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

Technology Information	
Area	1 + 2 (Select the number from "Areas of Technologies Requested")
Title	**Process for Fukushima cooling water Solidification in Gypsum**
Submitted by	Dr. Jozef Hanulik / Deco-Hanulik AG, Switzerland

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

Untreated contaminated cooling water (inclusive salts, strontium, cesium, tritium etc.) is mixed with gypsum by remote control according to the chemical reaction:

$$CaSO_4 + 2H_2O \rightarrow CaSO_4.2H_2O$$

This liquid gypsum and water mixture is pumped into already existing, in some cases leaking tanks, box-shaped maritime containers, oversized tanks or specially prepared ultra-large dumping grounds, situated above the groundwater level and protected against rainfalls.

The mixture solidifies after 1-2 hours. The gypsum to water ratio (by weight) can be for example 1:1. The weight of the processed water is hereby doubled, but the volume increases only by 50 percent.

That means:
1,000kg gypsum + 1,000kg (Liter) = 1,500Liter solidified and hardened gypsum block.

The processing is carried out with existing high-performance mixing machinery of the same kind that are commonly used on construction sites with routinely througputs of 100-300m^3/hour.

The freshly mixed gypsum-water continues to be liquid and can be pumped for 20-40minutes. With high-troughput pumps used in the construction industry the gypsum-water mixture is pumped into reservoirs/tanks for storage for the next 150-300years. This is equivalent to 5-10 radioactive half-lives of Sr-90 or Cs-137 respectively.

The process digests all activities including Tritium and makes the safe , longtime storage of the produced secondary waste possible. The process is technically approved and consists of 2 treatment lines:

a. with capacity 30 m3 per hour for daily produced liquid quantities
b. with capacity 100- 300 m3 per hour for treatment 300'000 T already stored quantities. These quantities could be treated in 4 - 12 months, depending on equipment investment.

The process is patent pending in Switzerland (see Appendix 1).The necessary equipment for the process are standard parts, available in short time. The process costs are much smaller than the standard technologies, as osmosis, destillation etc.
When designing the process an important factor was the protection of the people from radiation, therefore all relevant steps are remote control and still economical.

Advantages of the proposed method:

- For mixing and pumping high-throughput machinery and equipment is utilized that are proven and are commonly used on conventional construction sites.
- Routinely troughputs of 100-300m^3/hour are achieved.
- No new construction of machinery is required. The machinery used on construction sites are cost-efficient and can be quickly commissioned.
- It is also possible to operate several independent processing lines. This increases the operating flexibility. Should one processing line be down for whatever reason, then there are still other processing lines able to work. There is no such thing as everything is working or nothing is working. A very high operational availability does exist.
- Due to the solidification of the contaminated cooling water in the gypsum mixture any kind of receptacles can be used for the storage. Almost any kind of forms and sizes of receptacles, boxes, containers are suitable.

- Utilizable as receptacles for the solidification process are also the already existing tanks used for the storage of the contaminated cooling water.

- Due to the storage of the solidified contaminated cooling water as a gypsum ingot mold, no leakage can occur. No maintenance and repair work in a highly radioactive radiation field are necessary.

- Compared with the storage of a liquid, the solidified contaminated cooling water is insensitive to the dangers of earthquakes.

- Gypsum ($CaSO_4$) has a solubility in water of only 2gram/Liter. In case of a water penetration only a small amount of activity is taken away. Should a water inleakage occur a subsequent eluate emerging could easily be detected by measuring the concentrations of the [Ca^{2+}] and [SO_4^{2-}] ions in the solution.

- The treatment of the original liquid cooling water with the solidification does not need deionization of the water. Compared with osmosis the treatment of the cooling water with gypsum produces no secondary wastes. Additionally, by the omission of the expensive osmosis treatment a lot of maintenance work in an intensive radiation environment will not be necessary.

The problem with tritium

As a result of the solidification of the untreated contaminated cooling water the tritium problem is also solved in the same process step. The gypsum matrix is stored for at least 5 radioactive half-lives (approx. 60years).

