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APPLICATION OF ADSORPTION PHYSICS FOR HANDLING ENVIRONMENTAL POLLUTION- ONE METHOD OF DECONTAMINATION OF RADIOACTIVE SEAWATER-

Eiji Ishizaki[1*], Atsushi Minato[2], Masanori Itaba[3] & Satoru Ozawa[4]
[1*]Union Showa K. K., 1-8-40 Konan, Minatoku, Tokyo 108-0075, Japan.
[234]Graduate School of Science and Engineering, Ibaraki University, Hitachi 316-8511, Japan.
Correspondence Author:Eiji_Ishizaki@uskk.co.jp

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Abstract
In recent years, nuclear power plants are going to be introduced to developing countries to cover their increasing needs of electric power supply. In case of nuclear power plant accident, various top-level scientific and engineering techniques are needed to manage the accident. One of them is removal technique of radioactive materials from polluted soils or water. This paper reports the lessons learnt from the Fukushima nuclear power accident in 2011. One method is presented of the radioactive decontamination of the seawater polluted by the accident of Fukushima nuclear plant 1. The point is how to decontaminate huge amount of the polluted seawater in the harbor where the radioactive materials are accumulated especially in the neighborhood of the nuclear power plants. It has been shown a molecular sieve zeolite (MSZ) in a pillar buoy that floats in the harbor effectively collects ^{90}Sr from the polluted seawater.

Introduction
On the 11 March 2011, the northeast region (Tohoku region) of Japan was severely damaged by the earthquake and the associating tsunami attack. There were working two nuclear power plants, i.e., Fukushima Nuclear Power Plant 1 (FNPP1) and Fukushima Nuclear Power Plant 2 (FNPP2) along the coast of Fukushima prefecture. In the four Units of FNPP1, they lost all of the electricity supplying systems; therefore, the cooling system of the reactors completely stopped. The temperatures of the reactors were increased abnormally and the nuclear fuel melted down in the Units 1, 2 and 3 of FNPP1. Soon after the accident, a lot of plain water and sea water were sprayed over the damaged reactors for cooling. There appeared huge amount of water contaminated by radioactive materials. The radioactive water spilled out from the reactors and contaminated the ground, the harbor and the sea in the adjacent area to the nuclear power plants.
The author's previous paper [1] is concerned with the study of decontamination of the radioactive water inside of the nuclear plants. It has been shown that the academic and industry cooperation worked effectively for the development of a new recycling system of the cooling water of the plant. On the basis of the knowledge of the adsorption physics, they have succeeded to develop a new type of MSZ which is best suited for the decontamination of the radioactively polluted water inside the plants.
The present paper is concerned with the study of the method of decontamination of ^{90}Sr that is accumulated in the seawater in the harbor adjacent to the nuclear power plants. Since it is not allowed to pump out the polluted seawater from the harbor, the decontamination method should be in-situ type. In this paper, a new method of decontamination of huge amount of the polluted seawater in the harbor is proposed on the basis of the study of adsorption physics of MSZ.

Physics of adsorption on molecular sheave zeolite
Molecular sieve zeolite is a group of materials which have microscopic porous structures. The microscopic structure on the surface of MSZ determines its adsorption characteristic. Since one MSZ selectively adsorbs one material, it can be used as an adsorbent in separation processes of various engineering plants. There are two types of MSZ, i.e., the natural Zeolite and the synthetic MSZ. The former has a fixed character of adsorption. The latter is more expensive than the former; however, its character of adsorption can be tuned easily by modifying the microstructure of MSZ or by doping a foreign material into MSZ. Therefore, it is possible to synthesize a MSZ which has the best suited separation characteristic for the required purposes [2]. The knowhow of the synthesis is accumulated in MSZ companies.
The final purpose of MSZ adsorption physics is to understand microscopic adsorption processes occurred on the surface of MSZ and to explain the adsorption characteristic from a microscopic point of view. The essence of the phenomena is microscopic and dynamic; however, the commonly used methods to describe the adsorption phenomena on MSZ are thermodynamics that concerns quasi-static equilibrium states.
While the contaminated fluid is passing through the mass of MSZ, the contaminant adsorbs onto the surface of MSZ. The adsorption process occurs in the "mass transfer zone (MTZ) in the adsorber vessel (see Fig. 2 in the reference [3, 4]). As the fluid is continuously fed into the vessel, the MTZ is being pushed forward in the direction of the feed. When the front of the MTZ reaches at the end of the MSZ bed, the MSZ is almost consumed; this is called "breakthrough". However, in this paper the word

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"breakthrough" is used for the state that the MSZ is completely consumed. The dynamic process in the adsorber can be described by the method of rate equations [4]. The numerical method based on the rate equations successfully explains the movement of the MTZ in the direction of the feed. The most important result of the numerical study is that the occurrence of breakthrough and the length of MTZ are explained in terms of the basic adsorption parameters included in the rate equations. Actually, the authors have developed a computer simulator which works in Microsoft Windows environment and also in Linux environment [5, 6]. The dynamical process of adsorption can be shown in a movie on a computer display

