

“NORM-MANAGEMENT PLANNING FOR HYDRO-METALLURGICAL INDUSTRY AT SILLAMÄE, ESTONIA”

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1 ABSTRACT

The Sillamäe Metallurgical Plant was built in 1948 at Sillamäe, in North-East Estonia. Target product was uranium, mostly in form of yellow cake (U_3O_8) for Soviet nuclear program. Uranium ore processing continued from 1948 to 1977, totally 4,013,000 tons of uranium ore were processed at Sillamäe plant.

In early 1970s the plant introduced a new production line – rare earth elements. Rare earths were until 1991 produced from loparite (later from semi-processed loparite) – rare earths, niobium, tantalum and NORM-containing ore for Kola peninsula, Russia.

All wastes were, as typical to hydrometallurgical processing all over the world, discharged to a large, 40 ha liquid waste depository – tailings pond, what in Sillamäe case was designed to discharge all liquid constituents slowly to the Baltic Sea.

All uranium related activities were stopped in 1990, when only rare earth and rare metal production lines remained operational.

The plant was 100 % privatized in 1997 and is today operated by Silmet Ltd., processing annually up to 8 000 tons of rare earth and 2000 tons of niobium and tantalum ores.

The historical tailings pond, containing ca 1800 tons of natural uranium and ca 800 tons of thorium, was found geotechnically unstable and leaking to the Baltic Sea, in mid 90s.

Being a problem of common Baltic concern, an international remediation project was initiated by Estonian Government and plant operator in 1998.

In cooperation with Estonian, Finnish, Swedish, Danish and Norwegian Governments and with assistance by the European Union, the tailings pond will be environmentally remediated – dams stabilized and surface covered, by end of 2006.

Close-down and environmental remediation of the tailings pond provides plant an ultimate challenge of discontinuing the use of liquid waste depository and re-arranging completely entire waste management system.

One of the most complicated and not yet properly regulated areas is solid NORM-waste management: according to drafted concept of new waste management system, the plant will produce ca 1000...1500 tons of solid

NORM-waste with activity between 1000 and 5000 Bq/g annually; NORM is represented in wastes by U-238 and Th-232.

However, under conditions of tense work schedule, the plant is planning waste streams' separation, retrievable interim storage for separately NORM-containing and non-radioactive solid residue; and liquid streams pre-treatment with steps of acid regeneration.

2 INTRODUCTION AND BACKGROUND

The Sillamäe Metallurgical Plant was established in 1946...1948 to meet needs of Soviet nuclear program.

Since plant's launch until early 50s local Estonian alum-shale, containing about 0.03% of uranium, was processed; later the production was switched to richer ores from Central and East European countries.

Uranium ore processing continued to 1977, totally 4,013,000 tons of uranium ore were processed at the plant. Since late 70s to 1990 the plant refined nuclear fuel (enriched uranium) been produced in Russian plants.

All uranium related activities were stopped in 1990, when only rare earth and rare metal production lines remained operational.

The plant was 100 % privatized in 1997 and is today operated by Silmet Ltd., processing annually up to 8 000 tons of rare earth and 2000 tons of niobium and tantalum ores.

Until 1959, when the tailing pond was established, the waste from the processing was transported to a marine terrace nearby the plant and stored just on the surface. The tailings pond located at the shore of the Finnish Gulf has been constructed on a slope, consisting of several layers, tilted into the direction of the sea. The pond covers the area more than 40 hectares, with a built-up height of about 25 m.

The tailing pond contains about 12 million tons (about 8 million m³) of waste. Based on estimates the pond contains the following substances; 6.3 million tons of uranium processing residuals and 6.1 million tons of oil-shale residue and waste from processing of loparite. These wastes contain some 1,830 tons of pure uranium and 850 tons of thorium. The total amount of radium is estimated to 7.8 kg, corresponding to 2.9×10^{14} Bq of ²²⁶Ra.

