ISSN: 2349- 5197
Impact Factor (PIF): 2.138

INTERNATIONAL JOURNAL OF RESEARCH SCIENCE & MANAGEMENT

STUDY OF ADSORPTION PHYSICS FOR HANDLING ENVIRONMENTAL POLLUTION - AN APPROACH TO THE PROBLEM BY ACADEMIC AND INDUSTRY COLLABORATION -

Eiji Ishizaki[1*], Atsushi Minato[2], Masanori Itaba[3] and 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

Keywords: Nuclear accident, radioactive decontamination, adsorption physics, academic and industry collaboration

Abstract
Because of worldwide rapid development of industries, environmental pollution has now become a global problem. One of the techniques of handling the environmental pollution is development of adsorbent that removes contaminants from the polluted air, water and soil. This paper describes academic industry collaboration for developing an efficient adsorbent and its reverent system for the radioactive decontamination of Fukushima nuclear plant accident 2011. The Fukushima radioactive contamination occurred suddenly and unexpectedly by the nuclear plant accident which was triggered by the tsunami attack. The point was how to develop and supply a useful adsorbent in such an urgent situation. The lessons learned from the experience of the accident are summarized and some conclusive remarks are deduced regarding the study of adsorption physics for handling environmental pollution.

Introduction
Tohoku region pacific coast earthquake and Fukushima nuclear plant accident
An earthquake of the magnitude of 9.0 attacked the northeast region (Tohoku region) of Japan on the 11 March 2011. The earthquake occurred in Japan Trench area where the Pacific Plate sinks under the North American Plate. It was a trench-type earthquake. The earthquake produced tsunami waves, which devastated the coastal areas of Tohoku (Fukushima, Miyagi, Iwate, and Aomori Prefectures) and Kanto (Ibaraki and Chiba Prefectures) regions of Japan. The rising tsunami waves were as high as 41 meters at maximum. Nearly 18,500 people were killed or missed in the whole area damaged by the earthquake and the tsunami.

There were 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. The former had six units and the latter had four units in the plant. They were supplying electric power to Tokyo area. They experienced 550 Gal vibrations of the earthquake which damaged some equipment of the plant. The working reactors stopped automatically; namely, the reactor scram was successful. The first tsunami waves attacked the nuclear power plants 41 minutes after the occurrence of the earthquake. The height of the rising tsunami waves that attacked the plant was 14 meters at maximum. By the tsunami attack, they lost all of the electricity supplying systems including that for the emergency use in the four units of FNPP1, namely the station black out occurred, which resulted complete stop of the cooling system of the reactors. The temperatures of the reactors were increased abnormally and the nuclear fuel melted down in the Units 1, 2 and 3 of FNPP1. The high temperature and the nuclear fuel melt down naturally produced hydrogen gas in the reactors. The buildings of the reactors were blown away by the hydrogen gas explosion and a lot of nuclear contaminants were scattered into air. The wind carried the nuclear contaminates as far as 100 km from the reactors, in the northwest direction. The soil of the land was widely contaminated by radioactive materials, I131, Cs137, etc. The total amount of the radioactive materials exposed into the environment was estimated as about 900PBq, which was about 1/6 of that in the case of Chernobyl nuclear power plant accident 1986. Soon after the accident, as in case of emergency, a lot of plain water and sea water were sprayed over the damaged reactors for cooling. As the result, huge amount of water contaminated by radioactive materials was produced. The part of 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.

One of the urgent problems was to establish a cooling-water recycling system. We must have decontaminated the polluted water to reuse for the cooling. A typical method of decontamination is to use adsorbents that remove contaminants from the polluted water safely and efficiently. The Fukushima radioactive contamination occurred quite unexpectedly caused by the tsunami attack. The point was how to develop efficient adsorbers in such an urgent situation. In the following sections, it is shown that academic industry collaboration worked effectively for developing efficient absorbers and the relevant systems which were specially designed for Fukushima nuclear plant accident.