Due to the presence of cesium-137 and strontium-90 it is recommended to prolong the storage of the gypsum matrix for 250-300years. This seems a long period of time, but the storage can occur integrated in the landscape. After 250-300years have elapsed, hereafter the gypsum ingot molds of the different forms are identical with naturally occurring gypsum deposits.

Remarks:

To cope with all the necessary work as the consequence of the nuclear disaster in Chernobyl in 1986, the assignment of an enormous number of humans was used.
Over 500,000 soldiers were assigned for this mission. All the required procedures could only be accomplished with a self-sacrificing sense of duty.
Only because of this enormous effort of human power Europe was spared from a widespread contamination.
Dr. Jozef Hanulik was personally attendant in Chernobyl for a total of many months distributed over 3 years.

A minimalization of the radiation dose for the individual human and for the entire workforce was only of secondary relevance by reasons of lack of time and not optimally organised work scheduling.

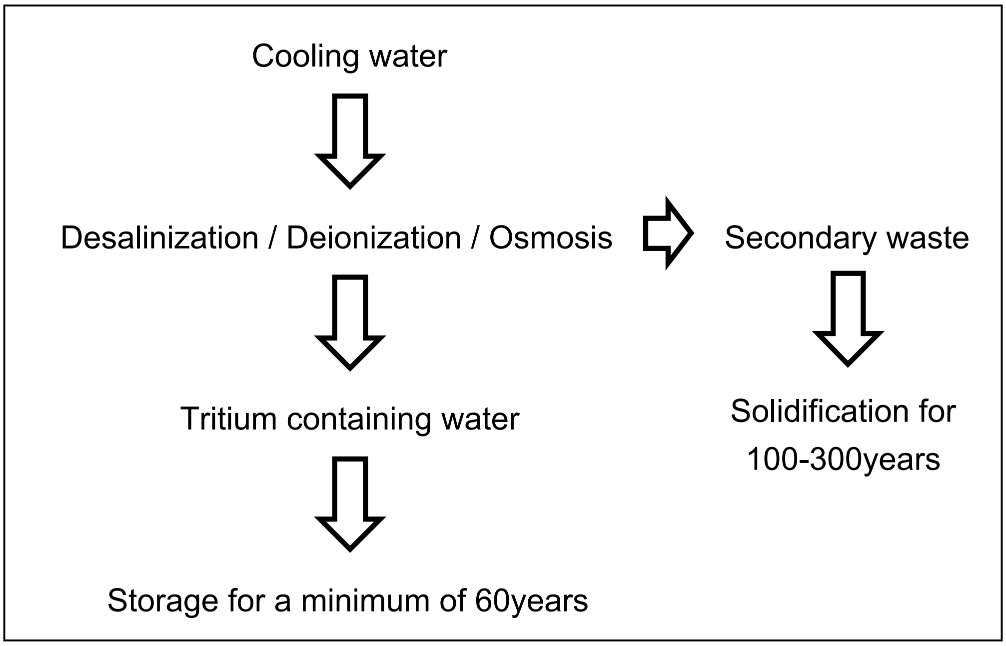
The experiences gained from Chernobyl can teach two things:

- In Fukushima the number of persons available for all the necessary work that has to be done is far less than in Chernobyl.
- For this reason the necessary processing steps must be analyzed critically and more time for the work planning must be provided.

In case a goal can be reached in two different ways, the process should be choosen with the least radiation dose for the entire workforce.

Example 1:

<u>A process that involves a high radioactive dose for the entire workforce</u>



This process includes many personnel-intensive steps. This process is also susceptible for repair work (in particular the osmosis process step) and needs a long term monitoring with the corresponding exposure.

The outcome of this process is a high collective radioactive dose for the entire workforce.

Example 2:

<u>Comprehensive solidification of the contaminated cooling water</u>

(This process is proposed)

The contaminated cooling water including the salts, cesium-137, strontium-90 and tritium is mixed with gypsum.
The whole process composed of the mixing, pumping, filling of the receptables/tanks is remotely-controlled.

