

## TANTALUM, NIOBIUM AND THORIUM CAKE PRODUCTION 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. Their original internally heated retorts were not successful, but after restarting in 1935 with the local tunnel ovens, good yields of shale oil from the brown kukersite shale were achieved. The factory was destroyed by the Soviet occupation forces and rebuilt after WWII for uranium production from the local black alum (dictyonema) shale. Uranium production was soon replaced by uranium processing, but the factory (P.O.B. P-6685) retained the old shale-related name. In 1970 tantalum, niobium and rare earths’ production from the Khibina (Kola Peninsula, Lovozero) loparite ore was added and operated until the demise of the Soviet Union in the end of 1991. The uppermost layer in the tailings dump consists of thorium-rich loparite waste while the lowermost represents the black dictyonema shale processing waste, rich in uranium. We compare these two sources of radioactive pollution.*

### Introduction

Altogether 152 379 metric tons of Lovozero loparite 90±5% concentrate were brought to the Oil Shale Processing Plant and fully used during the years 1970 to 1991. No loparite ore has been imported to Estonia thereafter. The loparite processing started in the second half of 1970. Tantalum was produced as hydroxide or carbonate and sold as oxide (and a small quantity as ingots and alloys), but inventory was kept for the metal (Ta). Niobium was produced as pentoxide and sold as oxide, metal powder, or even zone-refined ingots and some alloys, with loparite-processing inventory kept for Nb<sub>2</sub>O<sub>5</sub>. Other ores and sources for both Ta and Nb were also used so that the total metal output exceeds the resource available in loparite. The mixed light rare earth elements (LREE) were produced as (LREE) carbonate with

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inventory kept for the mixed trioxide. Contrary to widespread folklore, no rare earth elements were dumped into the tailings pond, but all was sold for various uses in metallurgy, as petrochemical catalysts, abrasives, or exported. Cerium, lanthanum and neodymium were also separated and purified in extraction cascades and sold as fluorides. Thorium was precipitated as insoluble fluoride and dumped in the depository together with other waste. Altogether 612.32 tons of tantalum and 9638.2 tons of niobium pentoxide were produced from loparite. 48676 tons of (LREE) trioxides mixture were produced between 1972 and 1988 [2], which means practically total recovery of all (LREE)<sub>2</sub>O<sub>3</sub> present in the imported loparite with no margin for intentional dumping or losses.

### Loparite processing

Table. Loparite concentrate (90±5%) processing at the Sillamäe Plant

Year	Loparite concentrate, tons	Ore composition, weight %				Production from loparite, tons		Yield from concentrate, %	
		Ta	Nb <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	(LREE) <sub>2</sub> O <sub>3</sub>	Ta	Nb <sub>2</sub> O <sub>5</sub>	Ta	Nb <sub>2</sub> O <sub>5</sub>
1970	2157	0.467	8.14	38.1	34.3	8.476	129.7	77.2	77.5
1971	6828	0.467	7.75	38.1	34.3	25.589	428.9	82.0	82.1
1972	5816	0.442	7.71	35.7	28.4	21.870	377.8	84.4	83.7
1973	5475	0.442	7.71	35.7	28.4	21.827	369.6	90.0	87.3
1974	2371	0.442	7.71	35.7	28.4	9.258	169.8	91.5	88.9
1975	3730	0.442	7.71	35.7	28.4	14.982	249.5	92.5	89.0
1976	4001	0.442	7.71	35.7	28.4	16.420	280.8	92.9	90.2
1977	4033	0.442	7.71	35.7	28.4	16.679	281.2	93.2	90.4
1978	4492	0.442	7.71	35.7	28.4	18.599	314.9	93.4	90.6
1979	4511	0.442	7.71	35.7	28.4	18.667	315.6	93.6	90.8
1980	5015	0.442	7.71	35.7	28.4	20.799	351.6	93.8	91.0
1981	5128	0.442	7.71	35.7	28.4	21.490	361.8	94.0	91.2
1982	5661	0.442	7.71	35.7	28.4	23.914	404.5	94.2	91.4
1983	5420	0.442	7.71	35.7	28.4	21.448	374.5	94.4	91.6
1984	5902	0.442	7.71	35.7	28.4	21.860	408.6	94.6	91.8
1985	10227	0.435	7.31	35.7	28.7	38.921	656.5	90.0	92.0
1986	10582	0.423	7.01	35.7	30.6	40.440	705.0	90.1	91.1
1987	11332	0.423	6.76	35.5	30.2	44.765	631.5	90.2	91.2
1988	12640	0.425	6.82	35.7	30.1	52.720	747.8	91.7	86.7
1989	12271	0.437	6.54	35.7	30.4	49.715	692.6	94.9	89.0
1990	11357	0.480	6.20	35.7	30.7	50.373	654.8	93.7	88.0
1991	13430	0.410	6.39	35.7	31.4	53.510	731.2	93.6	86.8
Total	152379					612.32	9638.2		