Studies of adsorption physics carried out before the accident

ISSN: 2349- 5197
Impact Factor (PIF): 2.138

INTERNATIONAL JOURNAL OF RESEARCH SCIENCE & MANAGEMENT

Before describing the academic industry collaboration to develop the new adsorbent and the relevant systems, let us summarize what was known for the adsorption physics before the accident. The basic scientific knowledge on adsorption phenomena was accumulated in the academic side, while actual adsorption data and the plant level experience were in the industry side. Let us see this more in details in the followings.

Typical adsorbent used in adsorbers is molecular sieve zeolite (MSZ). There are two types of MSZ, i.e. the natural and the artificial. The both types of MSZ have characteristic porous structures [1]. The size of the microscopic structure of MSZ determines the character of adsorption. Namely, one MSZ selectively adsorbs one material depending upon the pore size of MSZ and the molecular size of adsorbate. The adsorption character can be modified also by doping foreign material into MSZ. Therefore, quite a lot of MSZ with different characteristics can be produced. The commercial MSZ adsorbents are shaped in pellets or beads of which diameter are 0.5 – 4 mm. As shown in Fig. 1, a mass of MSZ (adsorbent bed) is supported in an adsorber vessel. There are an inlet and an outlet of fluid in the vessel.

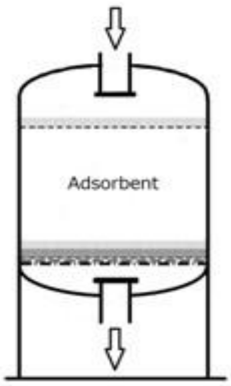

Figure 1: Schematic construction in the adsorber vessel

While the contaminated fluid is passing through the adsorbent bed, the contaminant adsorbs onto the surface of MSZ. This process is illustrated in Fig. 2. The adsorption process occurs in the region of "mass transfer zone (MTZ) in the adsorber vessel. In this region, the concentration of adsorbate is spatially distributed from zero value at the mass transfer front to a definite value (saturated value) as shown in Fig. 2. As the fluid is continuously fed into the vessel at a constant rate, the MTZ is pushed forward in the direction of the feed. When the mass transfer front reaches at the end of the adsorbent bed, which is called "breakthrough", the adsorber is almost consumed. If we observe the adsorbate concentration at a fixed position in the vessel, the value changes in time from zero to the saturated value. Although the adsorption process in MTZ is dynamic in nature, it has usually been described by using static quantities (thermodynamic quantities) such as adsorption energy, adsorption entropy, and isothermal adsorption data. These thermodynamic quantities and data have been accumulated for various kinds of MSZ at academic side as well as at industry side. When all the adsorbent is consumed by the adsorption, the used adsorbent must be replaced by another new adsorbent; or it must be refreshed by a suitable method [2].

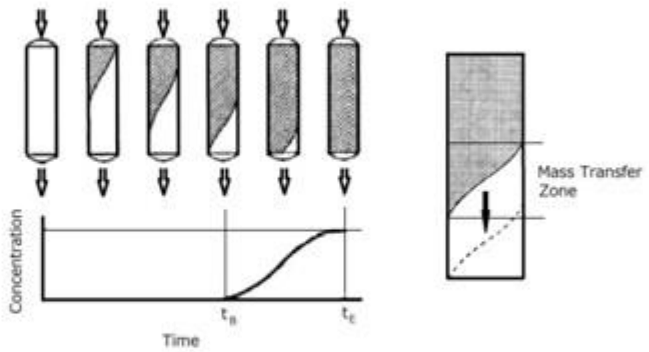

Figure 2: Illustration of adsorption process in absorber vessel. The graph shows the time variation of the concentration of adsorbate on MSZ. Here, t_B is the breakthrough time and t_E is the effluent time.

One challenging work for the study of the dynamic process in the adsorber vessel is to use the rate equation method. In the simple one-dimensional model, a set of rate equations to describe the adsorption kinetics in the vessel is given by the following:

ISSN: 2349- 5197
Impact Factor (PIF): 2.138

INTERNATIONAL JOURNAL OF RESEARCH SCIENCE & MANAGEMENT

$$\frac{\partial S}{\partial t} = -C_1 Sn\sqrt{T} + C_2(1-S)\exp(-T_1/T)$$

$$\frac{\partial n}{\partial t} = -C_3 Sn\sqrt{T} + C_4(1-S)\exp(-T_1/T) - C_5\frac{\partial n}{\partial x}v + C_6\frac{\partial^2 n}{\partial x^2}\sqrt{T}$$

$$\frac{\partial T}{\partial t} = C_7 Sn\sqrt{T} - C_8(1-S)\exp(-T_1/T) - C_9\frac{\partial T}{\partial x}v + C_{10}n_{carrier}\frac{\partial^2 T}{\partial x^2}$$

