Development of high-efficiency cesium adsorbent(HECA) for cesium removal from cesium contaminated water

Byungwoo Lim[a*], Jongshik Joo[a]

[a] *Nuclear Environment Engineering & Development Co., Ltd.(NEED):*

260, Changnyong-daero, Yeongtong-gu, Suwon-si, Gyeonggi-do, Republic of Koera

**Corresponding author : limbau@need4u.co.kr*

1. Introduction

There are many different types of substances contaminated by radioactive cesium leaked into the environment due to the accident at the Fukushima nuclear power plant, and the quantities of them are huge. For intermediate storage and final disposal of radioactive waste, the purification and volume reduction of contaminants is a very important strategic technology development task. [1]

Cesium is water-soluble and volatilizes at a high temperature of 650°C or higher. In order to separate and recover cesium from contaminants, decontamination by using a washing method or a melting method is generally applied. However, in the decontamination technology using the melting method, a lot of energy is input, additives are added, and the complicated process of sintering and solidifying high-concentration waste to fix cesium is applied, so it is expensive due to the large scale of the facility and the volume reduction of waste is disadvantageous. Therefore, there is a limit to practical use. In addition, the decontamination technology using a conventional washing method uses prussian blue having excellent cesium adsorption characteristic, but there is a problem in the process of using the cohesive precipitation method to recover the mixture of coagulant and prussian blue nanoparticles adsorbed with cesium. Therefore, this method was not successful as a practical decontamination technique.

Therefore, in order to effectively recover cesium from radioactive cesium contaminated water, it is necessary to selectively adsorb and fix cesium among various competing ions mixed with contaminants, and the adsorbent itself must be easy to recover. In addition, the cesium-concentrated adsorbent to be treated as radioactive waste should be capable of excellent volume reduction in terms of disposal and long-term safety management. To solve these concerns, Nuclear Environment Engineering & Development Co., Ltd.(NEED) has developed a manufacturing technology for mass-producing a high efficiency cesium adsorbent (HECA) in the form of beads which contain the prussian blue as a base element.

The HECA has the merits of high selective adsorption performance for cesium, stability of cesium immobilization, high waste volume reduction rate, and long-term safety of waste management. Therefore, the decontamination technology using HECA enables a simple operation process of the decontamination facility. Thus, it can be effectively used for removing cesium from water, incineration fly ash, and soil at low cost.

2. Characterization of high-efficiency cesium adsorbent (HECA)

2.1 Prussian blue and HECA

Prussian blue is a royal blue pigment and is a hydrate of ferrocyanide with a uniform lattice structure. The length of one side of the prussian blue lattice is about 0.5 nm, which is similar to the size of hydrated cesium, so it is particularly excellent in selectivity adsorption for radioactive cesium ion. [2] [3]

NEED has confirmed that the cellulose hydrogel containing prussian blue can remove cesium efficiently and selectively in aqueous solution. Hydrogel is a hydrophilic polymer material having a three-dimensional network structure that can contain a large amount of water. It is thermodynamically stable after formed as beads in an aqueous solution, and due to its unique hydrophilicity and flexibility, it is used in various fields. NEED developed mass production technology of HECA by using such principle simply and economically.

2.2 Structure of HECA

Figure 1. shows the SEM image of HECA. When HECA is freeze-dried, it can be seen that it has a three-dimensional structure with a large number of pores inside (Figure 1A). Fig. 1B shows that prussian blue nanoparticles are well deposited on the HECA internal surface, and Fig. 1C shows that the prussian blue was uniformly deposited on the 1 and 2 dimensional structures inside the HECA to form a 3D structure and

effectively synthesized.

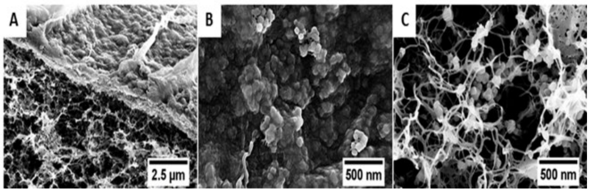

Figure 1. SEM image of HECA, (A) cross section, (B) surface, (C) inside.

2.3 Analysis of cesium adsorption mechanism of HECA

Figure 2(A) shows the adsorption isotherm results comparing the adsorption amount in equilibrium when HECA adsorbs cesium at the various cesium concentrations. This is analyzed to understand the mechanism by which HECA adsorbs cesium to reach chemical equilibrium, and the adsorption performance of HECA to cesium can be analyzed using the Langmuir and Freundlich isotherm model of adsorption experiment results. The maximum adsorption amount (qmax) of cesium in HECA is estimated as 15.38 mg/g, which means that 15.38 mg of cesium can be removed using 1 g of adsorbent (Table 1). This shows that 1 liter of a solution of 15 ppm cesium can be purified by using 1 gram of HECA. The adsorption strength (n) of HECA to cesium is 4.55, which has a value between 1 and 10, indicating that HECA has a strong affinity for cesium (Table 1).

