

Absorbers for Removal of Sr-90 from Sea Water at FUKUSHIMA Site - 14184

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ABSTRACT

The FUKUSHIMA reactors have been cooled with huge amounts of sea water, resulting in more than 100 000 m³ of contaminated water, which, after some purification steps, may contain the ions of sea water in even higher concentration than the normal approx. 3.5 %. After the removal of radioactive Cesium, Sr-90 remains, with concentrations of up to 100 MBq/L, one of the leading radiological relevant nuclides. The challenge with regard to Strontium in sea water is – besides the high salinity- twofold: Inactive Strontium is contained in sea water with relatively high concentrations of approx. 8 mg/L (very different from e.g. Cesium with 0.0003 mg/L), resulting in the requirement for high capacity. Chemically similar ions like Magnesium and Calcium are found with together 1,700 mg/L, accordingly high selectivity for Strontium is a second requirement. The Russian Academy of Science, in its Institute of Chemistry of the Far East Branch, has gained significant experience with the treatment of Sr-90 contaminated sea water. They developed inorganic absorbers, which do not, like other absorbers, apply ion exchange mechanisms, but make use of highly selective sulfate precipitation inside nano crystalline structures. Tests with sea water simulates, spiked with Sr-90 have been conducted successfully, Kd values of about 20.000 could be verified. Investigations with real water and planning for a pilot plant are ongoing.

INTRODUCTION

On March 11, 2011 a seaquake happened on the east side of Japan. The epicenter was 130 km east from the city Sendai on Japan's main city Honshu. The Tohoku-Chihou-Taiheiyou-Oki seaquake was the strongest ever measured in Japan and the 5th strongest worldwide causing a tremor at the magnitude of 9.0 and several tsunamis. Some of the tsunamis were more than 10 meters high, the maximum level reported was almost 40m.

In consequence of the seaquake all power plants on the northeast coast of Honshu disconnected themselves from the grid and turned into the emergency power supply mode, meaning that the emergency diesel generators were switched on in order to remove the residual heat. Among these power plants were also the ones at the Fukushima-Daiichi and Fukushima-Daiini sites.

Until then all events relating the nuclear power plants were in agreement with their design. However the nuclear power plants at the Fukushima sites were hit by a tsunami of 14m height. Due to the fact that the nuclear power plants at both Fukushima sites are only 10m above sea level and the emergency generators are not secured or sheltered against such flooding the generators were flushed with water and failed. In fact the generators were housed in the basement of the turbine buildings and the doors of the buildings were simple roller shutter doors that collapsed under the pressure of the water pushing against them (Fig. 1).

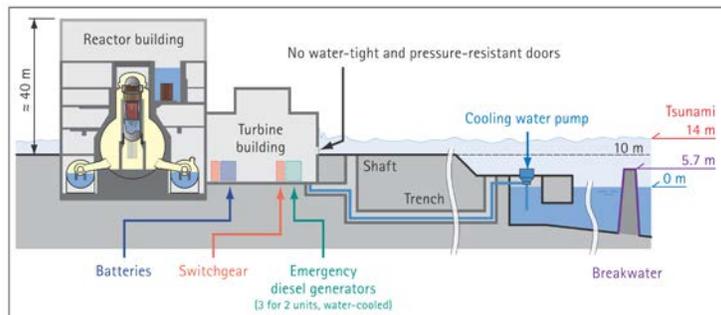


Fig. 1. Cross section of Fukushima-Daiichi, blocs 1-4
Source: atw [1]

Due to this loss of power accident and the ongoing production of heat caused by radioactive decay of fission products it was necessary to cool the reactors externally.