Here, S is the ratio of the used surface area of MSZ to the initial virgin surface area; n is the concentration of the adsorbate in the fluid (carrier); T is the temperature of the fluid and MSZ; v is the drift velocity of the fluid; n_{carrier} is the density of the fluid; and C_i (i = 1, 2,…10) are the numerical parameters. It should be noted here that the fluid and the surface of MSZ are assumed to have a same temperature and $T_1 = E_{ad}/k$, where E_{ad} is the adsorption energy, k is the Boltzmann's constant. The parameters, t and x represent time and distance from the top of the adsorbent bed, respectively.

Since the rate equations are non-linear type, it is impossible to solve these differential equations analytically. However, it is possible to see the behavior of the solutions with the aid of numerical method. In author's previous study [3], the rate equations were numerically integrated for variety of parameters with changing their values systematically. It has been found from the numerical works that there are five types of adsorption modes on MSZ [4]. An example of numerical results obtained from the rate equation is shown in Fig. 3.

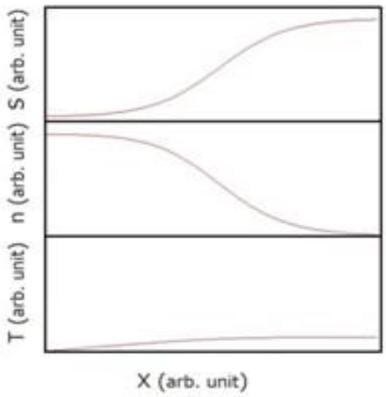

Figure 3: The typical results of numerical calculations of adsorption kinetics based on the rate equations. S is the used surface area of MSZ; n is the concentration of the adsorbate in the fluid; T is the temperature of the fluid and MSZ; x is the distance from the top position of the adsorbent bed.

Here, the numerical results of adsorption kinetics are represented by the corresponding curves of S, n, and T, which shows the spatial distribution of each quantity in the direction of the feed in the adsorber bed at a fixed time after the start of feeding. The overall feature of the spatial distribution of these quantities fits well with the illustration of adsorption process shown in Fig. 2. After the detailed systematic examinations of the numerical results at different adsorption times, it has been concluded that the adsorption process on MSZ is successfully described by the proposed model. This means that computer simulation of adsorption based on the rate equation method can be a convenient tool for designing adsorber equipment. Actually, this computer simulation method was used in the initial stage of designing a new adsorber system that is required from industries. The authors developed a computer simulator which works in Microsoft Windows environment and also in Linux environment [5]. If the parameters included in the rate equations are given, the simulator calculates the values of $S(x)$, $n(x)$ and $T(x)$ and these curve are plotted on the display of computer. Since these drawing is repeated with increasing time, the dynamical process of adsorption can be seen in a movie. This tool has been used not only for designing but also for education and knowledge sharing of adsorption physics. It was used quite conveniently in training courses of adsorption physics in some companies [4]. It was one of the successful results of academic and industry collaborations.

Development of a new adsorber for the use of radioactive decontamination

Soon after the accident, Union Showa K.K. (USKK), an expert company in adsorption engineering decided to develop a new absorber for the use of decontamination of the polluted water produced by the accident of FNPP1. They could have technical supports from its parent companies, Showa Denko K.K. (SDK) and UOP LLC (UOP). One of the parent companies, UOP had

ISSN: 2349- 5197
Impact Factor (PIF): 2.138

INTERNATIONAL JOURNAL OF RESEARCH SCIENCE & MANAGEMENT

accumulated knowhow of radioactive decontamination in the accident of Three Mile Island (TMI) nuclear power plant in 1979. The related parties to this problem, i.e., the people from USKK, SDK, UOP, JAEA (Japan Atomic Energy Agency), Hitachi, Toshiba, CRIEPI (Central Research Institute of Electric Power Industry), FNPP1, etc., had meetings to discuss about decontamination techniques of radioactive I, Cs and Sr from air and water. They set up a new project to develop a MSZ adsorbent which is effective especially for FNPP1 accident. They decided the target of the project, the constitution of the project team, the planning of the development, and the time schedule of the work. These are summarized in Table 1.

