

## Technology for Treatment of Salt Residue Stored at NPPs

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### ABSTRACT

At Moscow SIA "Radon", three (3) options for NPP salt residue treatment were developed and tested. Option 1 consists of dissolving the salt residue and subsequent treatment by ozonization, separation of the deposits formed from ozonization and selective cleaning by ferrocyanide sorbents. Option 2 consists of fusion of the salt residue, addition of glassforming additives and melting of borosilicate glass in a melter such as a "cold crucible". Option 3 consists of dissolving the salt residue, oxidation of the solution obtained, removal of radionuclides by collectors and the separate handling of formed deposits and the solution. The deposits containing more than 99 % of the activity are directed to vitrification and the solution is directed either to a concentrates dryer or to cementation. The vitrified waste product is placed in repository for solid radioactive waste storage and the solidified product from the solution goes to an industrial waste disposal site or a repository specially developed at NPP sites for "exempt waste" products by IAEA classification.

### INTRODUCTION

Significant amounts of salt residue have accumulated at NPPs with PWR reactors in Russia and Ukraine. At each NPP where concentrates drying is used to produce salt residue from evaporator concentrates, the accumulated quantity of drums is 10 thousand or more. The salt residue is a mixture mainly of sodium nitrates and sodium borates of specific activity  $1 \text{ E}+7 - 1 \text{ E}+8 \text{ Bq/kg}$ . The salt residue is stored in 200-l drums with a life of no more than 5 years. Such storage represents a serious threat to the environment.

### MAIN PART

At Moscow SIA "Radon", three (3) options for NPP salt residue treatment were developed and tested.

Option 1 consists of dissolving the salt residue and subsequent treatment by ozonization, separation of the deposits formed at ozonization and selective cleaning by ferrocyanide sorbents. As a result of such treatment, secondary radioactive waste products are formed:

- Solids from the filtration stage which can be immobilized in a matrix material,
- Exhausted sorbent placed in a filter – container.

The solution cleansed of radionuclides can be treated by one of the following methods:

- Discharged to the sea; such practice is used at Loviza NPP, Finland;
- injected underground;
- directed to industrial waste disposal sites after drying (deep evaporation)

Advantages of this option of salt residue treatment are the following:

- An opportunity to treat the legacy salt residue drums at a plant and future evaporator concentrates with the same system;
- Very high radioactive waste volume reduction factor (~ 50 - 100).
- Creation of systems for selective cleaning of the evaporator concentrates at Russian NPP. (At the Kola NPP a system for ion selective cleaning of evaporator concentrates with a capacity 500 l/hour has been put into operation.)

A drawback of option 1 is the generation of a large quantity of the spent filters - containers of high cost (~ 30000 \$/ps.).

Option 2 consists of fusion of the salt residue, addition of glassforming additives and melting of borosilicate glass in a melter such as a "cold crucible".

Advantages of this option are:

- High radioactive waste volume reduction factor (~ 3 - 5);
- Excellent quality of the conditioned waste product (leaching rate <math>< 1 \text{ E-} 6 \text{ g/cm}^2/\text{day}</math>).

Drawbacks of option 2 are:

- High treatment cost because of high power consumption of vitrification process ;
- Significant amount of secondary LRW.

Option 3 consists of dissolving the salt residue, oxidation of the solution obtained, removal of radionuclides by collectors and the separate handling of formed deposit and the solution. The deposits containing more than 99 % of the activity are directed to vitrification, and the solution is directed either to a concentrates dryer or to cementation. The vitrified waste product is placed in repository for solid radioactive waste storage, and the solidified product from the solution goes to an industrial waste disposal site or a repository specially developed at NPP sites for "exempt waste" products by IAEA classification. Disposal cost of such waste products in global practice is hundreds of times less than intermediate level radwaste disposal costs.

Advantages of option 3:

- Very high radioactive waste volume reduction factor (~ 50 - 100);
- Considerably lower treatment cost in comparison with direct vitrification (the volume of deposits is less than 1 - 2 % of the salt residue volume);
- Excellent quality of the conditioned product. More than 99 % of the activity from the salt residue is immobilized in a glasslike product.

