CONCEPTUAL ASPECTS OF LOW-LEVEL LIQUID RADIOACTIVE WASTE (LRW) DECONTAMINATION

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ABSTRACT

The report contains a review of different treatment methods of Liquid Radioactive Waste, developed in Russia in the period between 1986 and 2000.

The author conducts a comparative effectiveness analysis for the following methods:

1. Sorption with use of selective inorganic sorbents, which were used in Murmansk at the Enterprise RTP “Atomflot” from 1988 to 1998.
2. Sorption-membrane methods with use of electrical membrane and reverse osmosis concentration developed for:
   - The project “Murmansk Initiative” on reconstruction of RTP “Atomflot”, conducted under the program of economic cooperation of three countries: Russia, USA and Norway;
   - LLRW Project on treatment of LRW produced as a result of decommissioning of Russian Navy submarines, financed with the technical assistance to Russia from the U. S. (“Nunn-Luger” program).

The author examines new methods of LRW treatment, which are applied in order to minimize the amount of solid radioactive waste, and significantly simplify the treatment process itself.

Based on comparison of different process charts, the author draws conclusions on prospective development of technological charts for selective treatment of radionuclides, which provides for their concentration in solid phase, and excluding formation of salt solutions, which predominantly contain non-radioactive salts. Such process layouts are the most efficient, reliable, and less energy consuming.

REPORT

The report reviews diverse methods of nuclear fleet LRW decontamination developed in Russia in the period of 1986-2000.

Activities aimed at creating systems for nuclear fleet LRW treatment were started in the USSR soon after the Chernobyl accident in 1986-1987. Researchers and specialists from All-Union Research Institute of Chemical Technology, Kurchatov Institute (under the Ministry of Medium Machine Building) and Physical Chemistry Institute within the USSR Academy of Sciences were at the head of them.
The activities from the R&D stage to construction of a pilot facility were completed in a short space of time. The facility was based on selective sorption of radionuclides using specially synthesized synthetic inorganic sorbents.

The efficiency of the synthesized selective ferrocyanide sorbents of the "SELEX-TsFN" type proved more than 100 times higher than that of traditional zeolite sorbents of the "DURASIL-230" type, which permitted actually complete decontamination from cesium radionuclides of all types of the LRW, their composition being provided in Table I.

The first in the USSR pilot facility for nuclear fleet LRW decontamination, its capacity 1 m\(^3\)/h, was put into service at “Atomflot” Repair and Technological Enterprise (RTE) in 1989. It was successfully operated at RTE for 10 years. In the period mentioned more than 10 thousand m\(^3\) of diverse LRW (primary circuit water and salt decontaminating solutions) were decontaminated in it to levels complying with NRB-76 (Radiation Safety Standards). It permitted, whenever necessary, simultaneous decontamination from radionuclides of special laundry sewage, as well. It featured maximum simplicity and permitted attaining radionuclides concentrating degree in solid phase (radiation resistant inorganic sorbents) of approximately 1000. Solutions actually decontaminated from radionuclides and containing chemical impurities were fed to conventional centralized chemical treatment.

In 1995 it was decided to modernize the facility mentioned. The decision was dictated by a number of reasons. The available sorption facility could not be used for treating high-salt waste produced and built up in the Navy bases for a long time. Simultaneously the facility capacity was to be increased and brought to 5,000 m\(^3\)/year (1.5 m\(^3\)/h).

Analysis of the state of solutions accumulated in the Navy bases suggested that LRW featured unstable chemical composition and major part of the solutions had salt content up to 30 g/l. For assuring the necessary decontamination indices for all types of LRW complying with the ones required by the standards, i.e.: in terms of \(\sum \beta\)-activity<10\(^{-10}\) Ci/l at initial content of 10\(^{-5}\) Ci/l, it was decided to supplement the sorption facility with the following main units:

- fine mechanical filtration,
- precipitation of water hardness salts,
- solution electromembrane treatment and desalination,
- brine cementing.

In the course of the design approaches implementation a few fundamental errors were made, including the system of the work arrangement, which resulted in failure to put the facility mentioned in pilot operation 5 years later. During initial testing activities it was revealed that the feasible degree of radionuclides concentration in the modernized facility would be 10 at most, which is more than 100 times worse compared to the initial indices.