Existing high-performance mixing and pumping machinery from the construction industry with capacities of 100-300m^3/hour are used.

Processing Procedure

Contaminated cooling water

⇩

Remotely-controlled mixing with gypsum is performed in one or several processing lines with an individual capacity of 100-300 m^3/hour

⇩

Remotely-controlled pumping of the liquid gypsum into casting molds / tanks / maritime containers or very large dimensioned constructed tanks. Storage occurs above groundwater level and with protection from rainfalls. These solidified gypsum blocks are stacked in a kind of artificial hills for 300years.

Abstract:

Radioactively contaminated cooling water without any pretreatment (like osmosis) is solidified with gypsum. The gypsum is stored in maritime containers of a volume of ca. 90m^3 each. The maritime containers can be stacked closely and can take the shape of hills.

Already existing cooling water tanks, or newly constructed ultra-large tanks/basins with volumes of 1,000-10,000m^3 can also be used for solidification. These deposits are built similar to state-of-the art waste deposits.

Additional information:

Extract and summary from patent application: Process for the large-scale treatment and safely storage of heavily loaded radioactive water

The storage of the solidified radioactive water is secured against earthquakes, leakage and possible terrorist attacks. The proposed storage tanks are secured against a possible airplane crash and also against small remotely piloted aerial vehicle attacks.

Large-scale process for the treatment of radioactively loaded water at which the radioactive cooling water is solidified within gypsum according to the chemical reaction

$$CaSO_4 + 2H_2O \rightarrow CaSO_4.2H_2O$$

Figure 1: Transfer of radioactive cooling water into gypsum tanks
Figure 2: The storage in a tank or other receptacles
Figure 3: The storage in a basin of a volume of 10,000 to 100,000m^3
Figure 4: The storage in a maritime container

One part of the water is bound as hydration water and the other part is bound into the porous mineral structure of the gypsum. Similar to a dry sponge. the mass balance is as follows :

1 part by weight gypsum and 1 part by weight water = 2 parts by weight of moist $CaSO_4.2H_2O$. Which is not different than moist gypsum. This represents a doubling of the mass or an increase of the volume by the factor 1.5 based on the quantity of water.

Sodiumchlorid (NaCl), Strontium (Sr), Cesium (Cs), Cobalt (Co) and tritium are thereby adsorbed, bound and immobilized in the mineral matrix. The newly formed, emerging solid block can be stored for long periods of time. The blocks can easily be manipulated and can easily be transported.

The procedure is visualized in Figure 1. No leakage can occur by dripping because there is no hydrostatic pressure inside the tanks. The tank is soley filled with the solidified gypsum. The tank is leakproof and closed. The drying-out is completely prevented. At the drying the tritium leaves.

1 part by weight gypsum + 1 part by weight water → 2 parts by weight

0.5 part by volume gypsum + 1 part by volume water → 1.5 parts by volume

The storage can take place for example in maritime containers.They can be stacked up to six layers and can be placed side by side in a dense array. See Figure 4 for an illustration. The maritime containers can be placed closely spaced to each other because they are leakproof due to the solidified gypsum. Therefore there is no space necessary for maintenance repairs. A remotely controlled crane can be used to handle the maritime containers. At seaports there exists a great operating experience with managing big maritime container depots.

The mixing of the gypsum with the radioactive cooling water is carried out with already existing equipment used in the construction industry. These machinery can handle great capacities of up to 200-300t/hour.
Standard large-scale industrial cement mixers are available for wholesale prices. There is no need for expensive specially designed equipment necessary. The use of proven technologies in the construction industry enables the processing of the daily accumulating radioactive cooling water of 300t. It is also possible to process the already existing 300,000t that have been accumulated during the past 2 years.