A drawback of option 3 is:

- The need for three types of systems at one NPP (cleaning of radionuclides, vitrification of the deposits, concentrates drying or cementation of the solution)

The three options mentioned above were tested under laboratory conditions on salt residue from the Novovoronezh NPP.

Chemical and radionuclide composition of the salt residue from Novovoronezh NPP are given in tables 1, 2.

Table 1. Chemical composition of the salt residue, mass%.

Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Fe <sup>2+</sup>	Al <sup>3+</sup>	NO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	BO <sub>3</sub> <sup>-</sup>	SiO <sub>2</sub>
12 - 20	1 - 4	3 - 5	< 1	< 1	18 - 23	10 - 15	< 1	25 - 33	1 - 5

Table 2. Results of radiometric and gamma-spectrometry analyses of the salt residue, Bq/kg.

$\Sigma \beta$ on <sup>137</sup> Cs	$\Sigma \beta$ on <sup>90</sup> Sr+ <sup>90</sup> Y	$\Sigma \beta$ on Y <sup>90</sup> E $\beta$ > 1,0 MEV	$\Sigma \alpha$ on Pu <sup>239</sup>	Cs <sup>137</sup>	Cs <sup>134</sup>	Co <sup>60</sup>
7,5•10 <sup>6</sup>	4,3•10 <sup>6</sup>	4,2•10 <sup>4</sup>	<1,5	6,7•10 <sup>6</sup>	6,6•10 <sup>3</sup>	2,9•10 <sup>3</sup>

Experiments for option 1 included three stages:

1. Experiments on dissolving the salt residue at various pH to determine solubility.
2. Oxidation of the obtained radioactive solution with use of various oxidizers.
3. Cleaning of the obtained solution with NZHS or Termoxid T-35 sorbents.

Dissolving the salt residue was carried out in the following way. Three aeration vessels were filled with 100 ml aliquots of distilled water, pH in the second vessel was adjusted up to 12, in the third vessel- up to 13. The salt residue was introduced into each vessel in of 2 g increments, the next increment was introduced after complete dissolution of previous portion. In the second and third vessels after introducing the next portion of the salt residue pH was adjusted (in the second vessel up to 12, in the third vessel up to 13). Vessels were equipped with magnetic mixers. If the next portion of the salt residue was not dissolved completely in 4 hours, the dissolution process was considered to be completed.

Results of experiments on dissolution of the salt residue are given in table 3.

Table 3. Chemical and radionuclides composition of the Novovoronezh NPP salt residue solution.

№	pH	Salt content, g/l	TOC, mg/l	BO <sub>3</sub> , g/l	Σβ, Bq/l	Σα, Bq/l	Cs <sup>137</sup> , Bq/l	Cs <sup>134</sup> , Bq/l	Co <sup>60</sup> , Bq/l
1	9	30,76	239	10,7	3,9*10 <sup>5</sup>	<1	3,4*10 <sup>5</sup>	3,8*10 <sup>2</sup>	1.2*10 <sup>2</sup>
2	12	121,20	552	43,3	8,7*10 <sup>5</sup>	<1	8,5*10 <sup>5</sup>	9.5*10 <sup>2</sup>	3.7*10 <sup>2</sup>
3	13	134,00	790	47,1	9,6*10 <sup>5</sup>	<1	9,5*10 <sup>5</sup>	1.4*10 <sup>3</sup>	3.4*10 <sup>2</sup>

\* TOC – total organic carbon.

Further dissolution of the salt residue was carried out at pH = 12.

For preliminary oxidation of the salt residue solution the following were tested:

- Hydrogen peroxide;
- Peroxide - permanganate oxidation;
- Ozonization.

Hydrogen peroxide has high oxidizing potential and it is widely used for sewage treatment. More than 50 % of hydrogen peroxide being manufactured in the world is used for sewage treatment. To increase the oxidizing ability, the peroxide is used together with the catalyst (Fe+2) according to Fenton reaction. When using peroxide in a solution to be treated no additional components are added, and, hence, it does not result in the formation of secondary waste products.