2.1 Reasons for changing the waste management system

Environmental studies, conducted at the plant and tailings pond in early 90s showed that the tailings pond – although having free capacity for many years – was environmentally unsafe and steps were necessary to be taken to eliminate potential threats to the Sillamäe region and entire Gulf of Finland.

Measurements indicated that the dam of the tailing pond was sliding down along a layer of clay into the Baltic Sea. The waves of the sea, at high tides and in bad weather, were attacking the foot of the dam. Stabilising the dam was

found necessary to prevent a collapse of the dam and subsequent landslide of the total tailing pond into the Baltic Sea.

The second problem with the pond was that the pond acted as a large-scale filter: water entering the pond was moving rather quickly into the sea through a gravel layer located at the bottom of the pond.

After plant's privatisation in 1997 the decision was taken to close down and remediate the tailings pond site. For initiation and management of the respective project a public-private environmental company – ÖkoSil Ltd – was established by Government of Estonia and new owner and operator of the plant Silmet Group Ltd.

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2.2 Present Processing

Rare Earth Process

The rare earth chloride mix from Solikamsk Magnesium Works is used as a raw material for rare earth production. The chloride mix contains 38-42% of the mostly light group rare earth elements and is obtained by the chlorination of loparite concentrate.

The Rare earth elements in the raw material are mixed with impurities (calcium, strontium, sodium, potassium, iron, aluminium and silicon) and also with NORM (natural uranium and thorium) and products of their decay. The chemical composition of the rare earth chloride mix is presented in the Table 1.

Component	%	Component	%
Ln ₂ O ₃	38-42	Na ₂ O	7.8
U ₃ O ₈	0.01	K ₂ O	0.2-0.3
ThO ₂	0.15-0.72	Fe ₂ O ₃	0.1-0.2
CaO	5-6.2	SiO ₂	2.5-3.2
SrO	2.1-2.7	Cl	44-52
BaO	0.13-0.15		
Insoluble Residue	~3-7	Activity ($\Sigma\alpha$) Bq/g	330-470

NORM Flow Chart of the rare earth processing

The Rare Earth Plant flow chart includes the following processes:

Dissolution - The rare earth chloride mix is dissolved in river water using heat, intense agitation and compressed air bubbling for iron oxidation.

Deactivation 1 - After the dissolution, the resulting slurry is treated with ammonium sulphate solution for precipitation of calcium and strontium sulphates. Most of the radium sulphate is co-precipitated with these sulphates.

Precipitation of Thorium Hydroxide - Thorium is precipitated with dilute ammonia solution at pH of 3.8-4.1 while heating. Together with thorium, hydroxides of trivalent iron, aluminium, uranium and a small amount of rare earth elements are precipitated.

Filtration - After precipitation, the slurry is filtered. The precipitate, consisting of insoluble residue, sulphates and hydroxides of calcium and strontium, is washed with water for the removal of the remaining solution and is discharged into the tailings pond as an aqueous slurry. Washing water is utilized for the chloride mix dissolution and the dilution of slurries. The main filtrate is directed to the "Deactivation 2" step.

Deactivation 2 (Purification from SO_4^{2-}) - The rare earth solution containing an excess of sulphate ions is treated with barium chloride solution. Final purification of radium and SO_4^{2-} occurs as a result of barium sulphate precipitation and the co-crystallization of radium. The resulting slurry is filtered. Crystalline radioactive barium sulphate precipitate is combined with the thorium hydroxide precipitate. The deactivated solution is directed to further processing.

Rare Metal Process

Columbite concentrates and ferroniobium are used as raw materials in the production of tantalum and niobium. The composition of raw materials varies depending on deposit. Niobium and tantalum in the mineral concentrates are combined with iron, tin, titanium, manganese, NORM (natural uranium and thorium) and their decay products. The chemical composition of the raw material is presented in Table 2.