A new method of decontamination of hyuge mounts of seawater in harbor

First of all, the quality of the seawater in the harbor adjacent to the FNPP1 was investigated. The quality test showed the following results: the concentration of the target contaminant, i.e., the radioactive ^{90}Sr in the seawater = 6.75×10^{-13}mol/L, and that of the natural Sr in the seawater = 9.13×10^{-5}mol/L. It should be noted that the seawater contains various minerals including the natural Sr and the concentration of the radioactive ^{90}Sr is much less than that of the natural Sr. The total amount of the contaminated seawater in the harbor was estimated to $3.6\times10^{5}m^{3}$. Therefore, the total amount of ^{90}Sr to be removed is $(6.75\times10^{-13}mol/L) \times (3.6\times10^{5}m^{3}) = 2.4\times10^{-4}$mol.

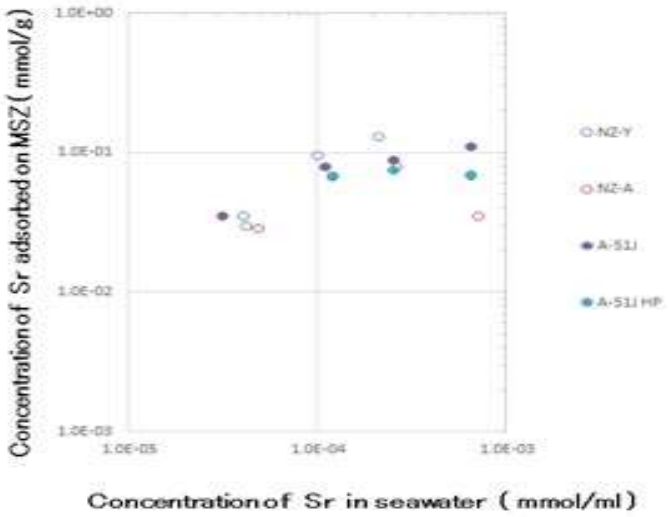

Figure 1: The equilibrium concentration of Sr adsorbed on the various MSZs versus the concentration of Sr in the seawater.

The adsorption efficiency of MSZ depends, in general, on the concentration of adsorbate in the solution. Figure 1 shows the measured data of the equilibrium concentration of Sr adsorbed on various MSZs from the seawater with different concentration of Sr. It is seen from the figure that the 1.14×10^{-5}mol of Sr can be adsorbed on the 1g of the synthetic MSZ (A-51 HP) from the seawater that contains 1.0×10^{-4} mol/mL of Sr which is almost the same level of the actually observed concentration of the natural Sr in the polluted seawater [7]. Namely, the 1-ton of the artificial MSZ adsorbs the 11.4mol of Sr in the seawater. In the case of the natural MSZ, however, the adsorption efficiency is lower by factor some 2 than that of the synthetic MSZ [8].

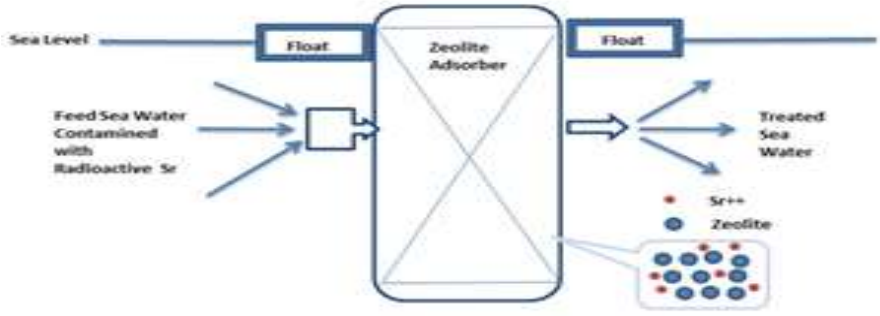

Figure 2: The pillar buoy containing the mass of MSZ that adsorbs Sr in the polluted seawater