Table 1. Variables of the isotherm model for the adsorption of cesium in HECA

Langmuir isotherm model			***Freundlich isotherm model***		
K_L (L/mg)	q_{max} (mg/g)	*R2*	K_F (L/mg)	n	*R2*
0.23	15.38	0.95	3.67	4.55	0.90

Fig. 2(B) shows the kinetic results of cesium adsorption of HECA and is used to analyze the rate of adsorption of cesium of HECA. HECA reaches equilibrium within 30 minutes in the 0.1, 1, and 5 ppm of Cs waters respectively which means that the three-dimensional HECA can effectively pull cesium and fix it.

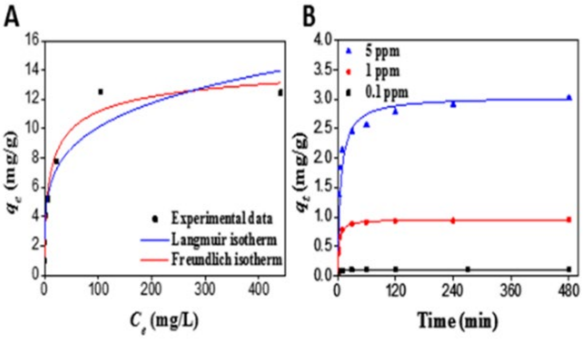

Figure 2. Results of cesium adsorption experiment of HECA, (A) Modeling of adsorption test results using isothermal adsorption test results and Langmuir, Freundlich isothermal adsorption model equations. (B) Modeling of adsorption test results using adsorption motion test results and secondary adsorption motion equations.

Figure 3 shows SEM-EDS image for the distribution of Fe and Cs atoms in HECA after the cesium adsorption reaction. Fe represents the distribution of prussian blue nanoparticles (Figure 3B), and Cs represents the distribution of cesium atoms adsorbed and recovered inside HECA. It can be seen that prussian blue nanoparticles are uniformly coated and distributed inside HECA, and cesium ions are effectively diffused and adsorbed into prussian blue.

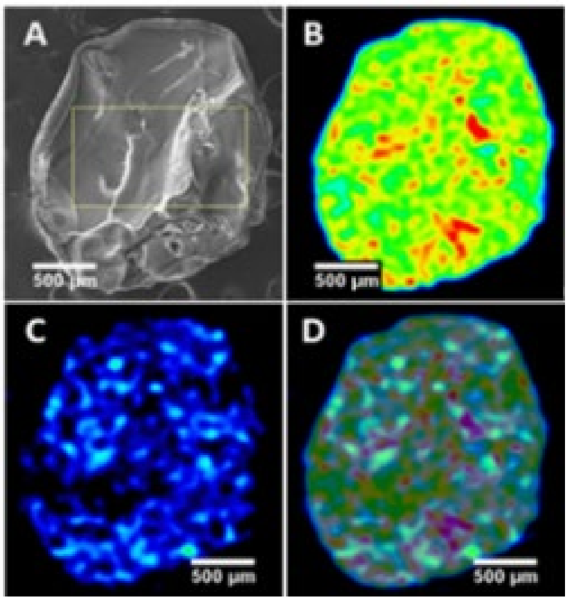

Figure 3. (A) SEM image inside HECA after cesium adsorption reaction. (B) Distribution of Fe atoms. (C) Distribution of Cs atoms. (D)) Merging of Fe and Cs atomic distributions.

2.4 Physicochemical stability analysis of HECA

Physicochemical stability against radiation is important because radioactive cesium adsorbents adsorb cesium isotopes that emit gamma rays, which are high-intensity energy. Figure 4 is an experiment to analyze whether prussian blue nanoparticles are eluted from HECA by measuring the UV absorbance of the aqueous solution after irradiation with gamma rays of 0, 6, and 60 kGy, assuming the adsorption of radioactive cesium of HECA. In the aqueous solution in which prussian blue nanoparticles are dispersed, a specific absorbance peak appears at 690 nm, but there is no difference in absorbance of HECA even after irradiation with gamma rays, which means that the physicochemical structure is stably maintained without eluting prussian blue nanoparticles.

