[Form 2 (to be reported to Committee on Countermeasures for Contaminated Water Treatment and to be disclosed to public)

Technology Information	
Area	(3) Removal of radioactive materials from the seawater in the harbor
Title	Realization of a method for decontamination of the sea water in the harbor of NPP Fukushima
Submitted by	Theta-Consult Ltd

1. Overview of Technologies (features, specification, functions, owners, etc.)

Considering the urgency of the issue, we have created an “ad hoc” team of three companies – Theta-Consult Ltd, Alpha Industrial Group Consortium and Techceramic-M and including experts from other Bulgarian organizations, coordinated by the Director of “Decommissioning” department in SE “RAW”. The goal of the team was in the time since the invitation of the Japanese government until October 23rd, 2013 to motivate and propose to the Japanese government’s Committee on Countermeasures for Contaminated Water Treatment technical measures for increasing the efficiency of the contaminated water treatment process

Analysis of the requirements

1. **The goal is to decontaminate the sea water from the harbor and in front of the entrance channels of Reactors 1 to 4 in NPP Fukushima, to levels lower than the radioactivity limits set in a public notice (Cs-134 < 60Bq/L, Cs-137<90Bq/L and Sr-90<30 Bq/L).**

The sea water volume in the entire harbor is approximately $2,3.10^6$ m^3 ($2,3.10^9$ l). The sea water in front of the incoming cooling channels of Reactors 1 to 4 is around $1,6.10^5$ m^3 ($1,6.10^8$ l).

One gram of:

- Cs-137 has an activity of 3,215 terabequerels - $3,215.10^{12}$ Bq;
- Cs-134 has an activity of 44,4 terabequerels - $4,44.10^{13}$ Bq;
- Sr-90 has an activity of 5,55 terabequerels - $5,55.10^{12}$ Bq.

Accordingly 1 liter of sea water with activity of Cs-134= 60Bq/L, Cs-137=90Bq/L and Sr-90=30 Bq/L contains:

- (60 Bq/l):($4,44.10^{13}$ Bq/g) = $1,35.10^{-12}$ g/l Cs-134;
- (90 Bq/l):($3,125.10^{12}$ Bq/g = $2,88.10^{-11}$ g/l Cs-137;
- (30 Bq/l):($5,55.10^{12}$ Bq/g) = $5,40.10^{-12}$ g/l Sr-90.

2. **The decrease of removal efficiency due to absorption of materials other than the targeted materials, such as Mg, should be limited.**

Composition of Ocean Water (%): O-85,7; H-10,8; Na-1,05; Cl-1,9; Mg-0,135; S-0,0885; K-0,038; Ca-0,04; C-0,0026;

Main competing ions during the absorption of Cs radionuclides are K^+ and Na^+, and during the absorption of radioactive Sr-90 – Mg^{2+} and Ca^{2+}. The concentration of these ions in the intended for decontamination water are approximately (g/l):

- K^+ - 0,38;
- Na^+ - 10,5;
- Mg^{2+} - 1,35;
- Ca^{2+} - 0,4.

3. The amount of waste produced by Cs and Sr absorption should be limited.

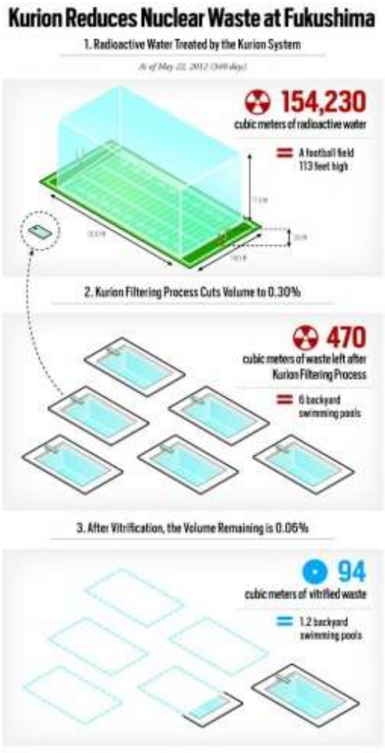
Quantities of radioactive waste, which will result in the decontamination processes depend mainly on:

- Concentration of competing (interfering) ions in decontaminated water;
- Selectivity of absorbent material to relative radionuclides.