A mobile facility for LRW treatment (“Sharya” facility) was developed in parallel with the work at RTE on the instructions of the Navy Technical Board by “Ecoatom” Research and Production Company.
The facility based on the principle of reverse osmosis desalination was constructed in 1996. Its capacity was 0.3 m$^3$/h. The facility was intended for treating LRW built up in special Navy vessels (special tankers). Their filling up gives rise to a critical situation necessitating measures aimed at reducing the volume of accumulated waste. The fact, that settling of current problems relating to reduction of accumulated LRW volume did not mean solution of the problem as such, was specific feature of the facility operation. Solutions decontaminated to the levels complying with NRB-87/86 were discharged to the water area, while concentrates, containing all radionuclides and toxic chemical impurities, were returned to the same reservoirs in the special tankers. Finally, after a four-year period of the facility operation (mainly in the Far East region) the following occurred:

- the volume of the LRW kept in the special tankers was somewhat reduced,
- the volumetric radioactivity, on the contrary, increased, whereas radionuclide and chemical composition grew more complicated giving rise to additional problems in its treatment.

Currently, the situation necessitating treatment of total amount of LRW accumulated in the Far East region in recent 6 years using more complicated and expensive methods, has taken shape. It is the task to be coped with using facility, which is being constructed according to the “Landysh” project. The design capacity of the facility to be arranged on board a barge shall be 7000 m$^3$/year. Cemented blocks, like in the case of the Murmansk facility under modernization, are assumed as the final product to be disposed. The radionuclide concentration factor in it does not exceed 15.

It is worth noting that fundamental errors were committed while creating the facility, so, 5-year efforts aimed at its development did not permit its putting into pilot operation.

Finally, in the course of cold and hot tests it was revealed that the “Landysh” facility cannot provide the design indices. When operated at design capacity it does not assure decontamination from cesium radionuclides and ammonium ions, whereas operated in the mode of normal treatment it does not permit attaining the design capacity.

Further progress of the activities in the trend, which are undertaken in the framework of international cooperation, involves implementation of the LLRW project on complex treatment of low-level waste formed during nuclear submarines utilization.

The project was implemented in the framework of assistance to the CTR program (“Nunn-Luger” program) by international consortium headed by LMET division of the Lockheed Martin Company. The main efforts aimed at development of apparatus and flowsheet for LRW treatment, development of design approaches and manufacture of nonstandard equipment were made by Russian specialists, Aspect Association being the leader.

Collaboration of Russian, US and French specialists permitted essential improvement of the apparatus and flowsheet for LRW treatment and construction of the first facility for treating low-level solid radioactive waste (SRW) formed during nuclear submarines utilization. All the facilities mentioned were constructed according to unitized module principle permitting separate treatment of different types of LRW.
and SRW. The activities as such, beginning from the designing stage and ending with construction stage, were completed very expeditiously – in the course of two years. In the complex constructed and put into service at SME “Zvezdochka” the following types of solutions are treated separately:

- primary circuit-drainage water – in the amount of 200 m$^3$/year, decontaminating and mixed solutions - 800 m$^3$/year,
- special laundry sewage - 2500 m$^3$/year,
- biological protection tanks water - 700 m$^3$/year).

The module principle employed permitted essential increase in the efficiency of treatment compared to the one envisaged in the “Murmansk Initiative” project or in the “Landysh” project. In the project to be implemented alongside with sorption preliminary treatment using selective inorganic sorbents a number of new technological approaches were employed:

- microfiltration and reverse osmosis treatment for radionuclides and chemical impurities,
- two-stage high concentrating of the brines with preparation of dry salts using a rotor-type concentrator and the “Ohmtemp” dryer,
- disposal of spent sorbents and dry salts in special protective containers, including the HIC-MUC type ones, without preliminary cementation.

The basic approaches permitted attaining a 200-300-fold radionuclide concentration in solid phase and more than a two-fold reduction of the treatment process energy intensity for the project implemented at “Zvezdochka” compared to the two complex projects described above.

Thus, comparative analysis of efficiency of the considered methods suggests that:

1. Purely sorption method of low-level LRW treatment using selective inorganic sorbents proved the most simple, reliable and energy efficient.

2. In the series of complex treatment methods using sorption-membrane separation processes (electromembrane and reverse osmosis concentrating) developed for the North-West and Far East regions of the RF the project implemented at SME “Zvezdochka” proved the best one.

The current projects that involve the treatment of liquid radioactive waste of the nuclear-powered fleet are described in Table II, whereas their main characteristics are provided in Table III.

- At the moment by virtue of new developments by Aspect certain prerequisites for further improvement of low-level LRW treatment flowsheets are created. The membrane-centrifugal apparatus on the basis of the “TRUMEM” cermet membranes developed by Aspect permits selective removal of actually all radionuclides from low-alkaline media without reverse-osmosis separation.

- Now we are engaged in the development of a new apparatus and flowsheet for radionuclide treatment as applied to the project envisaging construction of mobile
facilities for LRW decontamination. The flowsheet will permit attaining radionuclides concentration degree in solid phase comparable with purely sorption one and simplifying essentially the process of the waste treatment as such. Minimization of secondary SRW amount, simplicity of the apparatus flow diagram and energy efficiency are of crucial significance for the mobile systems of LRW treatment.