Lovozero (Mt. Selsurt) loparite with average composition (Na<sub>0.45</sub> LREE<sub>0.35</sub> Ca<sub>0.14</sub> Sr<sub>0.04</sub> Fe<sub>0.005</sub> Th<sub>0.004</sub>)(Ti<sub>0.90</sub> Nb<sub>0.10</sub> Ta<sub>0.008</sub>)O<sub>3</sub> and average molecular

weight of 172, classified as calcian niobian loparite-(Ce), is actually a solid solution of loparite ( $\text{Na}_{0.5} \text{LREE}_{0.5} \text{TiO}_3$ ) with perovskite ( $\text{CaTiO}_3$ ) and tausonite ( $\text{SrTiO}_3$ ) in the thorium-substituted A-site and with lueshite ( $\text{NaNbO}_3$ ) in the tantalum-substituted B-site. The light rare earth element components (Ce, La, Nd, Pr) are listed together with other relevant oxides in wt.% [1] as:  $\text{Na}_2\text{O}$  7.99;  $\text{La}_2\text{O}_3$  8.61;  $\text{Ce}_2\text{O}_3$  18.26;  $\text{Pr}_2\text{O}_3$  1.94;  $\text{Nd}_2\text{O}_3$  4.20;  $\text{CaO}$  4.44;  $\text{SrO}$  2.56;  $\text{ThO}_2$  0.58;  $\text{Fe}_3\text{O}_3$  0.22;  $\text{TiO}_2$  41.42;  $\text{Nb}_2\text{O}_5$  7.49;  $\text{Ta}_2\text{O}_5$  0.94. The uranium oxide content is very low, only 0.03 wt.%. The  $^{232}\text{Th}$ -containing ore is radioactive through formation of the short-lived  $^{228}\text{Ra}$  and  $^{228}\text{Th}$ , and the short-lived thoron  $^{220}\text{Rn}$  forms stable progeny  $^{208}\text{Pb}$  in little more than an hour.

The exact amount of loparite concentrate brought to Estonia is thus established as 152 379 tons precisely. All waste generated from this ore is still present in the gray upper layer (4 million tons) of the waste depository, which thus contains 800 tons of thorium or 910 tons of  $\text{ThO}_2$  unevenly dispersed in hardened shale ash in the upper gray layer.

### The thorium problem

Interestingly, the presence of thorium is not even mentioned in the extensive and formerly Top Secret yearly planning and production report (Techprom-finplan) volumes – not as product and not as waste, not even as a component in the tailings depository. However, it was not forgotten. Thorium is both radioactive and polluting, but can be potentially as useful as uranium in the more sophisticated forms of nuclear reactor technology. It is mentioned in the schemes for further development and extension of the factory (P.O.B. P-6685) during the next three five-year periods from 1982 to 1996. In the document prepared by P.O.B. A-7631 in 1982, three schemes for solving the thorium problem were considered, but action was slow. Just three years before the end of loparite processing in Estonia, it was decided to start in 1989 with the development of new technology for commercial production of pure 98.8% thorium oxide  $\text{ThO}_2$  through selective extraction from the nitric acid solution of technical thorium oxycarbonate. In loparite processing the ore is first dissolved in mixed acids (4 tons of sulfuric acid and 0.55 tons of 40% hydrofluoric acid for 1 ton of loparite concentrate). During this treatment most Nb, Ta and LREE are dissolved, but thorium remains as insoluble fluoride in the moist thorium cake (2.5%  $\text{ThO}_2$ ) that also contains about 27%  $\text{BaSO}_4$  from  $^{228}\text{Ra}$  (mesothorium) coprecipitation, 12%  $(\text{LREE})_2\text{O}_3$ , 6.8% F, 3%  $\text{TiO}_2$ , 3.7%  $\text{CaO}$  and 7.9%  $\text{SiO}_2$ . This thorium cake was considered and treated as useless waste and dumped as a minor component in the depository together with other waste from uranium and loparite processing and a large amount of oil shale ash from the local power plant. This moderately  $\gamma$ -active waste forms the upper 5 to 10 meters of the dump profile as the “upper gray layer” and covers the much more  $\gamma$ -active

uranium production waste (“brown layer”) that contains at least a hundred-fold more (several kilograms) of radium  $^{226}\text{Ra}$ , though in a very insoluble form (barium-coprecipitated radium sulfate).