Table 2 Composition of the Raw Materials for Rare Metal Production (content of the constituents in % of physical weight)													
Ta ₂ O ₅	Nb ₂ O ₅	TiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MnO ₂	SiO ₂	P ₂ O ₅	SnO ₂	WO ₃	MoO ₃	CaO	ThO ₂	U ₃ O ₈
Columbite, Nigeria total α- activity, ~100-120 Bq/g													
4.9-6	50-60	4-7	~22	0.39	2.5-3	1-2	1-1.5	4-6	~1.4	<0.01	<0.05	0.4-1	~0.05
Columbite, Brazil total α- activity, ~15-20 Bq/g													
3.7-4	39-41	6.7-9	37-40	-	-	-	-	~1.5-2	-	-	-	~0.12	~0.04
Ferroniobium total α- activity, ~7-10 Bq/g													
~6.5	65-70	1.5-3	38-43	7.5-9	5-6	6.5-12	~0.5	7-11	~0.5	~0.02	-	<0.03	~0.11

The balance between different ores may vary in the future – however, considering the similarity of compositions of the different raw materials used, considerable changes in the composition and quantity of technological waste formed during the processing should not be expected.

NORM Flow Chart of the rare metal processing

The NORM flow chart from the Rare Metal Plant includes the following processes:

Crushing - The concentrates are crushed in vibrating kinetic ball mills to a particle size of 0.3-0.16 mm. Ferroniobium is crushed to a particle size of 1-5 mm.

Decomposition - Crushed raw material is dissolved in a mixture of concentrated acids (92.5% H₂SO₄ and 40% HF). Dissolution is conducted in a batch mode in actively stirred reactors. The raw material is fed to the acid mixture at a slow rate as a large amount of heat is liberated in the dissolution process (hydrogen is also liberated in the ferroniobium dissolution process). The slurry is heated to 70 – 85⁰C. Liberated gases are condensed in cooled heat exchangers, then purified of fluorine to meet the sanitary regulations by trapping and scrubbing with soda solution.

Filtration and Washing of Precipitate - After the decomposition, the slurry is filtered. Insoluble residue is washed for the removal of remaining solution with the mixture of sulfuric and hydrofluoric acid. Washing solutions are combined with the main filtrate. The free fluorine content in the solution is adjusted, and the solution is fed to a solvent extraction circuit. The washed precipitate/insoluble residue is slurried in process waste solutions and discharged into the tailings pond as an aqueous NORM-containing slurry.

2.3 The new waste management concept

Like many industries, inherited from Soviet times, Silmet plant is today facing a serious challenge to upgrade technologies towards waste minimization and increase of the process efficiency.

Present operator of the plant – Silmet Group Ltd – is now planning the new waste management system.

Close-down and environmental remediation of the tailings pond provides plant an ultimate challenge of discontinuing the use of liquid waste depository and re-arranging completely entire waste management system.

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Factors, examined in the development of alternatives for the waste management system:

- ability to meet regulatory compliance standards;
- ability to be implemented within the time frame required (early 2003);
- initial capital and long term operating cost of the total waste management system; and
- selection of only proven technologies with known performance and qualified vendors.

2.4 Potential options observed

There exist numerous proven waste treatment technologies potentially relevant to the Silmet plant NORM waste streams. Most of these technologies produce some quantity of secondary waste, often as a contaminated aqueous phase, which would be treated in the chosen water treatment system. In order to deal with Silmet NORM waste, following techniques were observed and evaluated:

Solidification/Cementation

This technology involves cementation of the radioactive waste stream using some combination of Portland cement with a binder matrix such as concrete or fly ash to produce a solid mass with low leaching potential. Since the NORM waste is incorporated into the matrix of cemented mix, it is rendered immobile in the environment, although still considered hazardous or radioactive.

The benefits of this technology are that it is widely used and is a mature technology, readily adaptable to many different waste streams. It is also the least capital and initial treatment cost intensive. Since the treatment technology itself results in no air or water discharge, regulatory permitting is usually not very complicated.