In our opinion, development of flowsheets for “selective treatment” for radionuclides, envisaging their concentrating in solid phase and ruling out formation of brines, which mainly contain non-radioactive salts, are fundamental trends in treating all types of LWR featuring low and intermediate radioactivity levels. The flowsheets are low-cost, reliable and energy efficient.
Table I. Amount and type of liquid radioactive waste (LRW) formed in utilization of one decommissioned nuclear submarine.

<table>
<thead>
<tr>
<th>Type of radioactive waste</th>
<th>Radioactivity, Ci/l</th>
<th>LRW volume, m³</th>
<th>LRW composition</th>
</tr>
</thead>
</table>
| 1. Salt-free (primary circuit water) | $10^{-5} - 10^{-6}$ | 50 | pH ..................10-11
dry residue, mg/l..............20-70
chemical impurities,
preservatives, mg/l ........100-120
radionuclide composition:
Cs radionuclides, % .........60-80
Sr radionuclides, % ..........5-10
$\sum$ (Co, Mn, Cr etc.), % ..........8-15 |
| 2. Salt-containing (decontaminating solutions) | $10^{-5} - 10^{-6}$ | 100 | pH ..................7-11
dry residue, g/l..............1-6
hardness, mg-equiv./l ........≤5
K, Na, g/l ........................≤1
nitrates, carbonates,
phosphates, g/l.............≤0.1-0.2
chlorides, oxalates, g/l ....≤1
Trilon B (EDTA), g/l ..........≤0.1
ammonia, surfactants mg/l ≤ 0.05
Fe, mg/l ..................≤0.01
radionuclide composition:
$^{137}$Cs, $^{134}$Cs, % ...........70-80
$^{90}$Sr ..............................10-15
$\sum$ ($^{124,125}$Sb, $^{58,60}$Co, $^{141,144}$Ce, $^{103,106}$Ru, $^{152,154}$Eu) ..........1-5 |
| 3. Special laundry sewage | $6 \times 10^{-8} - 8 \times 10^{-9}$ | 600-700 | pH ..................9-10
surfactants, mg/l..............25-50
soda, g/l ..........................0.4-0.6
oxalic acid, g/l ..............0.1-0.15
radionuclide composition:
$^{137}$Cs, $^{134}$Cs, % ............90-95
$^{90}$Sr ..............................5-10
$\sum$ (the rest radionuclides) - 5-20 times below MPC according to the NRB 76/87 standards. |
Table II. Radioactive waste treatment projects being implemented in the Russian nuclear fleet

<table>
<thead>
<tr>
<th>No.</th>
<th>Project name</th>
<th>Scope of work</th>
<th>Major participants (arrangement) of the work</th>
<th>Project period</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Development of sorption facility at RTE Atomflot.</td>
<td>R&amp;D, arrangement of inorganic sorbents production, construction of the facility.</td>
<td>ARRICT, IAE «Kurchatov Institute», PCI under the Academy of Sciences (direct economic contracts)</td>
<td>1987-1989</td>
</tr>
</tbody>
</table>
Table III. Major indices of various flowsheets for treating low-level LRW in nuclear fleet.

<table>
<thead>
<tr>
<th>Design indices</th>
<th>LRW treatment flowsheets</th>
<th>Sorption flowsheet at Atomflot RTE</th>
<th>Landysh</th>
<th>Flowsheet modernized in line with Murmansk Initiative project</th>
<th>Membrane-sorption flowsheet at SME Zvezdochka</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of secondary SRW, (m$^3$/m$^3$ of initial LRW)</td>
<td>0.001</td>
<td>0.07</td>
<td>0.12 (0.36)</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Type of waste to be disposed</td>
<td>Solely sorbents</td>
<td>Sorbents, pulps and brines as cemented matrix</td>
<td>Solely pulps and brines as cemented matrix</td>
<td>Sorbents, pulps and dry salts in double protective containers</td>
<td></td>
</tr>
<tr>
<td>Cost of 1 m$^3$ LRW treatment ($)</td>
<td>100</td>
<td>380</td>
<td>280</td>
<td>180</td>
<td></td>
</tr>
</tbody>
</table>

Note:
Final amount of secondary SRW to be disposed according to the “Murmansk Initiative” project will be three times higher than the actually formed one, due to the use of a special protective container, which does not require additional external protection, i.e. a square ferroconcrete container with the following external dimensions $L \times ? \times H = 1.52 \times 1.52 \times 1.4$ (m), its walls 220 mm thick, envisaged in the project.