

Economic Feasibility Analysis and Potential Design Suggestion of Novel Cesium Adsorbents

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1. Introduction

Severe accident and decommissioning can be source of cesium contamination. Therefore, for long-term operation of nuclear facilities, environmental remediation and waste management remain a key priority. Due to its long half-life and water-soluble character, it easily transfers in the soil and groundwater. Because it is chemically similar to potassium, it is difficult to decontaminate cesium.

To decontaminate cesium from liquid solution, there are some technologies such as coprecipitation, evaporation, and adsorption/ion exchange. In cases of large-scale release or decommissioning, due to their large volume and extremely low cesium concentration, adsorption with ion exchange is suitable for decontamination.

A variety of cesium adsorbents such as zeolite, crystalline silicotitanates, aluminum molybdophosphate, chalcogenides have been considered for cesium decontamination from liquid solution. However, there are some problems remained. Current adsorbents' low selectivity, radiation stability, and adsorption capacity limit their application in real situation.

Although there are a variety of commercially available cesium adsorbents, there is not enough information of cesium adsorbents cost. Due to the lack of cost-benefit analysis information, it is difficult to apply cesium adsorbents for specific situations.

In order to apply cesium adsorbents during the severe accident, it is necessary to design an engineering system considering the situation at the time of severe accident.

The first objective of this research is to develop novel cesium adsorbents, and analyze their chemical and radiation stability. The second objective of this research is to assess cost-benefit analysis of novel cesium adsorbents, and design an engineering system to apply novel cesium adsorbents for a real situation.

2. Methods

2.1 Development of Two New Novel Cesium Adsorbents, and Analysis of Mechanical and Radiation Stability

Korea Advanced Institute of Science and Technology (KAIST) Chemical & Biomolecular Engineering Energy Fundamental Design Laboratory developed two novel adsorbents: HCF-gels and HPC.

The first novel Cs⁺ adsorbent is HCF-gels. We performed three test. pH stability test was evaluated by

submerging 10 mg of HCF-gel in 20mL of 2mmol L⁻¹ Cs⁺ solution of varying pH for 24h. Removal efficiency test was evaluated with a batch-shaking method. Here, adsorbent was immersed in CsCl (¹³³Cs) aqueous solution with ratio of 2000mL g⁻¹. Selectivity test was evaluated by submerging 25 mg of HCF-gel in 50mL seawater(Na⁺, Mg²⁺, K⁺, Ca⁺) of various Cs⁺ solution for 24h.

The second novel adsorbent is HPC. Experimental design of HPC is similar to that of HCF-gels. pH dependent removal efficiency test was evaluated by submerging 50 mg of HPC in 50ml Cs⁺ solution at 25°C of varying pH for 24h.

The followings are the processes of radiation stability experiment. First, prepare adsorbent. HCF-gel was used for the adsorbent here. Set realistic decontamination scenario, and calculate time, distance, and dose using MCNP code. Second, irradiate the adsorbent using radioactive cesium 137 (Here, 8.51*10⁹ Bq, 0.851 ratio, Gy=J/kg). Third, conduct adsorption test and XRD test, and compare removal efficiency and material stability before and after irradiation.

2.2 Cost Benefit Analysis, and Potential Design Suggestion for Severe Accident

Commercially available cesium adsorbent was evaluated under the same experimental condition to compare with HCF-gels and HPC in terms of adsorption capacity and selectivity.

New pool scrubbing system was suggested for engineering system design to apply novel Cs⁺ adsorbents under severe accident condition. Jet impaction at the orifice, convection/diffusiophoresis during steam condensation, thermophoresis, sedimentation, centrifugal impaction during bubble rise, and Brownian diffusion were considered for modeling aerosol removal mechanism.

3. Results

3.1 Development of Two New Novel Cesium Adsorbents, and Analysis of Mechanical and Radiation Stability

The first novel Cs⁺ adsorbent is HCF-gels. As we can see here, potassium copper hexacyanoferrate is immobilized in a cellulose-based hydrogel. Cesium adsorption occurs both in KCuHCF and carboxylate of carboxymethyl cellulose in HCF-gels.