The downside of this technology is that since cement-forming compounds and water are added to the waste stream, its volume and mass is greatly increased, often as much as two fold. Since depositing costs are usually based on a volume or weight, this also increases the disposal cost. Another downside to this technology is that chemical salts historically do not react well with most stabilization formulas and usually require significant pre-treatment to decrease their solubility.

Incineration

This technology uses combustion to decompose wastes and convert them to oxides of their respective elemental components. This technology is well developed and understood, and several different systems are available from a variety of vendors worldwide.

The downside of this technology is that since the majority of the converted waste forms discharge from the incineration system via the stack exhaust, a great deal of effort and expense is spent in permitting and monitoring stack exhaust quality. Quite often may the exhaust gas treatment system be more costly than the incinerator itself. Permitting has proven to be complicated worldwide due to public prejudice.

Incineration would be considered to be relatively high cost per kilogram of waste treated. In addition, final disposition of the incinerator bottom ash and fly ash usually requires additional treatment to meet regulatory leachability guidelines.

A specific concern regarding this technology and its applicability at Silmet would be the treatment of off-gas, both to meet regulatory concerns and to prevent severe corrosion of the off-gas treatment system. Specifically, high sulfur wastes such as those from the extensive use of sulfuric acid in the rare metals production would cause very high levels of SO₂ in the off-gas emissions. Likewise, the high levels of nitrogen compounds would cause high levels of NO_x. Both of these compounds are highly regulated.

Vitrification

This technology involves combination of glass-forming compounds with the waste to be treated in a melt chamber heated to a temperature of 950 to 1,350 °C. Organic compounds, if present in the waste stream, are destroyed or combined with the glass matrix. Metals and radionuclides present in the waste are combined within the glass matrix. Heat to accomplish the vitrification is usually supplied by electrical energy, either directly via resistance heating between electrodes within the melt chamber, or externally via resistance heating of the melt chamber. Induction heating via coils external to the melt chamber is also used.

Unlike solidification / stabilization which greatly increases final waste volume, this technology significantly reduces the final waste volume similar to incineration. The final glass matrix results in the most durable waste form currently known and has caused e.g. the US Environmental Protection Agency

to label this technology as best demonstrated available technology (BDAT) for high level radioactive waste.

The cost of this technology is similar to incineration both in capital and operating costs. The permitting of a vitrification facility is usually less complicated because it is usually not classified as an incinerator even though the same air discharge standards must be met. Off-gas from a vitrification facility results in much lower discharges of NO_x, SO_x, and CO because of a lower operating temperature and the ability to 'trap' many volatile compounds within a 'cold top' vitrification unit. Cold top units maintain a layer of partially solidified glass on top of the glass melt to increase retention of volatile organics and metals. Waste feed to the molten glass pool, and discharge of the vitrified waste there from, occur under this 'cold top'.

The vitrified NORM-waste could be easily stored on-site awaiting availability of a final low level radioactive waste repository.

Some potentially negative aspects of this technology include:

- the requirement to blend waste feedstock to achieve a uniform mix;
- control of pH to prevent undue wear of melt chamber refractory; and
- high electrical energy cost required per unit of waste fed to the unit.