TABLE 1
FEATURE OF THE PROJECT TO DEVELOP A NEW MSZ SUITABLE FOR DECONTMINATION OF FNPP1

Target	Decontamination of radioactive Cs and Sr from recycling cooling-water of FNPP1	
Project team	MSZ design group, Manufacturing group of practical MSZ, Quality estimation group of trial and practical MSZ, and Customer responding and data management group	
Schedule	Step 1	Selection of MSZ type and determination of suitable microscopic structure of MSZ and their characteristic parameters: 1- 4 months
	Step 2	Study of Cs adsorption on various MSZ: 2 - 6 months, Study of Sr adsorption on various MSZ: 24 months, Study of effects of obstacle material on the adsorption behavior: 2 - 12 months.
	Step 3	Establishment of production method of the new MSZ: 6 months
	Step 4	Optimization of the structure and the dimensions of the absorber vessel: 12 months
	Step 5	Preliminary study of the method of processing the used adsorbents: 36 months

Steps 1 and 2 are executed in parallel and cooperatively. Regarding the decontamination technique of radioactive material, a lot of data and experience have been accumulated since the TMI nuclear power plant accident in 1979. This knowledge was conveniently used in these steps. However, the situation of the polluted water of FNPP1 accident was not exactly the same as that of the TMI nuclear power plant accident. The polluted water in the former case was mixed with sea water, and the contaminants, Na, Ca, Mg, etc. decreased the adsorption efficiency of Cs and Sr on MSZ The influence of such contaminants on the adsorption behavior must have been studied in detail for various MSZ [6][7]. The examples of the obtained data of the efficiency of decontaminations of Cs and Sr are shown in Figs. 4 and 5. It is seen in Fig. 4 that the adsorption of Cs on MSZ (IE-96) is suppressed by a factor ~1/100 by the existence of salt water minerals as compared to the case of pure water. Figure 5 shows the equilibrium concentration of Sr adsorbed on various MSZ from the polluted water with different densities of Sr. It is seen that the measured values of the concentration of Sr adsorbed is decreased in particular for the cases of Sr concentration > 10^{-3}mmol%. This effect has been improved by adding ferrocyanide into the adsorbent [8][9].

INTERNATIONAL JOURNAL OF RESEARCH SCIENCE & MANAGEMENT

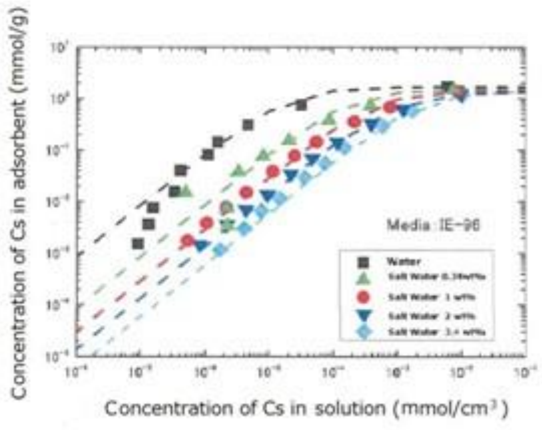

Figure 4: The equilibrium concentration of Cs adsorbed on the MSZ (IE-96) from the polluted water with different densities of Sr and salt water

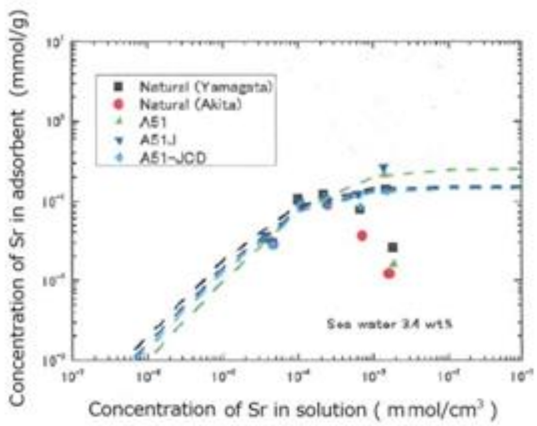

Figure 5: The equilibrium concentration of Sr adsorbed on various MSZ from the polluted water with different densities of Sr and sea water (3.4wt%).