Since thorium may turn out to be a very useful element and not only in nuclear technology, but also as catalyst and in solid state electrochemistry, interim storage of the cake in large  $5000\text{ m}^3$  concrete reservoirs was also considered. This form of storage completely avoids any leakage of radioactive material, but shall vent some thoron into the air and can present a significant radiation load for the storeroom personnel. The third and best option was dissolution of the thorium cake in nitric acid, Ba-coprecipitation of  $^{228}\text{Ra}$ , extraction of thorium with tributylphosphate with following re-extraction into acid (pH 1.0) water phase and sedimentation of  $\text{ThOCO}_3$  with soda at 70 to 80 °C temperature. Thorium oxycarbonate yield was 0.55% from loparite. The technical product also contained 5.1%  $(\text{LREE})_2\text{O}_3$ . It was planned to keep the product in interim storage using sealed dust-free containers in a well ventilated, but unheated concrete construction. However, since market economy was rapidly replacing central planning and no commercial use was in sight, nothing was actually done and thorium dumping continued to the very end of loparite processing in Estonia. No interim or final storage facilities were built and no trace of any thorium transportation to remove it from the factory territory could be found in the detailed yearly reports.

### “Missing or lost thorium”

There has been considerable discussion about the “missing or lost thorium”, because the borehole  $\gamma$ -fluence measurements and some neutron activation analyses of two drillcore segments [4] have yielded 50% lower than expected results, consistent with the presence of only about 100 g/ton of  $^{232}\text{Th}$  in the  $4 \times 10^6$  tons of the upper gray layer material in the depository. This problem is obviously caused by the extremely non-uniform distribution of thorium along the depth profile with up to nearly tenfold variations in  $^{232}\text{Th}$   $\gamma$ -fluence even over a thin  $4.2 \pm 0.2$  m layer in the upper gray material drillcores DH4, DH5 and DH6, taken in the center of the depository (from 194 Bq/kg to 1830 Bq/kg [3, Table 4.2]). At 800 tons of  $^{232}\text{Th}$  in 4 million tons of waste, the average concentration would be 200 g/ton which would provide 800 Bq/kg activity, just close to the dump profile average value at 4 m depth. The estimate of Ehdwall about 850 tons of thorium in the dump just adds 50 tons of thorium from uranium ore processing to the 800 tons from loparite inventory data.

## Conclusions

The fate and amount of thorium in the waste depository is important, because the large recultivated dump has been declared harmless and thus can serve as a natural testing ground for a long term safe alkaline-sulfated burial site for large amounts of thorium together with all the daughter nuclei. The leaching and other forms of escape of radioactive  $^{232}\text{Th}$  progeny from the calcified mixture with alkaline calcium-rich shale ash can be checked exactly because all nuclei in the  $^{232}\text{Th}$  series are distinct and different from those in the  $^{238}\text{U}$  uranium-based series. Since most of the thorium was dumped more than 20 years ago, long term effects can be precisely studied and the behaviors of the thorium and uranium series nuclei compared under the same experimental conditions. Thorium radioactive waste long term interim storage or burial within a mixture with oil shale ash is definitely beneficial, perhaps even for final burial. The proposals presented by P.O.B. A-1997 in 1982 contain experimental data about  $^{232}\text{Th}$  and  $^{226}\text{Ra}$  leaching under these conditions, giving for thorium concentration in the leachate just  $5\ \mu\text{g/L}$  and for  $^{226}\text{Ra}$  activity  $0.3\ \text{Bq/L}$ , which are harmless values. Uranium together with the radioactive progeny appears to be the more mobile and dangerous pollutant than thorium, even if both leach from the same depository. Uranium salts are more soluble and their radioactivity is more persistent and widespread in North-East Estonia [5].

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