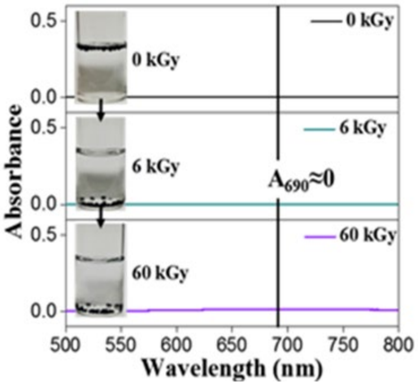

Figure 4. Results of stability test of HECA against gamma rays

2.5 Quantitative analysis of prussian blue nanoparticles eluted in HECA

If the prussian blue nanoparticles are eluted in the cesium removal process, this results in release of the radioactive cesium-adsorbed prussian blue to nature. The release of prussian blue may signify release of cyanide which can cause secondary contamination to the environment. So, prussian blue should not be eluted from the adsorbent. In order to confirm whether this problem is occurred in this process, the solution of the outer flow and the reservoir tank were analyzed with an ultraviolet and visible ray spectroscopy. (Figure 5)

Prussian blue nanoparticles show absorbance at a specific wavelength of 690 nm, and both the outlet water and the reservoir tank showed zero absorbance at the above wavelength. This reveals that prussian blue was not eluted from HECA, and it can be seen that cesium can be stably and effectively absorbed and settled in the HECA when applied to the actual decontamination industry site.

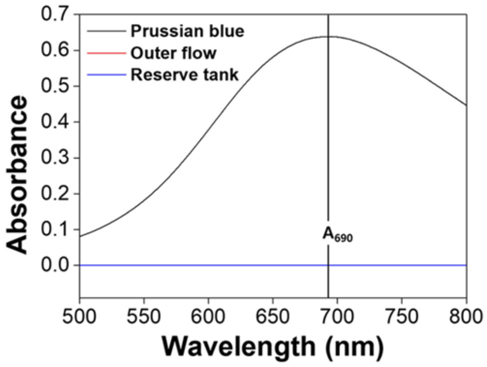

Figure 5. Prussian blue nanoparticle elution experiment results using a spectroscope.

2.6 Improvement to increase the amount of cesium adsorption

The above characteristic analysis described the contents that were tested based on HECA with a 5% prussian blue content at the beginning of HECA research and development. NEED has conducted research on diversifying the content of prussian blue to maintain the long-term performance of HECA, and developed the improved HECA showing more than twice the adsorption performance by increasing the prussian blue content than the initial stage. As a result of the performance test on the incineration ash washing water with TDS of 25,000~30,000 PPM and about 10,000 PPM of cesium competition ion (K, Ca, Na, etc.) using the improved HECA, the adsorption performance of 99.9% was continuously achieved for 4 days. This result reveals that the improved HECA has remarkably higher performance than the HECA of early stage.

3. Performance comparison of HECA & zeolite adsorbent

The adsorption capacity of cesium to prussian blue-based HECA and zeolite-based adsorbents was compared. The adsorbent used in the experiment was HECA and a zeolite-based fibrous radioactive cesium adsorbent manufactured by Kasai Co., Ltd. in Japan. In order to compare the adsorption rates of these adsorbents, an experiment was conducted in the same manner, in which samples were collected and analyzed 5 times a day and a total of 20 samples were analyzed for 4 days at 1-hour intervals. As a result of comparing and analyzing, HECA showed excellent performance as a cesium-selective adsorbent. Prussian blue-based HECA maintained a constant adsorption performance of almost 99.99% on average, while the zeolite-based fibrous cesium adsorbent decreased the adsorption rate (about 52% on average) as shown in Fig 7.

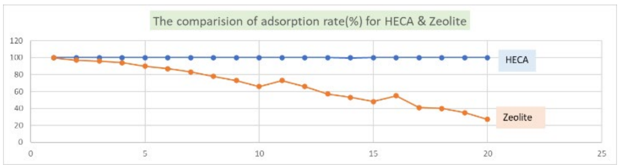

Fig 7. Trend of cesium adsorption performance for HECA and zeolite

4. Conclusion

NEED has developed a manufacturing technology that can mass-produce high efficiency cesium absorbent (HECA) by using prussian blue, which has excellent cesium adsorption, as a base material. It was manufactured in the form of beads in consideration of the easy recovery of the adsorbent, and the interior of the adsorbent has a structure in which multiple micropores are existing in order to maximize the cesium adsorption reaction area.

When the adsorbent is dried at a low temperature of 100°C or less, the volume of the adsorbent is reduced to 1/10 because the solid content of the adsorbent is about 10%, and the volume of waste is reduced while cesium is fixed. Therefore, HECA is very advantageous for the handling, storage and disposal of radioactive waste.

The decontamination technology of the advanced cleaning method using HECA simplifies the process, minimizes the exposure dose to work, and reduces the disposal cost due to the high-volume reduction rate of the adsorbent, thus minimizing the overall decontamination cost. It is expected that the decontamination process of the advanced cleaning method using HECA can effectively respond to the removal of radioactive cesium from contaminated water, incineration fly ash, and soil, etc.

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