In the current case the concentration of absorption interfering ions (K^+ and Na^+ for Cs radionuclides and Mg^{2+} and Ca^{2+} for Sr-90) is more than trillion (10^{12}) times higher than of the relative radionuclides.

Extremely high selectivity of the absorbent is necessary in order to produce relatively small volumes of radioactive waste for burial.

Since the restriction concerning the waste from sea water decontamination is only qualitative and there is no quantitative criterion (for example the quantity of used sorbent for cubic meter of decontaminated water), we will accept as a criteria the concentration level of Cs radionuclides from high active waters. It is about 330 times for a single pass of the water volume through the sorbent material.
The figure below shows the obtained results when using one of the most CS selective materials.



The concentration coefficient of the Cs radionuclides during the one step absorption process:
154 230 : 470 = 328
Overall concentration coefficient of the Cs radionuclides after vitrification (second step concentration) : 154 230 : 94 = 1 641
Specific activity of the end product (activity of Cs-137 in the vitrified product):
$4{,}4.10^{17}: 9{,}4.10^{4} = 4{,}7.10^{12}$ Bq/l

Assuming as a determining concentration coefficient the one reached in decontamination of high active waters – 330, during a single pass of the entire sea water volume from the harbor, we will receive:

- $2,3.10^{12}:330 = 6\ 970\ m^3$ secondary waste.

Concerning the fact that there is no way to perform a single pass of the entire sea water volume from the harbor through the decontamination system, while following the “simple structure” condition, with the current existing practice we would accumulate huge amounts of secondary waste. This is even more obvious when we consider the fact that for Sr-90 there are no sorbents with selectivity close to the one for Cs-134/137.

On the other hand the activity of the contaminating radionuclides in the entire radionuclide volume is commensurate to the activity in several liters of vitrified waste.

4. The removal systems should be of a simple structure.

The structure of the decontamination system is determined by the processes that take place in it, their efficiency and the appropriateness and efficiency of the constructions and facilities and their setting.

The analysis shows that there are no suitable routine ways for decontamination of large volume water solutions in the presence of relatively high concentrations of interfering ions and relative low activity of the targeted radionuclides.

That requires the development, testing and implementation of a new solution, consistent with the current conditions that have occurred after the NPP Fukushima accident in 2011.

Considering the conditions to be met by the water decontamination technology in NPP Fukushima, and based on their analysis and our experience, we have developed a decontamination method, which can assure the practical base for the realization of an effective technology.

Proposal

We possess our own developments and patents for regenerable sorbents for Cs radionuclides, chemical high-temperature plasma processes and highly resistant ceramics. On this basis a method for sea water decontamination has been developed.

The method consists of three main technological processes:

1. Decontamination of sea water to free release levels, using regenerable sorbents and initial Cs-137 and Sr-90 radionuclide concentration;
2. Secondary multi-level concentration of radionuclides to reasonably applicable levels;
3. Burning of saturated sorbents, vitrification and inclusion in a ceramic package of the resulting melt.

PROCESS 1:
Decontamination of the harbor waters in NPP Fukushima to free release levels

Decontamination of Cs-134, Cs-137 and Sr-90 contaminated seawater to levels lower than radioactivity limits set in a public notice is done by the following process:

$$[aSM_n]_{solid} + [iR + b(H_2O)]_{liquid} \rightarrow [aSM_{(n-i)}R_i\,]_{solid} + [iM + b(H_2O)]_{liquid} \qquad (1)$$

where:
$[aSM_n]_{solid}$ – regenerating sorbent;
$[iR + a(H_2O)]_{liquid}$ – water contaminated with the i-th radionuclide or group of radionuclides;
$[iM + a(H_2O)]_{liquid}$ – decontaminated water from the i-th radionuclide or group of radionuclides;

$[aSM_{(n-i)}R_i\,]_{solid}$ – radioactive regenerating sorbent;
S – solid carrier of the ion exchange layer of the regenerating sorbent;
M – exchanging ion for the ion exchange layer;
R – radionuclide or group of radionuclides number;
a – quantity of the solid carrier of the ion exchange layer of the regenerating sorbent;
b – quantity of contaminated, respectfully decontaminated water.