Potassium permanganate in an alkaline medium has higher oxidizing potential, than hydrogen peroxide. However, use of permanganate for oxidation of organic substances in a solution being treated forms plenty of manganese dioxide which is a secondary waste product. To reduce the quantity of secondary waste products from permanganate, it is necessary to use hydrogen peroxide first to oxidize all possible organic substances and then to carry out oxidation of other substances with permanganate.

The choice of the ozonization method for destructive oxidation of solutions was made based on its advantages in comparison with other treatment methods:

- 1 Ozone is synthesized from oxygen in the air and a product of its decomposition is also oxygen( i.e. during the treatment process there is no formation of secondary contaminants in the solution).
- 2 Ozone is one of few oxidizers participating in natural chemical and biochemical processes, therefore it is compatible (up to the certain limits) with the environment.
- 3 Use of ozone solves the problem of cleaning the solution of both organic and inorganic contaminants.
- 4 Formed during self-decomposition of ozone and its interaction with water molecules the products of radical character have a potential of oxidation higher, than an initial molecule of ozone that causes high efficiency of the use of ozone in technological processes.
- 5 Generation of ozone directly during solutions treatment eliminates the need for other reagents for solution treatment.
- 6 The emission of ozone into an environment can be quickly eliminated by switching-off the ozone generator.
- 7 Ozonization process equipment enables combined processing using other technological operations: adjusting pH, sedimentation of substances not readily soluble , etc.
- 8 Ozonization is widely used in industry for water-preparation and sewage treatment. Standard equipment capacity from 1 g up to 50 kg of ozone per hour are available.

**Ozonization of the dissolved salt residue.**

Ozonization was carried out at temperature 60<sup>0</sup> C and pH ~ 12. Temperature was maintained via a liquid thermostat. The vessel was filled with LRW to be treated. Ozone was introduced in the vessel by means of gas-distributing devices made of porous ceramics. Adjustment of pH was carried out by NaOH solution (500 g/l). During ozonization the following parameters were controlled:

- A portion of the ozone passed through LRW, % of stoichiometry;
- pH value;
- Optical density of a filtrate of taken sample;
- TOC (total organic carbon);

When pH fell below <11 an alkali was added to the solution. The ozonization experiment was carried out up to a constant optical density of a filtrate sample. During ozonization the color of the filtrate changed from yellow with green opalescence to colorless. The optical density of the filtrate after ozonization was compared to distilled water (0.01 at 1 cm wide troughs and wave length of 490 nanometers). After filtering through a dark blue tape the solution was cleansed by inorganic sorbents.

**Peroxide oxidation of dissolved salt residue.**

After adjusting pH, adding catalysts and heating the evaporator concentrates; the hydrogen peroxide was injected by peristaltic pump at the rate needed to maintain constant optical density (D) in a filtrate sample. The sample was passed through the filter « a dark blue tape ».

Results of peroxide oxidation of the salt residue solution are given in table 4.

Table 4. Results of peroxide oxidation of the salt residue solution

Time, min	0	30	90	120	150	210	240	270	300
T, °C	100	100	100	100	100	100	100	100	100
H <sub>2</sub> O <sub>2</sub> volume , ml/l	0	30	75	105	135	200	235	265	300
D <sub>490</sub> <sup>10</sup>	0,225	0,15	0,08	0,03	0,025	0,025	0,025		
D <sub>490</sub> <sup>50</sup>	-	-	-	-	-	0,076	0,06	0,045	0,045
pH	3	3	-	-	-	2,25↑ 3,15	2,05	1,7	1,25↑ 3,05

2,25 ↑ 3,15- pH was corrected.

**Peroxide - permanganate oxidation**

This process consisted of carrying out a peroxide oxidation, and then oxidation by potassium permanganate. Peroxide oxidation was carried out as it mentioned above. The pH of LRW was then adjusted into alkaline range and KMnO<sub>4</sub> solution (50 g/l) was introduced at 80 - 100<sup>0</sup>C. Introduction of permanganate was carried out up to constant violet color of KMnO<sub>4</sub>. Excess of permanganate was removed by hydrogen peroxide. The precipitate was removed by a filter.