In Steps 3 and 4, computer simulations have been carried out of adsorption processes that occur in the actual production line of the absorber vessel. With reference of the results of the computer simulations and also with the experimental try and error method, the optimizations have been executed of the structure and its dimension of the absorber vessel. The computer simulation was quite important for studying the breakthrough trace (see Fig. 2). On the basis of these works, it was possible to determine the actual absorber dimensions and its running plan.

In Step 5, which was carried out in parallel to Steps 2, the processing method of the used adsorbent was studied. The used MSZ is highly radioactive because radioactive Cs or Sr has been adsorbed on MSZ. A stable solidifying method has been studied in which the radioactive materials are fixed into the body of MSZ by sintering of the used MSZ. It has been found from the sintering experiments that the Cs does not come out from MSZ at temperatures < 1000℃ The MSZ structure is destroyed at temperatures > 1000℃ As the results of these studies, the targeted absorber plant was successively constructed, where a new complex MSZ mixed with insoluble ferrocyanide was used as the adsorbent which shows good selective adsorption for Cs (adsorption efficiency 95%) and also for Sr (adsorption efficiency 60%) even in salty water. It has been shown that the used adsorbent can be a stable solid that keeps the radioactive material in the body of MSZ mixed with ferrocyanide if it is sintered at temperatures below 1000℃ By this vitrification procedure, a method has been established that keeps the used radioactive adsorbent safely for many years. It should be noted that the steps 1, 2, and 5 were carried out in collaborations with industrial companies and academic parties (universities and national research centers).

Lessons learnt from the accident

In the nuclear power plant accident of FNPP1, one of the urgent problems was to establish the decontamination system of the cooling-water of the reactors that was polluted by radioactive materials. How this work was carried out has been described in the

INTERNATIONAL JOURNAL OF RESEARCH SCIENCE & MANAGEMENT

previous section. Here, we discuss, in general, some points that must be prepared for such emergent accidents. The efforts to prepare for emergency together are summarized in the followings.

The efforts before the accident

- The techniques and knowhow have been accumulated of producing absorbers with various different characteristics.
- Lots of data have been obtained on the adsorption phenomena, and they are well collated with each other.
- Physics of adsorption has been established to a level that can explain quantitatively actual phenomena of adsorption. It was possible to guess actual adsorption phenomena in absorbers from theoretical considerations.
- Computer simulations of adsorption kinetics have been carried out to study the process in absorber vessel. Some codes for the simulator have been developed and opened to public.
- Knowledge on the various type of adsorbent was shared with the people of industries and the academic.

The efforts after the accident

- Framework of academic and industry collaboration has been established soon after the accident. They helped each other by presenting techniques and knowhow of their specialties.
- A new project has quickly been set up to develop new MSZ adsorbents which are effective especially for FNPP1 accident. They decided a sharp schedule for this work. It was quickly put into execution.
- Computer simulation method of adsorption kinetics in absorber worked effectively in order to design the structure and the dimension of the absorber. The theoretical, experimental and computational methods worked cooperatively for designing the new absorber.
- Overall method has been developed of both effective decontamination and stable storage of radioactive material in the body of sintered MSZ.

Future efforts

- The decontamination method of radioactive cooling water has been executed successfully in FNPP1. As the result, a lot of high-level radioactive waste has been produced. We must decide how to manage the radioactive waste.
- The decontamination of radioactive Sr from sea water by using natural MSZ is proposed. It is executed; huge amount of low-level radioactive waste is expected to occur.
- The method of management of the radioactive waste has not been decided. It has become a serious social problem.
- The method of management of the radioactive waste must be studied scientifically. The academic and industry cooperation is needed in this field.