Therefore fresh and later seawater were fed in using fire-fighting pumps. However, this measure was started too late and the cladding tube material of the fuel rods overheated, hydrogen was produced and caused explosions, also the uranium fuel melted. [1, 2]

WATER TREATMENT SYSTEM

As a result of the incidents described above thousands of m³ of highly contaminated sea water flew into the basements of the reactor buildings. The contaminated sea water in the reactor buildings amounts to 400,000. The amount of the contaminated water increases daily due to penetration of rain and ground water into the damaged buildings. [2]

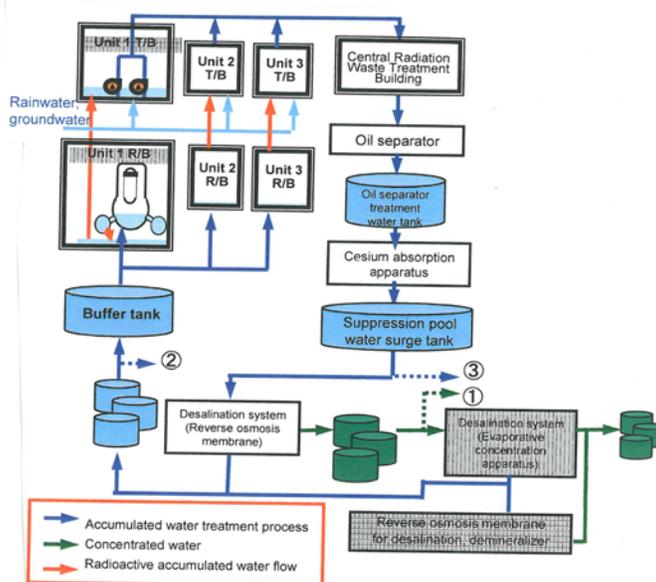


Fig. 2: Current Water Treatment System at Fukushima
Source: The Tokyo Electric Power Company [3]

Already in June 2011 The Tokyo Electric Power Company started a water decontamination system (Fig. 2), which initially used a decontamination system from AREVA. Later the system was supplemented by

two lines of Toshiba SARRY decontamination system and also improved by adding a return loop with a desalination step so that treated water could be used as cooling water for the reactors.

By the end of September 2013, the system had treated 350,000 m³ of water which is stored in huge tanks around the site. [11]

But the treated water is still highly radioactive, because the SARRY system only removes cesium isotopes, and according to [4] it mainly consists of retentate from reverse osmosis which is corrosive to the storage tanks due to its high salt content.

Thus The Tokyo Electric Power Company has started to build a new treatment system to treat all of the contaminated water. The new system will also remove not only caesium isotopes but a total of 62 radionuclides, among them also Sr-90. The new treatment system is shown in Fig. 3. It will be inserted into the current water system and treat water streams labeled 1 to 3 in Fig .2, mainly concentrated salt water from reverse osmosis.

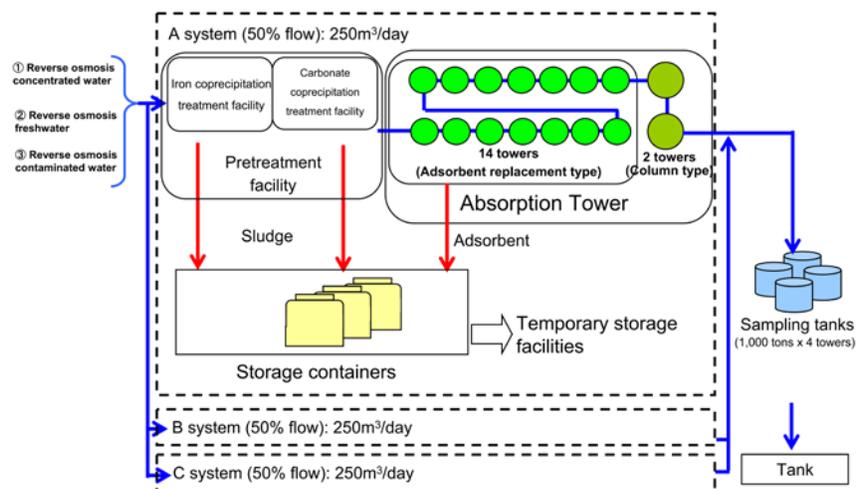


Fig. 3: New Water Treatment System at Fukushima
Source: The Tokyo Electric Power Company [3]

The core of the New Water Treatment System is the adsorption stage which contains 14 towers with ion-exchange media.