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The idea of the decontamination of the radioactive ^{90}Sr in the harbor is illustrated in Fig. 2. It is a pillar-shaped buoy in which the 1-ton of the MSZ is included. The vessel of the buoy stands in the sea in vertical direction to the sea surface with the aid of floats which are attached to the top part of the buoy. There is a pumping system on the side of the vessel. The polluted seawater is fed into the mass of the MSZ by the pump at a constant feed rate R_F. While the polluted seawater is passing through the mass of the MSZ, the natural Sr and the radioactive ^{90}Sr are adsorbed on the surface of the MSZ. Note the adsorption efficiency of the two is equal. The adsorption occurs in the mass transfer zone (MTZ) [8]. The shape of the MTZ in this case is not so simple as compared to that in the previous case where the flow of the polluted water is simple and geometrically symmetric [3,9]. Because of this symmetric condition, the simple one dimensional model for the dynamics of the MTZ was successful in the previous case [9]. When the mass transfer front reaches at the outlet position, the breakthrough occurs also in the present case. The breakthrough time can be estimated computationally by the numerical calculation, or experimentally by measuring the Sr concentration of the seawater at the inlet and that of the seawater at the outlet. The full breakthrough time of this decontamination unit was 12.5 days in the case of the feed rate 0.23 L/sec. When the full breakthrough occurs, the used MSZ must be replaced by a new one; or it must be refreshed by a series of chemical processes. The pillar buoy type adsorber is repeatedly used after refreshing the MSZ. We call this cycle the breakthrough cycle. The period of one breakthrough cycle is nearly equal to the breakthrough time t_B.

Now, let us estimate the total amount of the MSZ needed for decontaminating the polluted seawater in the harbor. Here, it is assumed that the K units of the pillar buoy type adsorber are used simultaneously. Each of which contains the 1-ton of the MSZ. The time variation of the concentration of the radioactive ^{90}Sr, $n(t)$ in the seawater is given by the following differential equation.

$$-M\frac{dn}{dt}=KA\frac{n}{N} \qquad (1)$$

Here, M is the total amount of the polluted seawater; A is the amount of the Sr adsorbed on 1-ton of the MSZ in one breakthrough cycle; N is the concentration of the natural Sr in the seawater; and t is time of which scale is normalize by the breakthrough time t_B. The term in the left-hand side of Eqn. (1) means the decreased amount of the radioactive ^{90}Sr in the harbor in one breakthrough cycle, and the term in the right-hand side means the amount of the radioactive ^{90}Sr adsorbed on the MSZ in the K units of the adsorber. It should be noted here that N does not depend on time because the harbor is open to the Pacific Ocean and the natural Sr is continuously supplied from the open sea. This has been experimentally confirmed by the measurements of the concentration of the natural Sr in the harbor and in the open sea. The differential equation is easily integrated and the solution is given by

$$n(t)=n(0)\exp(-KAt/NM)=n(0)\exp(-Ax/NM) \qquad (2)$$

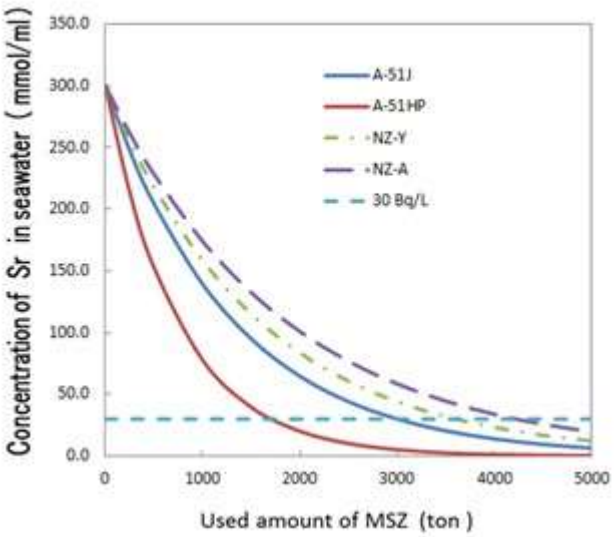

Figure 3: The time variation of the concentration of the radioactive ^{90}Sr in the polluted seawater in the harbor as the function of the used amount of the MSZ.

Here, $n(0)$ is the initial concentration of the radioactive ^{90}Sr in the harbor. It should be noted again that the parameter t is normalized by the breakthrough time t_B. Since the K–ton of the MSZ is used in one breakthrough time, the used amount of the MSZ is proportional to the normalized time t, namely, $x = Kt$. The curve of Eqn. (2) can be drawn as a function of x as well as a function t. The graph as a function x is shown in Fig. 3 where $K = 1$. In the figure, the allowable (legal) level of the concentration

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of the radioactive ^{90}Sr is shown by the horizontal broken line. The numerical values of the parameters used for the calculation are listed in Table 1

TABLE 1
NUMERICAL VALUES OF PALAMETERS USED FOR THE STUDY OF DECONTMINATION OF THE POLLUTED SEAWATER IN THE HARBOR

$n(0)$	6.75×10^{-13} mol/L = 300 Bq/L	
M	3.6×10^{5} m^3	
N	9.13×10^{-5} mol/L	
t_B	$1.2\times10^{4}\sim1.9\times10^{6}$ sec for the feed rate R_F = 0.23 L/sec	
A	A-51J	10.5 mol
	A-51 HP	11.4 mol
	NZ-Y	9.8 mol
	NZ-A	6.2 mol

It is seen from Fig. 3 that the 3000 tons of the MSZ (A-51J) is needed to decontaminate the harbor to the level allowable by the Japanese law. This amount corresponds to 100 years in the case that just one unit of the adsorber is used. If we use 20 units of the decontamination buoy simultaneously, it is possible to finish decontamination in the harbor in 5 years.