The liquid mixture of gypsum and radioactive cooling water is pumped into boxes or casting boxes. Suitable as receptacles or casting boxes are also the before mentioned maritime containers with a volume of approx. 90m^3 each.
After solidification and hardening of the liquid gypsum after 1h to 24h the ingots are transfered into standard maritime containers of lengths of 6 to 12m. Maritime containers can be stacked up on top of each other in up to six layers. In that way the stacking needs only a small base area for a comparatively big volume of solidified/immobilisied water. For the weather protection it is possible to cover the maritime containers with linings or to place them in a storehouse respectively. the storage for long periods of time is possible.

A possibility to implement the process is by pumping the radioactive cooling water into tanks as pictured in Figure 2.
Afterwards a layer of oil is put onto the water surface that serves as a barrier against the evaporation or vaporization of the water. subsequently, gypsum is slowly and uniformly added at the base of the tank. In this way the gypsum at the bottom of the tank solidifies gradually and grows upwards until the tank is filled with a hardened body of gypsum. The radioactive water is bound inside the body of gypsum.

In another variant, the maritime container coated with a water-tight lining can be filled directly with the liquid gypsum. This variant is shown in Figure 4.
After the hardening of the gypsum the lining prevents as desired the drying-up. It is possible to operate with a massive excess of water. The water that is left after 1 to 10hours and has not yet reacted with the gypsum is later withdrawn by suction and can be used subsequently in the next pass.
During the hardening of the gypsum the radioactive nuclides are bound/embedded and immobilized/fixated so that after the hardening is completed a whole block serves as a safety container for the radioactive nuclides. Gypsum is virtually insoluble in water and remains stable also after a water inleakage. The solubility of gypsum in wateer is approx. 2gram per liter. Tritium is also immobilized in the gypsum matrix.

The solidified gypsum containeers, boxes or slabs can be stored without difficulties in huge numbers in a rain-proof warehouse. For maritime containers a stacking of up to six containers is possible. The repairing of a leakage will not be necessary because a now solidified body (of a formerly liquid) is stored. If needed a monitoring and inspection of an individual maritime container is possible at any time due to a remotely controlled container crane. The container crane is based on rails or as a self-moving crane on tires.
In such a way the personnel is exposed only to a minimum radiation dose. The solidification of gypsum with contaminated cooling water is carried out with established and proven machinery and equipment used on large construction sites.
This machinery and equipment allows to execute the necessary process steps in an expeditiosly and cost-effective way.
The processing of 200 - 300t/hour gypsum is feasible. If demand requires it is always possible to build and operate a second operating line or even a third one. In this way the whole project and operating capacity can be accelerated significantly.
It is also possible to build a separate processing line for the daily incoming cooling water and a separate processing line for the already accumulated contaminted cooling water in the existing cooling water tanks.

The cost for the project is comparable with macinery and equipment on standard construction sites, i.d. construction sites without a radioactive contamination. The process is very robust and one can resort to comprehensive experiences with continously operated concrete mixers and concrete pumps.
The stored solidified and such immobilized radioactivity bound in gypsum is strongly

resistent against the danger of earthquakes and possible terrorist attacks, and is also resistent to unintended handling errors during operation. There is great inherent safty in the process flow. The period of storage can be years to decades.

After the expiration of 1-10 radioactive half-lives, i.e. 30-300years the gypsum will correspond to naturally occuring gypsum in respect of cesium-137.
Despite the huge volume of processed radioactive cooling water the solidified water can be stored in a very dense manner. It is also viable to integrate the solidified gypsum in the nearby hilly landscape.

The following practical examples are shown for some mixtures.

Example 1:

a) 1 kg Gypsum + 1kg radioactive contaminated cooling water is mixed with 0% NaCl
b) After 7 hours a 2kg ingot solidifies, it feels moist, but is kockproof

Example 2:

a) 0.200kg gypsum + 1kg cooling water
b) After 4 hours the ingot is knockproof, 0.820kg water has not reacted
c) After 3 days the ingot weighs 0.380kg

Example 3:

a) 1kg gypsum + 1Liter 35%-NaCl solution, density 1.1g/cm^3
b) After 1 hour it solidifies, after 3 hours noticable hard, the unreacted volume of water is 0.150Liter
c) After a 3 days drying period the mixture weighs 1.830kg, but the gypsum is not very hard