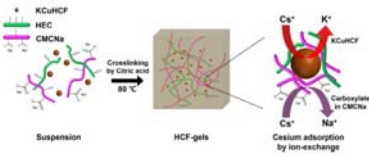


Fig. 1. Schematic diagram of cesium adsorption of HCF-gels

Figure 2 shows pH effect and removal efficiency of HCF-gels. 1.5-1.9 mmol/g of Cs^+ is adsorbed over a wide pH range of 4-11. At low pH, the decrease is related to a competition effect between H^+ and Cs^+ . However, it is still quite high. In terms of removal efficiency, the HCF-gel-1 was observed to remove more than 99% of Cs.

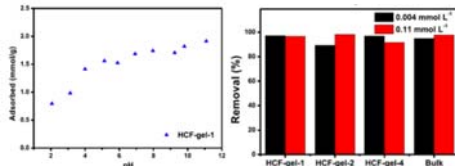


Fig. 2. pH effect and removal efficiency of HCF-gels

K_d is used to evaluate the Cs^+ selectivity and calculated the order of 10^4 - 10^5 mL/g. These values in seawater comparable with DI water. Remarkably, there is rapid Cs^+ removal (90.1% for 0.15 mmol L^{-1} of Cs^+ in 1h). Adsorb Cs^+ selectively in seawater containing 0.11 mmol L^{-1} of Cs^+ .

Table I: Distribution coefficient (K_d) values of HCF-gel

Sample	K_d (mL/g) [#]	K_d (mL/g) ^{##}	K_d (mL/g) ^{###}
HCF-gel	3.81×10^4	1.81×10^5	6.09×10^4

[#] K_d for DI water solution (0.07 mmol L^{-1} of Cs^+).

^{##} K_d for seawater solution ($0.004 \text{ mmol L}^{-1}$ of Cs^+).

^{###} K_d for seawater solution (0.11 mmol L^{-1} of Cs^+).

The second novel adsorbent is HPC. As we can see here, HPC represents potassium copper hexacyanoferrate-embedded poly(vinyl alcohol)-citric acid hydrogel film (HPC).

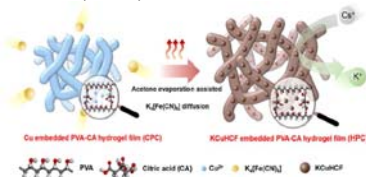


Fig. 3. Schematic diagram of cesium adsorption of HPC

HPC shows almost 99.9% Cs^+ removal efficiency over a wide pH range of 2-10. At pH 12, the removal performance slightly decreased due to the decomposition of HCF in a high alkaline condition.

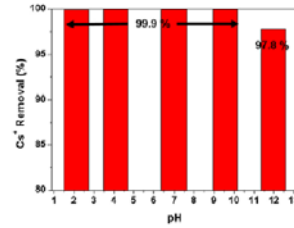


Fig. 4. pH effect and removal efficiency of HPC

HPC also has high distribution coefficient K_d value at an extremely low Cs^+ concentration (0.67 ppm , $\text{V/m} = 1000 \text{ ml/g}$). Remarkably, there is rapid Cs^+ removal (99.5% for 9.18 ppm of Cs^+ in 30 min). Adsorb Cs^+ selectively in seawater containing 0.67 ppm of Cs^+ .

Table II: Distribution coefficient (K_d) values and removal efficiency of HPC

Sample	C_0 (ppm)	K_d (mL/g)	% Removal
HPC	10.30 ppm in seawater	2.33×10^5	99.57
HPC	2.92 ppm in seawater	2.95×10^5	99.66
HPC	0.67 ppm in seawater	7.74×10^5	99.87

Figure 5 shows schematic diagram for MCNP simulation. The red color represents HCF-gel on the paper which color is yellow. The blue color represents cs-137 and sky blue is shielding. The calculated dose, time, and distance was 0.5 Gy/hr , 24hrs, and 0.4 cm respectively.