Recycling of used MSZ

The used MSZ contains the radioactive ^{90}Sr. The maximum value of the radioactivity of the used MSZ is $n(0)\ t_B\ R_F$ = in the first breakthrough cycle. The radioactivity of the used MSZ is gradually decreased to the value $n_{legal}\ t_B\ R_F = 3.8\times10^4$ Bq/Kg in the final breakthrough cycle. The mean value of the radioactivity of all the used MSZ is 2.1×10^3 Bq/Kg for the case of MSZ (A-51J). Therefore the used MSZ in even the case of non-regeneration case is classified into the "low-level radioactive waste". The problem is not the level of radioactivity but the volume of the waste. In order to solve this problem, recycling of the used MSZ is considered.

Figure 4 shows the flow chart of chemical processes needed for the recycling of the used MSZ. The total process is composed of the following steps:

1. The 1st step: the units of the adsorber are landed and the used MSZ is taken out from the adsorber vessel.
2. The 2nd step: The used MSZ is put into Na_3PO_4 aqueous solution. The existence of Na^+ ion in the solution helps desorption of the Sr from MSZ. The desorbed Sr forms coagulated solid.
3. The 3rd step: The coagulated solid is separated from the solution by using filtering technique.
4. The 4th step: The coagulated solid is dehydrated and put into suitable vessels.

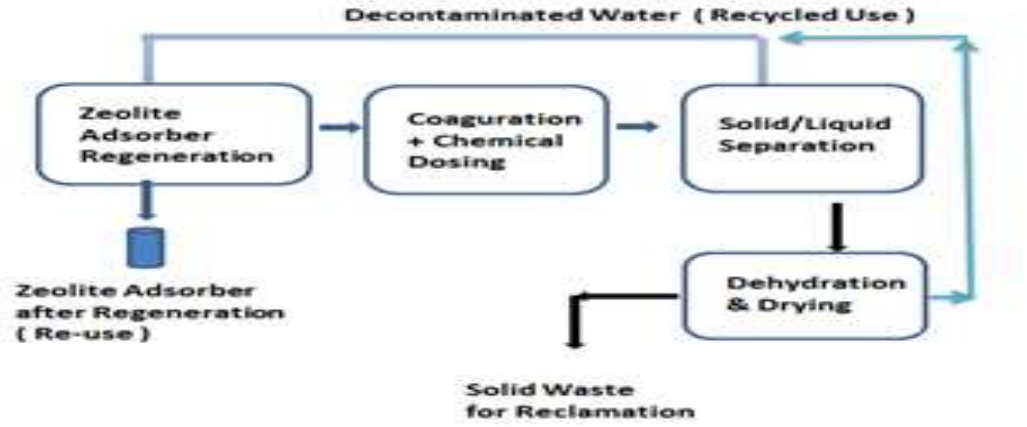

Figure 4: The flow diagram of chemical processes needed for recycling the used MSZ

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It has been found from the detailed analysis of the above processes that the chemical processing of the 3000 tons of MSZ (A-51J) produces 250 tons of the processed waste which has the radioactivity of $4.6\times10^{5}\sim4.5\times10^{4}$ Bq/Kg . The processed MSZ is able to reuse about 15 times repeatedly [9,10,11].

Conclusion

The method has been studied of the radioactive decontamination of the seawater produced by the accident of Fukushima nuclear plant 1. The point was how to decontaminate the huge amount of the polluted seawater in the harbor adjacent to the nuclear power plant. It has been shown that the MSZ in the pillar buoy type adsorbers that float in the harbor effectively collects ^{90}Sr from the polluted seawater. The study is still in laboratory level, however, some important information has been obtained: (1) the 250-tons of MSZ (A-51J) is needed to decontaminate the harbor to the level allowable by Japanese law; (2) the mean value of the radioactivity of the used MSZ is $3.8\times10^{4}\sim3.5\times10^{3}$ Bq/Kg just after one breakthrough cycle in the case of MSZ (A-51J); (3) the total volume of the radioactive waste is very much reduced by the chemical processing of the used MSZ. If the 3000-tons of the used radioactive MSZ is chemically processed, only 250 tons of the radioactive waste is to be produced. The reduction of the volume of the radioactive waste is very attractive because it is difficult to find a suitable disposal place of the huge amount of the radioactive waste. However, the chemical processing needs an additional coast. The less expensive alternative is to use natural Zeolite as the adsorbent and adopt the direct disposal method. Which to choose is not the matter of science but of management and politics.

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