Cooling water containing a lot of tritium

Radioactive cooling water is solidified with gypsum at the ratio of 1 : 0.5 (by weight) (gypsum to cooling water) until the ratio reaches 1 : 1 but it is prevented that the newly developed gypsum is able to dry. The exchange of tritium is prevented due to linings inside the receptacles or outside the receptacles. Also possible is a combination of a lining inside and outside the receptacles. Or the solidified gypsum is stored in sealed receptacles or silos. Possible is also a storage in especially sealed big dumps/cavities. These dumps/cavities are lined with a waterproof layer (i.e. asphalt) and sealed on the top afloat with an oil layer.

As a variant, the gypsum mixed with the radioactive cooling water can be filled into pool-like, water-tight built trenches or basins in the soil that act as forms where the blocks can solidify and harden. This is shown in Figure 3.

After filling of the holes, trenches or basins the hardened blocks are covered with an oil layer, and then covered with a lining that prevents the evaporation oft he water. Then the lining is covered with a layer of asphalt which is followed with a layer of soil. This soil layer can be planted with plants or with trees.

Such a basin is built and structured like a state-of-the art waste deposit. In such a way it is possible to safely store huge volumes. It is feasible to fill by pumping basins with volumes of up to 10.000 – 100,000m^3.

Figure 1

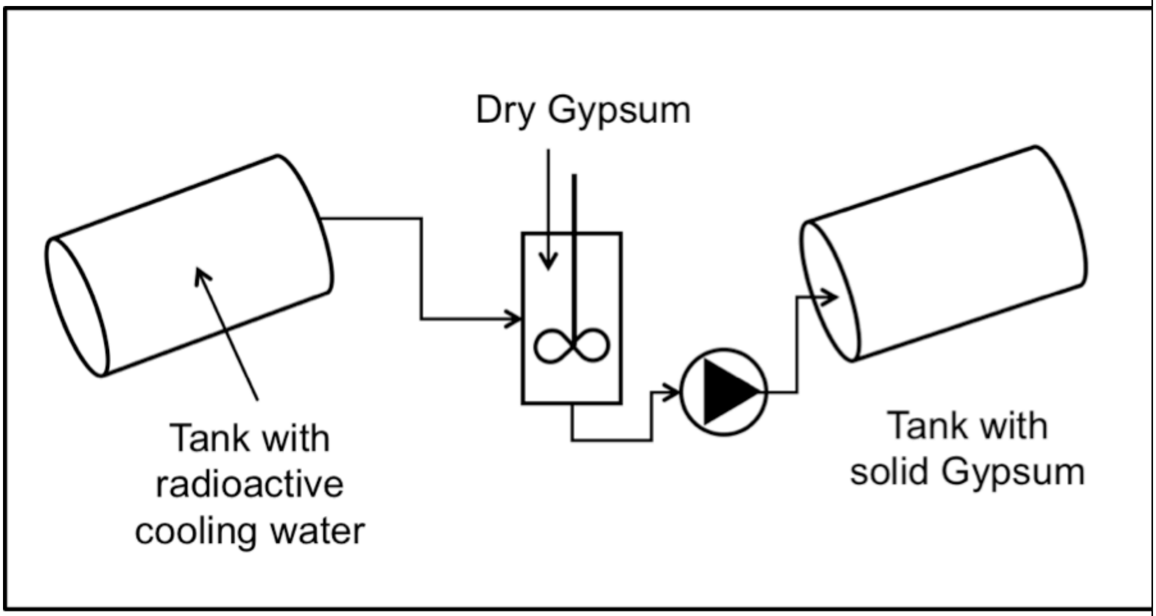


Figure 2

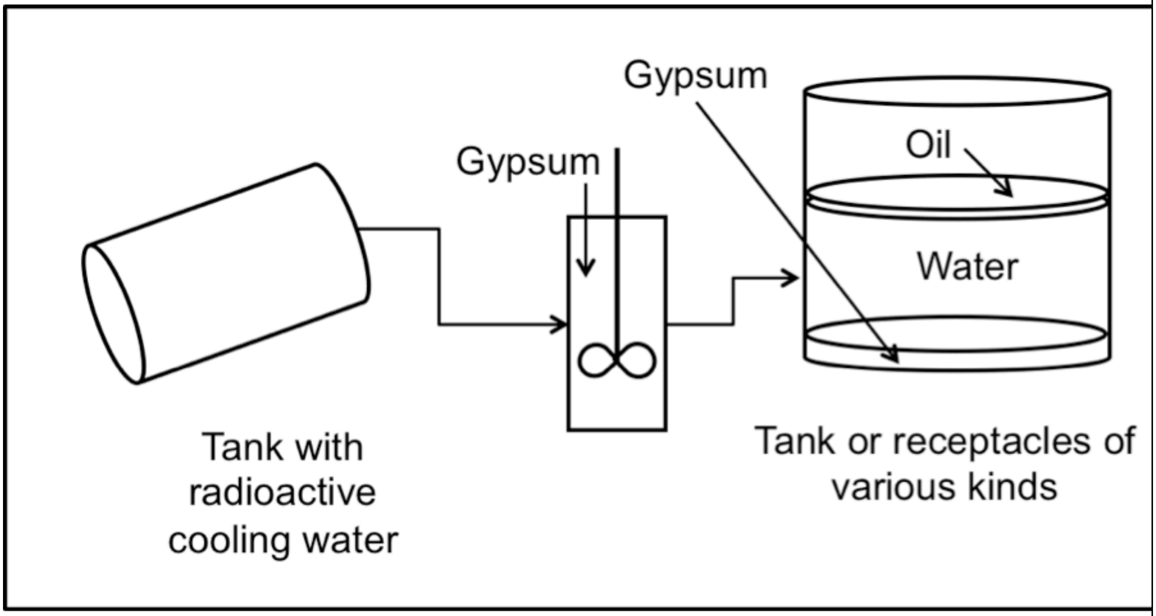

Gypsum
Gypsum
Oil
Water
Tank with
radioactive
cooling water
Tank or receptacles of
various kinds