Along with the decontamination of the water from radionuclides their initial concentration takes place as well. Depending on the selectivity of the regenerating sorbent the concentration level can reach 1 000 and more.

Decontamination is performed as sea water is passing through three consecutive filters, each and every one of them filled with 2,5 m^3 regenerating sorbent $[aSM_n]_{solid}$. Filtration speed is $25m^3l/h$ for the Cs radionuclide absorbents. Using this process we can decontaminate around 600 m^3 of sea water for 24 hours. Decontamination coefficient is expected to be above 10 000 for the first 1 000 column volumes and to decrease gradually. Reaching activity levels higher than norms is expected after processing 7 500 m^3 of sea water. At that time the first filter is taken for regeneration and a new filter is placed on the last place of the three consecutive filters.

The activity concentrated on the sorbent in filter 1, for example for Cs-137 with initial specific activity of 1000 Bq/l, after passing of 7 500 m^3 contaminated water, is expected to be about $7{,}5.10^9$ Bq.

The specific activity of the sorbent material for Cs-137 reaches $3{,}0.10^6$ Bq/l. (First step concentration).

PROCESS 2:
Secondary multi-level concentration of radionuclides (second step concentration)

After the initial concentration of the radionuclides in the water decontamination process two more steps for additional concentration are performed. That way we can reach specific activity levels of the radionuclides close to the one of the high active waste produced in NPP Fukushima.

Multi-level concentration of radionuclides is done by the following sub-processes:

SUB-PROCESS: Elution of the exchanging ion and destruction of the ion exchange layer

Using special eluent the ion exchange layer is destroyed and at the same time the radionuclides transfers from the solid to the liquid phase. The main part of the exchanging ion also transfers to liquid phase.

$$[aSM_{(n-i)}R_i\,]_{solid} + E \rightarrow [aS]_{solid} + [E + iR + M_{(n-i)}]_{liqid} \qquad (2)$$

where:
E – eluent;
$[aS\,]_{solid}$ – solid carrier of the regenerating layer sorbent;
$[E + iR + M_{(n-i)}]_{liquid}$ – eluate with dissolved radionuclude/es and exchanging ion.

SUB-PROCESS: Separation of the eluent from the liquid phase

The eluent is separated from the dissolved ions and radionuclides using evaporation.

$$[E + iR + M_{(n-i)}]_{licuid} \rightarrow [\,E\,]_{gas} + [\,(n-i)M + iR]_{solid} \qquad (3)$$

After condensation of the eluent it is returned to the cycle for regeneration of sorbents.

SUB-PROCESS: Dissolution and removal of the i-th radionuclide from the solid phase

$[(n\text{-}i)M + iR]_{solid}$

The melt left after the evaporation of the eluent is dissolved in water.

$$[(n\text{-}i)M + iR]_{solid} + cH_2O \rightarrow [(n\text{-}i)M]_{solid} + [iR + H_2O]_{liquid} \qquad (4)$$

where:
$[iR + cH_2O]_{liquid}$ – liquid phase with dissolved radionuclide/es;
c – quantity of water in the liquid phase with radionuclide/es.
$c \ll b$

SUB-PROCESS: Secondary concentration of the radionuclide/group of radionuclides

The secondary concentration of the radionuclides is done as the water solution containing the radionuclides from the first level of concentration, because of its lower volume, is passed through 20 liters of new or regenerable sorbent.

$$[dSM_n]_{solid} + [iR + c(H_2O)]_{liquid} \rightarrow [dSM_{(n-i)}R_i]_{solid} + [iM + c(H_2O)]_{liqiud}$$

where:
$[dSM_n]_{solid}$ - new or regenerated sorbent;
d – quantity of sorbent;
$d \ll a$
$c \ll b$

Reaching the abovementioned concentration coefficient we could expect several tens of cubic meters waste from the sea water decontamination.

The specific activity of the sorbent material for Cs-137 reaches $3{,}75.10^8$ Bq/l. (First step concentration).