Conclusion

- Study of adsorption physics and its application to radioactive decontamination technology have been described in relation to Fukushima nuclear plant accident 2011. Many specialists of various fields of sciences and technologies must have worked hard to manage the dangerous situation soon after the accident. They helped each other by presenting techniques and knowhow of their specialties. In this sense, academic and industry collaboration worked effectively in the urgent situation. The reasons why they have succeeded to develop a useful absorber in short period are: (1) before the accident, they have accumulated lots of data and technologies concerning MSZ; (2) soon after the accident, they quickly set up a project to develop a new absorber plant on the basis of the academic and industry collaboration; and (3) The cooperative use of theoretical, experimental and computational methods of adsorption physics worked effectively to develop the new absorber plant.
- The decontamination of radioactive cooling water by using MSZ was executed successfully in FNPP1. As the result, a lot of radioactive waste has been produced. The management method of the radioactive waste has become the next urgent problems to study. The academic and industry cooperation is also needed to obtain a scientific solution of this problem.

Acknowledgment

The part of this work was supported by JSPS KAKENHI Grant Number 20500825 and Grant Number 24300278. The authors express sincere thanks to Prof. Hitoshi Mimura of Tohoku University for his guidance in developing MSZ doped with ferrocyanide. The author's thanks are also to Central Research Institute of Electric Power Industry and Showa Kankyo System K. K. for giving their knowhow of decontamination of radioactive Sr from polluted sea water

References

1. D.W.Breck: "Zeolite Molecular Sieves – Structure, Chemistry,and Use –" Capter 2) Structure of Zeolite, John Wiley & Sons, Inc., P29-P133, 1974

INTERNATIONAL JOURNAL OF RESEARCH SCIENCE & MANAGEMENT

2. D.W.Breck: "Zeolite Molecular Sieves – Structure, Chemistry,and Use –" Capter 8) Adsorption by Dehydrated Zeolite Crystals, John Wiley & Sons, Inc., P715-P718, 1974
3. E. Ishizaki, A. Minato, and S. Ozawa, Application of Graphic Computer Simulation Method and E-Learning Method in the Fields of Stuff Education and Sales Enginering in the Case of Adsorption System Producing Company, CIEC Vol.21 P88-94, 2006
4. E. Ishizaki, A. Minato, and S. Ozawa, 4th Asia-Pacific Forum on Engineering and Technology Education, Academia and Industry Collaboration in the Field of Sales Engineering, Keynote Address, P31-34 UICEE ,2005
5. S. Ozawa and D.W. Heermann, Computer Simulation under UXIX Environment, Gakujyutsutosho Publishing Company, Tokyo, Japan, 2005
6. Takatoshi Hijikata, Koichi Uozumi, Kenta Inagaki, Takeshi Tsukada, Tadafumi Koyama, Eiji Ishizaki, Minoru Matsukura, Study on the Radioactive Wastewater Treatment System at Fukushima Daiichi Nuclear Power Station (7) Adsorption Properties of Chabasite and CST for Cesium Removal from the Contaminated Water Simulant, Proc. of AESJ Spring, March 26-March 28, Osaka, Japan, 2013
7. Takeshi Tsukada, Takatoshi Hijikata, Koichi Uozumi, Kenta Inagaki, Tadafumi Koyama, Eiji Ishizaki, Minoru Matsukura, Study on the Radioactive Wastewater Treatment System at Fukushima Daiichi Nuclear Power Station (8) Adsorption Properties of Zeolite Type Sorbent for Strontium Removal from the Contaminated Water Simulant, Proc. of AESJ Spring, March 26-March 28, Osaka, Japan, 2013
8. Yuki Ikarashi, Rana Syed Masud, Tomonori Nakai, Hitoshi Mimura, Eiji Ishizaki, Minoru Matsukura, Selective Adsorption Properties and Stable Solidification of Cs by Insoluble Ferrocyanide Loaded Zeolites, Proc. Of ICONE21, July 29-August 2, Chengdu, Chine, 2013
9. Hitoshi Mimura, Yuki Ikarashi, Eiji Ishizaki and Minoru Matsukura, Selective Decontamination and stable Solidification of Cs-Insoluble Ferrocyanide by Zeolites, Proc. Of CIMTEC 2014, invited lecture, Montecatini, Italy, June 15-19, 2014