Figure 3

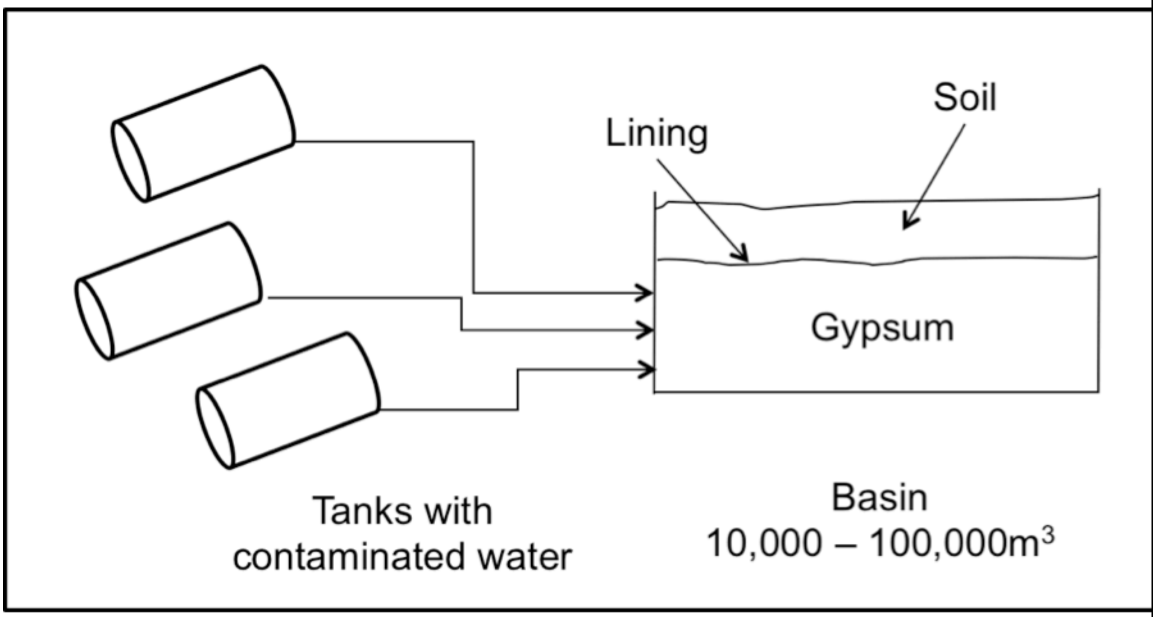
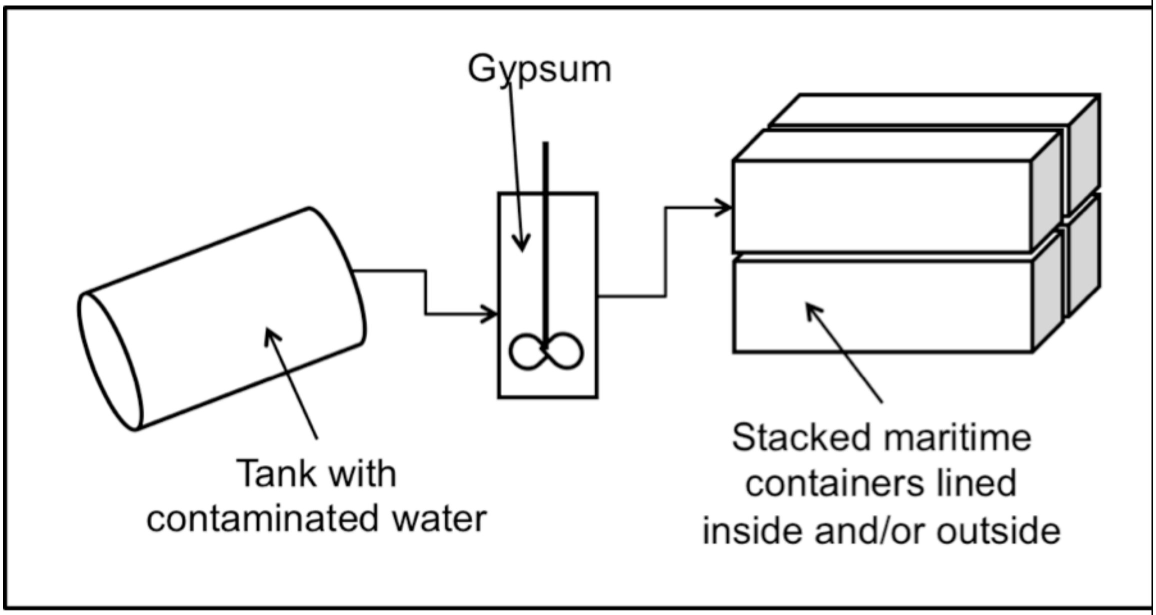

Soil
Lining
Gypsum
Tanks with
contaminated water
Basin
10,000 – 100,000m3

Figure 4



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

- Technology readiness level (including cases of application, not limited to nuclear industry, time line for application): see above.
- Because of the simplicity and low risk of the process and the not expensive equimpent the problem with the contaminated cooling water can be solved within a few weeks/ months and makes possible to store the contaminated and solidificated water safe and "forever".

- Others (referential information on patent if any)

Others: information about Dr. Jozef Hanulik and patent situation

Dr. Jozef Hanulik (see the attachments) has personally spent several months in Chernobyl where he has overseen the construction and operation of a radioactive decontamination process plant. This decontamination plant is based on Fluoroboric Acid (HBF_4) and has a processing capacity of 5tons/hour for stainless steel. Dr. Jozef Hanulik is the inventor of the HBF_4-Decontamination process, the Decoha-process.

Appendix:

- presentation of Dr. Jozef Hanulik (CV, work experience)
- letter from Swiss Federal Institute of intellectual Property, confirming Patent application of October 1, 2013