SUB-PROCESS: Recovery of the regenerable sorbent

Recovery of the sorbent is accomplished by recovering the sorption layer of the organic base. For that purpose a specially developed procedure is performed to assess the purity of the base, some physical and mechanical characteristics and etc.

We possess patented sorbent material and method for implementing it for multiple concentration of Cs radionuclides.

The method and material are tested in real conditions with evaporation concentrates from WWER-440 reactors. Concentration level of 100 000 was reached, without this being the limit. The limitation was imposed by radiation safety measures. Using the appropriate protection and shielding this level could be significantly higher.

Using a similar pattern to that of Cs radionuclide sorbents we have started the development of regenerable sorbents for Sr-90.

PROCESS 3:
Combustion of the organic base of the regenerable sorbents, melting and inclusion in ceramic packing of the radionuclides extracted from the sea water (third step concentration)

After wear the organic basis of the regenerable sorbents is burnt in the flame of oxy-hydrogen plasma. Appendix* 1 shows possible basis and their burning in laboratory conditions.

We are manufacturing industrial generators with production rate of 5 000 l/h oxy-hydrogen. Generators are owned by a company, which is a member of our team.

After reaching the desired concentration level with regenerable sorbents the radioactivity is absorbed by modified aluminosilicate absorbents. Together with the mineral oxides left from the combustion of the basis of the regenerable absorbents they are mixed with appropriate flux and are in-situ vitrified in highly resistant ceramic containers.

During the third step the concentrated radionuclides from 10 second step processes are absorbed on 1 liter of aluminosilicate sorbent, which is vitrified together with the oxides from the combustion of the organic bases of the regenerating sorbents.

The specific activity of the sorbent material for Cs-137 reaches 2-4.10^{9} Bq/l. (Third step concentration).

The ceramic containers are industrial production of one of our team members. They are tested under different conditions and have shown very high resistance to corrosion, air-tightness and high temperatures.

Appendix* 2 and 3 demonstrate part of the thermal shock resistance tests of the ceramic containers.

In combination with the combustion and vitrification with the help of oxy-hydrogen plasma, and the specific characteristics of the ceramics of which the containers are made, an “in situ” inclusion of the radioactive concentrate produced by the sea water decontamination processes from Cs and Sr radionuclides and their multiple concentration can be implemented. The specific activity of the end product is close to those produced when processing high active waters from NPP Fukushima.

Using that technique the overall concentration coefficient reaches as high as 1 000 000. Reaching the abovementioned concentration coefficient we could expect several tens of cubic meters additional waste from the sea water decontamination.

That way we can satisfy the condition for minimal quantities of radioactive waste from the sea water decontamination at NPP Fukushima.

We believe that the process proposed by our team satisfies the conditions set by you and can become one good basis for solving the issue with sea water decontamination at the harbor of NPP Fukushima. We are convinced that approach that we propose can help solving similar cases with other contaminated waters.

*Appendices can be found on the following link:
https://www.dropbox.com/sh/151hlxxjnwe606w/J7hbLakjch

2. Notes (Please provide following information if possible.)

- Technology readiness level (including cases of application, not limited to nuclear industry, time line for application)

The proposed method is based on working modules, periphery and absorbents developed by our companies with the possibility to set a technology conveyor. If interest is demonstrated from your side, we are ready to manufacture an industrial prototype in 12 months time. The prototype will demonstrate the effectiveness of the method. Along with the review of the technological process all necessary technical information and relevant additional documents will be prepared.

- Challenges

Assistance from your experts is welcome and appreciated as they can consult and participate in the design and manufacturing of the facilities. This will allow easier migration to industrial system, according to your requirements and to the status development in NPP Fukushima

- Others (referential information on patent if any)

【Areas of Technologies Requested】

(1) Accumulation of contaminated water (Storage Tanks, etc.)
(2) Treatment of contaminated water (Tritium, etc.)
(3) Removal of radioactive materials from the seawater in the harbor
(4) Management of contaminated water inside the buildings
(5) Management measures to block groundwater from flowing into the site
(6) Understanding the groundwater flow