In front of the adsorption stage a pretreatment stage is installed. The pretreatment stage consists of two different chemical processes: first, a ferric flocculation process for removal of ruthenium isotopes; second, a co-precipitation process that removes calcium, magnesium and strontium as carbonates. This co-precipitation step is crucial since Ca, Mg and Sr represent competing ions to the most of the ion-exchange resins and lower its efficiency. This is also true for CsTreat and SrTreat which Fortum supplies for caesium and strontium removal. According to Fortum the competing ions lower the efficiency of its products by as much as three times. [4]

THE RADIOTOXIC IMPORTANCE OF SR-90

Strontium-90 (⁹⁰Sr) is a radioactive isotope of strontium produced by nuclear fission with a yield of about 6%. It has a half-life of 28.8 years and undergoes β^- decay into Yttrium-90 (⁹⁰Y), with a decay energy of 0.546 MeV. [5]

Strontium-90 is a major radionuclide in spent nuclear fuel, high-level radioactive wastes resulting from processing spent nuclear fuel, and radioactive wastes associated with the operation of reactors and fuel reprocessing plants. [6]

It is considered one of the more hazardous constituents of nuclear wastes. Strontium-90 is chemically similar to calcium, and tends to deposit in bone and blood-forming tissue (bone marrow). Thus, strontium-90 is referred to as a "bone seeker." Internal exposure to Sr-90 is linked to bone cancer, cancer of the soft tissue near the bone, and leukemia. When people ingest Sr-90, about 70-80% of it passes through the body. Virtually all of the remaining 20-30% that is absorbed is deposited in the bone. About 1% is distributed among the blood volume, extracellular fluid, soft tissue, and surface of the bone, where it may stay and decay or be excreted. [7]

Most of the risk is associated with the high-energy beta particle (2.282 MeV) emitted by its daughter nuclide ⁹⁰Y. [6]

According to Dalrymple [4] Sr-90 is one of the main radionuclides in the waste water at Fukushima. Besides Sr-89 it has the highest activity concentration in concentrated salt water as well as in the desalinated water, with 1.6E7 Bq/L and 1.2E8 Bq/L respectively.

SORBENTS FOR STRONTIUM REMOVAL

The Institute of Chemistry, FEBRAS, has been developing sorbents for strontium removal for about 15 years and thus has a wide experience in this field. In 2001 Avramenko et. al has demonstrated the advantages of the SRM type materials [8] by comparing them with different other sorbents. In his study following sorbents were tested:

IE-911 and TiIE-96 (UOP, Des Plaines, IL, the United States); Duolite C-464 (Rohm&Haas); crystalline sodium tita-nate (TiNa) (pilot sample; Allied Signal, Des Plaines, IL, the United States); DMT [granulated thermally treated manganese dioxide, provided by V.M. Gelis (Institute of Physical Chemistry, Russian Academy of Sciences)]; FMM (fiber-supported hydrated magnesium manganite; Institute of Chemistry, Far-East Division, Russian Academy of Sciences); and SSW, SRM-V, and SRM-N [sorption reagents based on sili-cotitanates containing exchangeable Ba; developed at the Institute of Chemistry, Far-East Division, Russian Academy of Sciences].

