter without harming the perfectly spherical shape. The microspheres were further calcined and sintered for 5 to 7 hours at 1650°C in a 10^{-2} to 10^{-5} mm Hg vacuum. Treatment at 1650 °C in a reducing atmosphere (4% H_2 in argon) for 2 hours may follow. A 80 to 85% (9.0 g/cm^3) density was achieved and the spheres were thoroughly detergent-washed to remove any adhering uranium oxide dust.

As the next step a triple coating was deposited in a preheated fluidized bed reactor, flushed with pure argon gas. The first 35 to 40 μm thick low density (1 to 1.15 g/cm^3) porous layer was formed in 15 min at 1300 °C in a 4% propane-butane argon mixture. The second 10 to 15 μm thick medium density (1.3 to 1.5 g/cm^3) fixing layer was formed in 2 hours at 1500 °C in a 0.8% propane-butane argon mixture. The third 50 to 70 μm thick high density (1.8 to 1.9 g/cm^3) layer was formed in 14 hours at 1500 °C in a 0.4% propane-butane argon mixture. Thereafter the coated microspheres were treated for 48 hours at 90 °C with 8N nitric acid and checked for surface

α-activity. The perfectly coated spheres could be separated by flotation in bromoform, thoroughly washed and dried. The 90 to 110 µm thick silicon carbide shell (density 3.15 to 3.5 g/cm^3) was made in 16 hours at 1500 °C in argon with additional hydrogen gas (250 to 400 L/h), saturated at 25 °C with 4% methyltrichlorosilane that decomposes into SiC and HCl. The tightness of carbide shell was checked by heating the microspheres in air. This treatment destroys the microspheres with damaged carbide coating. Finally a dense (5 to 10 µm thick) pyrolytic carbon coating is deposited upon the carbide shell at 1300 °C in a 0.4% propane-butane argon mixture.

The fuel spheres, about 60 mm in diameter are formed from a graphite (84%) glycerine (16%) mixture that binds the central 40 mm diameter core of HEU fuel microspheres in a graphite outer shell of 10 mm thickness. All this is pressed together at 60 kg/cm^2 for the inner core and 30 kg/cm^2 for the outer shell. The fuel spheres are thermally compacted with pyrolytic carbon formed from methane (preferred) or propane-butane in argon at 860 to 1000 °C, 0.3 to 0.7 ata pressure for 80 hours. Direct coking without the use of pyrolytic carbon requires a very high 1800 °C temperature for direct graphitization that can harm the fuel microspheres. The compacted spheres are finally polished to 60 $^{+0.65}/_{-0.05}$ mm diameter.

The first model-making experiments were carried out with natural uranium dioxide or even without a fuel particle. Altogether 3600 such models were produced from 1982 to 1986, but one hundred 21%-enriched HEU fuel spheres were also produced. Preparations were carried out to produce 30 000 HEU fuel spheres per year, to be extended to 200 000 per year.

However, political climate was changing. All development and production activities with HEU were abruptly terminated already in early 1987, or three years before complete closure of the uranium production in Estonia.

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