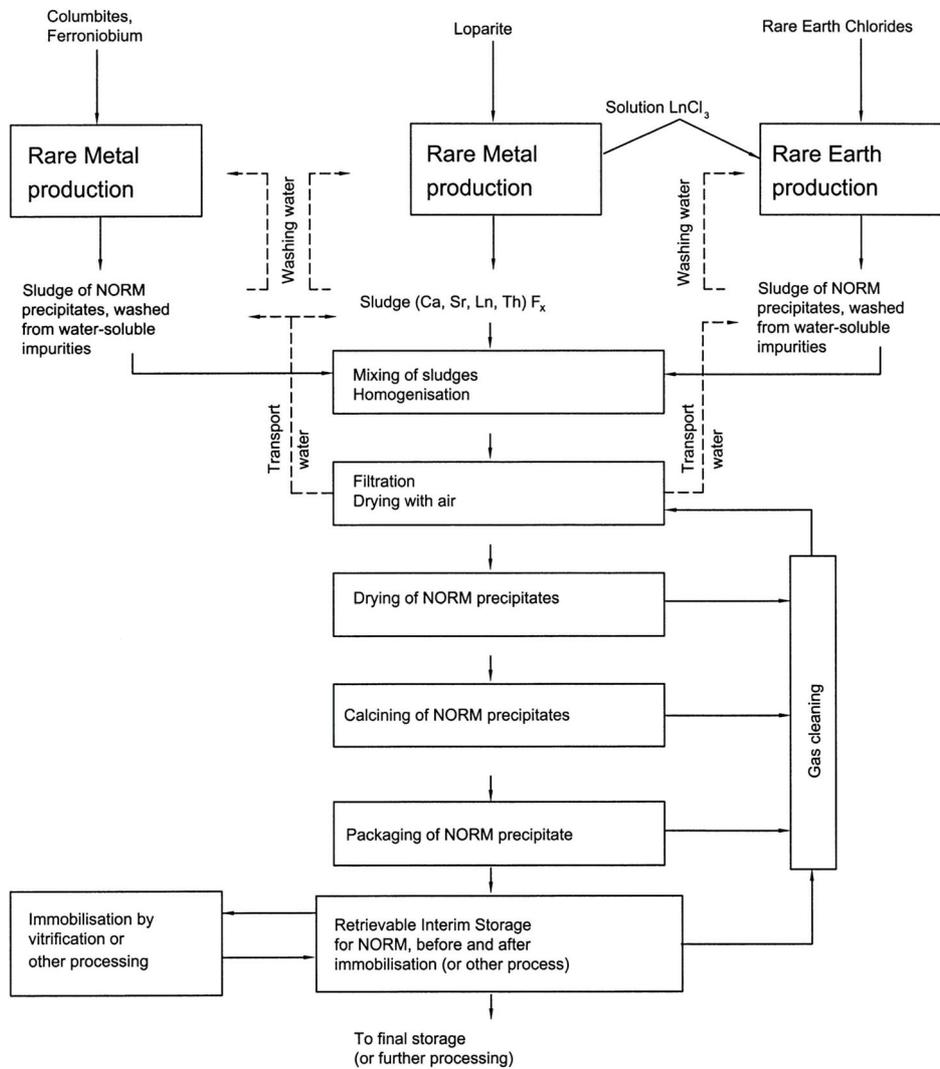
This last point is mitigated by the presence of an oil-shale fired power plant at Silmet.

This technology is a mature technology that is widely used throughout the world, particularly in France, Germany, and Japan. Several vendors of this technology exist.

3 SELECTED METHODS

After thorough evaluation and many discussions, involving also independent consultants, the following principal concept for general waste management was presented:

- Neutralization and precipitation for recycle or treatment and discharge to the sea;
- Thermal evaporation of salts and precipitates;
- Acid regeneration;
- Interim storage of radioactive (NORM) waste;
- Vitrification of radioactive (NORM) waste.



Drawing 1. Conceptual NORM flow chart at AS Silmet

Radioactive Waste Interim Storage

Interim storage for radioactive wastes in an on-site facility is a requirement for management of feedstock to a vitrification plant or for long-term management of the solid waste streams. The amount of space for such storage absent a

vitrification unit is significant, but available. Size of the storage will depend on implementation schedule the next phase – vitrification – and needed buffer capacity (2...3 years).

Later storage of the vitrified materials is less complicated than of non-vitrified material.

Waste Vitrification

This technology involves combination of glass-forming compounds with the waste to be treated in a melt chamber heated to a temperature of 950 to 1,350 °C. Organic compounds within the waste stream are destroyed or combined with the glass matrix. Metals and NORM present in the waste are also combined within the glass matrix. The vitrified materials stable character, and the fact that the volume of vitrified material produced by the process is significantly less than the feed waste, combine to make the technology favourable for application at Silmet.

4 REFERENCES

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