The comparison of the sorbents was performed in static experiments using seawater of the Gulf of Ussuriisk (Japanese Sea). The composition of the seawater is given below:

Cations in [g/L]		Anions in [g/L]	
Na ⁺	10.29	Cl ⁻	18.51
Mg ²⁺	1.23	SO ₄ ²⁻	2.59
Ca ²⁺	0.39	F ⁻	0.0012
K ⁺	0.38	Br ⁻	0.064
Sr ²⁺	0.0074	HCO ₃ ⁻	0.133
Organic carbon	0.004	H ₃ BO ₃	0.024

TABLE I. Composition of seawater of the Gulf of Ussuriisk

The procedure for static experiments is quite simple. The material is weight into a PE-tube, sea water spiked with Sr-90 is added to the material (typical solid to liquid ratio S/L is in the range of 1:100 up to 1:1000), tube is shaken for several minutes and stood calm for 24 hours. Afterwards the liquid is filtered using a 0.45µm filter and measured with a beta-spectrometer.

The distribution coefficients were determined as

$$K_d = \frac{(A_0 - A)}{A} \cdot \frac{V}{m} \quad (1)$$

where A₀ is the initial activity of strontium, A the equilibrium activity of strontium, V is the solution volume in mL, and m is the sorbent weight in g.

The results of these experiments are given below, showing by far the highest K_d for SRM:

Sorbent	K _d
SSW	4143
SRM	12600
FMM	315
DMT	125
IE-911	70
TiIE-96	11
TiNa	70
Duolite C-467	7

TABLE II. Distribution coefficients of different sorbents

Interesting results were obtained in studying the effect of dilution of seawater with distilled water, i.e., salinity, on the Sr distribution coefficients (Fig. 4).

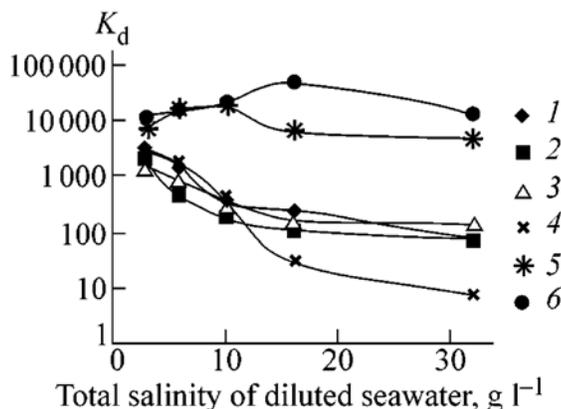
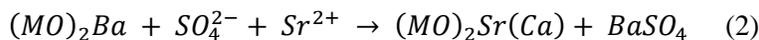


Fig. 4. Distribution coefficient of Sr as a function of the dilution of seawater. Sorbents: (1) IE-911, (2) TiNa, (3) DMT, (4) Duolite C-467, (5) SSW, and (6) SRM Source: Radiochemistry [8]

The results show that K_d increases with dilution, except for SSW and SRM. This demonstrates that the efficiency of SSW and SRM sorbents are not effected by Ca, Mg and Sr ions. The reason for such behaviour of these sorbents can be find in their sorption mechanism:



Thus, Sr can be fixed by both ion-exchange path via sites in the sorbent matrix and by coprecipitation on finely dispersed BaSO₄ formed in the sorbent matrix or on its surface. [8]

It has to be point out that the SRM sorbent has been produced at the pilot plant of the Federal State Unitary Enterprise “DalRAO” and has been applied for decontamination of high-salinity (≥30 g/l) LRW since 2003. [9]

Recently the Institute of Chemistry, Far Eastern Branch of Russian Academy of Sciences, has developed an enhanced sorbent for Sr-90 removal. The sorbents are based on SRM type sorbents, thus the sorption mechanisms of new sorbents are comparable to the SRM type sorbents.

The new materials were tested by NUKEM Technologies using simulated sea water. The composition of the simulated sea water corresponds to the composition of sea water in Table 1.