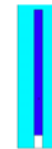


Fig. 5. Schematic diagram for MCNP simulation.

These are the results of removal efficiency and XRD result comparison. As we can see here, there is no big difference between before and after irradiation. Although RE after irradiation is slightly increased, it is ignorable. In terms of XRD result, the peak position did not change, and the intensity (Y-axis) did not change as well. Therefore, it is possible to say HCF-gel has good radiation stability.

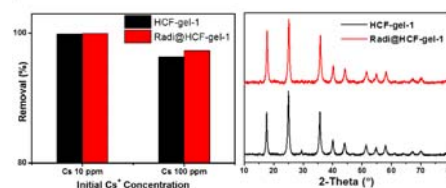


Fig. 6. Comparison removal efficiency and XRD result with

and without radiation

3.2 Cost Benefit Analysis, and Potential Design Suggestion for Severe Accident

First, cost of HCF-gel and HPC were calculated based on the material price, labor expenses, and the other expenses. Zeolite and CST were estimated according to the reference.

Second, removal efficiency was evaluated for both DI and seawater. HCF-gels, HPC, and zeolite were estimated by experiment. And CST data from UOP reference.

In cases of K_d value, pH range, and time needed for 99% removal of HCF-gel and HPC were evaluated by experiment. Zeolite and CST were estimated according to the reference.

Based on our cost-benefit analysis, it is possible to use specific adsorbents for specific situation.

For example, zeolite can be applied for various situation with lower cost. It is not effective to use zeolite for seawater, it would be better to apply this material for the final stage of decontamination.

In terms of CST. It has excellent RE, selectivity, and time for removal. We can use CST for various situation, especially for the first stage of decontamination.

Time and cost savings were estimated when we use our KAIST Cs adsorbents for the Fukushima seawater treatment.

Table III: Cost-benefit analysis of various Cs adsorbents

		HCF-gel	HPC	CST
Cost (\$/ton)		23,250	52,560	1,595,000
RE	DI water	94%	99%	99%
	Seawater	96%	99%	99%
K_d , ml/g		10^4 - 10^5	$>10^5$	10^4 - 10^5
pH range 4-11		1.5-1.9 mmol/g	97-99% RE	10^3 - 10^5 K_d
Form		Flake	Flake	Beads Membrane
Specific situation		First stage, seawater	First stage, seawater	First stage, seawater

Potential design scenario for steam generator tube rupture (SGTR) under severe accident. Under SGTR, it is difficult to remove CsI which diameter is 0.1-0.5 μm .

On the other hand, HEPA filter can adsorb 0.2 μm of CsI very effectively. However, it cannot stand alone due to the pressure difference. Therefore, pool scrubbing system is needed. Pool scrubbing will be applied before HEPA filter.

Our design is "Pool scrubbing + Storage tank + HEPA filter". After pool scrubbing system, Cs contaminated water moves to storage tank. Here, using our Cs adsorbents, contaminated water will be decontaminated. And then it will go to HEPA filter. To

analyze pool scrubbing system, aerosol removal through gaseous injection into water was developed and verified.

Decontamination factor (DF) can be decided jet impaction multiplied by the other mechanism. At small diameter, Brownian diffusion is a dominant. For future work, maximum value of DF will be studied.

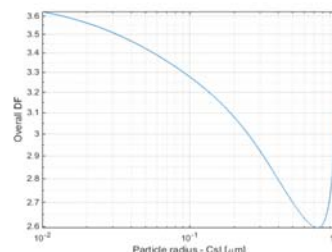


Fig. 7. Overall DF result of pool scrubbing system

3. Conclusions

Two novel adsorbent materials were developed. Their physical and chemical characteristics were investigated. Preliminary results show two adsorbents can be applied to a wide range of pHs while maintaining a high removal efficiency. The combination of testing and radiation stability results indicated that the performance of the material is maintained whether irradiated or not. The novel adsorbents can be applied for decommissioning radiation environment (0.5Gy/hr).

KAIST novel cesium adsorbents are cost competitive. Engineering system design specific to applying the KAIST adsorbents was developed.

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