**Sorption cleaning of the oxidized solution of salt residue.**

Sorption cleaning was carried out on NZHS and Thermoxid T-35 sorbents. The oxidized salt residue solution was passed at 20 - 40 ml/h through a column filled with a sorbent by peristaltic pump . Volume of the sorbent was 8 ml. Before sorption cleaning, the pH of the solution was adjusted to 9 - 11.

Results of sorption cleaning are given in table 5.

Table 5. Results of sorption cleaning of the oxidized solution

Oxidizer	Volume passed	Rate, ml/h	Volumetric activity of filtrate, Bq/l			Sorbent
			$\Sigma \beta$ on $^{137}\text{Cs}$	$\text{Cs}^{137}$	$\text{Co}^{60}$	
Initial (before oxidation )			$1.2 \cdot 10^6$	$1.2 \cdot 10^6$	$4.2 \cdot 10^3$	
ozone	100	40		$2.5 \cdot 10^3$	5,4	NZHS
ozone	100	40		$3.8 \cdot 10^1$	<	T – 35
	200			$7.2 \cdot 10^1$	-	
	300			$3.2 \cdot 10^1$	-	
	400			$4.4 \cdot 10^2$	-	
	500			$1.5 \cdot 10^2$	-	
$\text{H}_2\text{O}_2$	100	20	$4.7 \cdot 10^2$	$1.2 \cdot 10^2$	-	T – 35

For option 2 the composition of glass forming additives were chosen and laboratory glass samples with a various loadings of dry salt residue were obtained. The composition of the glass charge, mode of vitrification process and the visual description of glass samples are given in table 6.

Table 6. Characteristics and composition of glass samples

Index of glass sample	Charge structure	Content, mass. %	Parameters of vitrification process			Description of glass samples
			Temperature of heating $T_{\max}$ , $^{\circ}\text{C}$	Time of heating up to $T_{\max}$ , hour	Keeping at $T_{\max}$ , hour	
SNVP-1	Salt residue $\text{Na}_2\text{CO}_3$ CaO $\text{SiO}_2(\text{sand})$	30 15 10 45	1200	2	0,5	Melt poured out well. Glass sample has bubbles, colorless, transparent.
SNVP-2	Salt residue $\text{Na}_2\text{CO}_3$ CaO $\text{SiO}_2(\text{sand})$	60 0 5 35	1100	1,5	0,25	Melt poured out well. Glass sample has bubbles, colorless, transparent.
SNVP-3a	Salt residue $\text{Na}_2\text{CO}_3$ CaO $\text{SiO}_2(\text{sand})$	45 0 5 50	1100	1,5	0,25	Melt was viscous. Glass sample has large bubbles, colorless, transparent.
SNVP-3	Salt residue $\text{Na}_2\text{CO}_3$ CaO $\text{SiO}_2(\text{sand})$	45 0 5 50	1200	2	1	Melt poured out well. Glass sample has large bubbles, colorless, transparent.
SNVP-4	Salt residue $\text{Na}_2\text{CO}_3$ CaO $\text{SiO}_2(\text{sand})$	50 0 5 45	1200	2	1	Melt poured out well. Glass sample has large bubbles, colorless, transparent.

Results of the radiometric and gamma - spectrometer analyses of glass samples are given in table 7.

Table 7. Radionuclides composition of glass samples, Bq/kg

Index of sample	$\Sigma \beta$ on $^{137}\text{Cs}$	$\Sigma \beta$ on $^{90}\text{Sr}+^{90}\text{Y}$	$\Sigma \beta$ on $Y^{90} E\beta > 1,0 \text{ MEV}$	$\Sigma \alpha$ on $\text{Pu}^{239}$	$\text{Cs}^{137}$	$\text{Cs}^{134}$	$\text{Co}^{60}$
SNVP-1	$1,4 \bullet 10^6$	$8,2 \bullet 10^5$	$8,2 \bullet 10^3$	<2,9	$1,2 \bullet 10^6$	$1,3 \bullet 10^3$	$1,1 \bullet 10^3$
SNVP-2	$3,4 \bullet 10^6$	$2,3 \bullet 10^6$	$1,5 \bullet 10^4$	<4,3	$3,3 \bullet 10^6$	$3,0 \bullet 10^3$	$2,6 \bullet 10^3$

For option 3 after peroxide and peroxide-permanganate oxidation of the salt residue solution ferrocyanide sedimentation of radionuclides was conducted.