Distribution coefficients were determined in static experiments according to the procedure described above. K_d values were calculated according to eq. 1.

sample	weight [g]	Volume [ml]	cpma	Kd	Kd average
A0			25,240		
B-C-5	0.1017	10	147	23,059	22,872
B-C-5	0.1004	10	158	21,171	
B-C-5	0.1009	10	142	24,386	
B-C-10	0.1009	10	166	19,722	21,013
B-C-10	0.1012	10	138	25,310	
B-C-10	0.1016	10	177	18,006	
blank			40		

TABLE III. Data for new sorbents

From the results shown in Table 3 it can be derived that the new sorbents show distribution coefficients which are almost twice as high as those of SRM type sorbents.

In laboratory the sorbent B-C-5 was tested under dynamic conditions for three different salinities; 60 g/l, 30 g/l, and 1,2 g/l simulating concentrated, “normal” and 25 fold diluted sea water.

Therefore the sorbent was packed in columns and rinsed with the respective solution. Column volume applied was 10ml, space velocity 2 column volumes per hour. Rinsing procedure was continued until a decontamination factor of 10 was reached (defined breakthrough criteria for the columns).

The result of these tests is shown in Fig. 5.

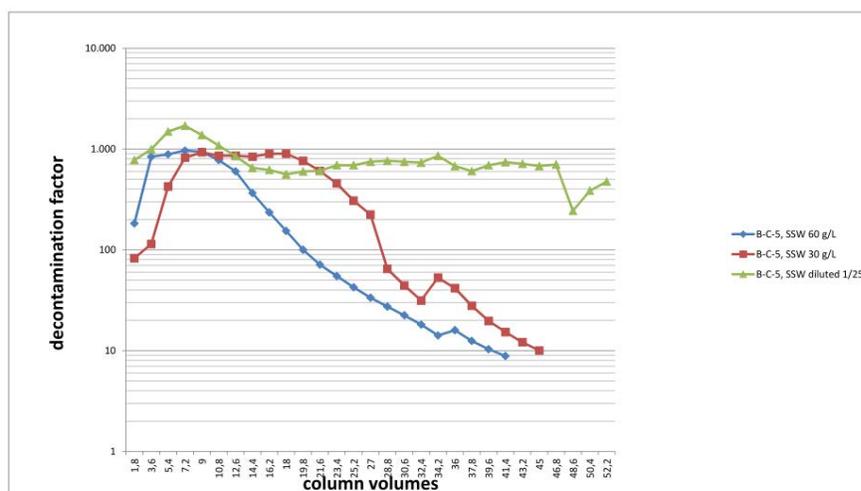


Fig. 5. Decontamination factor of B-C-5 depending on column volumes and salinity

The results show high initial decontamination factors and acceptable capacities of the sorbent B-C-5. Initial decontamination factors were determined to be 1000 and a solid to liquid ratio of 1 to approx. 250, meaning that for 1000 m³ of sea water or concentrated sea only 4 m³ of sorbent are necessary, for diluted sea water the amount of sorbent is even lower.

CONCLUSIONS

The seaquake and the tsunami have destroyed the nuclear power plants on the east coast of Japan. The accident and also the measures that were taken to cool the reactors resulted in a huge amount of highly contaminated waste water. The Tokyo Electric Power Company reacted very fast and set up a decontamination system to clean the waste water. However, the cleaned water has a high salt content and is stored in vessels around the site. The water is highly aggressive and measures should be taken fast to treat the water. Otherwise one runs the risk of leakages. According to the press [10] there is evidence that leakages already occurred.

The new water treatment system foresees two treatment steps: first step in order to remove the competing ions by precipitation and second step for adsorption of radionuclides through ion exchange resins. The efficiency of most sorbents that are available on market is highly effected by the competing ions [12-14].

All in all, for waste water treatment at Fukushima sorbents are required that can manage high salt contents and at the same time not effected by competing ions. Since the main component of the waste water is Sr-90, the used sorbents shall also have high selectivities for radiostrontium. Far Eastern Branch of Russian Academy of Sciences has experience of many years in the field of developing sorbents which meet requirements described above and which already were used in other projects that are comparable to the situation in Fukushima. Furthermore, in recent developments the properties of the sorbents could be even improved.

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