On completion of the oxidation process, before ferrocyanide sedimentation, the pH of the solution was adjusted to 9 - 9.7. Both nickel nitrate and potassium ferrocyanide were added to the solution. This resulted in a nickel ferrocyanide precipitate at a concentration of 1 g/l. After adding reactants the solution was maintained for 2 hours and then passed through the "dark blue tape" filter.

Results of ferrocyanide sedimentation are given in table 8.

Table 8. Specific activity of a filtrate after ferrocyanide sedimentation in the oxidized salt residue solution

Oxidizer	$\Sigma\beta$ , Bq/l	$\text{Cs}^{137}$ , Bq/l	$\text{Co}^{60}$ , Bq/l
$\text{H}_2\text{O}_2 + \text{KMnO}_4$	$1,7 \bullet 10^3$	$1,2 \bullet 10^3$	<10
$\text{H}_2\text{O}_2$		$1,1 \bullet 10^3$	$6,3 \bullet 10^1$

Several liters of the salt residue solution were prepared. The solution was oxidized by hydrogen peroxide and potassium permanganate, and then a ferrocyanide sedimentation was carried out. The precipitate (sludge) was separated and vitrified.

Because of high moisture content of the sludge (77 %) silicon dioxide, in the form of an aerosol, along with the glass forming additives were introduced to the solution to prevent the formation of a stratifying paste.

Results of experiments on sludge vitrification and charge preparation are given in tables 9 and 10.

Table 9. Characteristics of glass samples of sludge

Index of sample	Charge composition	Content, mass . %	Parameters of vitrification process			Description of sample
			Temperature of heating $T_{\text{max}}$ , °C	Time of heating up to $T_{\text{max}}$ , hour	Keeping at $T_{\text{max}}$ , hour	
SSHNP-1	sludge	50	1200	2	0,5	Melt poured out well. Glass sample is brown, opaque, homogeneous.
	$\text{Na}_2 \text{CO}_3$	10				
	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$	10				
	$\text{SiO}_2$ (sand)	28				
	$\text{SiO}_2$ (aerosil)	7				
SSHNP-2	sludge	50	1200	2	0,5	Melt poured out well. Glass sample is brown, opaque, homogeneous.
	$\text{Na}_2 \text{CO}_3$	20				
	$\text{Ca}_2(\text{BO}_3)_2 \cdot 2\text{H}_2\text{O}$	5				
	$\text{SiO}_2$ (sand)	20				

	SiO <sub>2</sub> (aerosil)	5				
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Table 10. Rheological properties of the sludge based paste

Index of paste	Structure	Content, mass. %	Moisture, mass %	Spreadability, cm
PSHNVP-1	sludge	50	61,3±1,2	16,5±1,0
	Na <sub>2</sub> CO <sub>3</sub>	10		
	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> *10 H <sub>2</sub> O	10		
	SiO <sub>2</sub> (sand)	28		
	SiO <sub>2</sub> (aerosil)	7		
PSHNVP-2	sludge	50	62,1±1,2	20,0±1,0
	Na <sub>2</sub> CO <sub>3</sub>	20		
	Ca <sub>2</sub> (BO <sub>3</sub> ) <sub>2</sub> *2H <sub>2</sub> O	5		
	SiO <sub>2</sub> (sand)	20		
	SiO <sub>2</sub> (aerosil)	5		

**Conclusion**

The experiments carried out have shown that treatment of salt residues, accumulated at NPPs in Russia and Ukraine, is possible by three options. Future work should be directed to:

- Carrying out integrated tests for all three options to optimize each stage and complete equipment selection;
- Carrying out technical and economic comparison of each salt residue treatment option based on the results of the integrated tests.