

## Feasibility Study in using Bismuth-embedded SBA-15 for Gaseous Iodine Adsorption during Nuclear Severe Accident Mitigation

Seong Woo Kang<sup>1</sup>, Man Sung Yim<sup>2</sup>

<sup>1</sup> Nuclear and Quantum Engineering at Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Korea.  
Email: seongwookang@kaist.ac.kr

<sup>2</sup> Corresponding Author. Nuclear and Quantum Engineering at KAIST.  
Email: msyim@kaist.ac.kr

### 1. Introduction

Since Fukushima accident, there have been many studies showing appropriateness of using the criteria of limiting the release of cesium-137 into the environment in excess of 100 TBq to be less than  $5 \times 10^{-7}$  per reactor-year. South Korean National Assembly amended the Nuclear Safety Act in 2015 to stipulate the regulatory control on severe accident in legal basis, by setting legally-binding limit for the nuclear power plants to keep the probability of cesium-137 exceeding 100 TBq under  $10^{-6}$  per reactor-year [Silva K, Okamoto K, 2018]. To meet such similar requirements, the nuclear industry has begun to develop not just the preventive but also the mitigative technologies that can limit the spread of radioactive materials into the environment.

Even when mitigative systems work properly to capture the radioactive materials, the amount of the steam and the radioactive materials released from nuclear severe accidents may be too large to contain in a closed system. Thus, these mitigative systems typically are designed to let the radioactive materials flow through filtration systems before ultimately releasing the treated materials into the environment. Since cesium and iodine are majority of the radioactivity released into the environment during severe accidents, the mitigative system should effectively capture and filter the cesium and iodine before releasing the filtered materials into the atmosphere.

While the technology for cesium capture is mature and cost-effective, iodine absorption technology can be improved. Sorbents developed to filter gaseous iodine include activated charcoal, macroreticular resin, silver-exchanged zeolites (AgX or AgZ), silver-functionalized silica aerogels, and metal-organic frameworks. Among these, silver-exchanged zeolites are most commonly used for filtering iodine. However, disadvantages of the silver-exchanged zeolites include high price and toxicity. Thus, bismuth-embedded SBA-15 (or Bi-SBA-15) has been researched as a possibly more cost effective alternative by [Yang, Jae Hwan, et al., 2015].

The purpose of this study is to examine the optimum synthesis process for bismuth-embedded SBA-15 for cost-reduction and its performance in open field application as gaseous iodine filtration material to be used during the environmental release accident mitigation.

### 2. Bismuth-embedded SBA-15 Synthesis with Reduction in Cost

The ratio of Pluronic P123, tetraethyl orthosilicate (TEOS), and MPTMS used in this experiment were 4g, 27mmol, and 14mmol, respectively because this combination gave optimal results in the reference [Yang, Jae Hwan, et al, 2015]. Following the general procedure from the aforementioned reference produced around 3g of Bi-SBA-15. The improved procedure listed in this section yields about 10g of Bi-SBA-15 as final product while saving time. The corresponding original times for the steps listed in this section may be found in the reference [Yang, Jae Hwan, et al, 2015].

First, 12g of Pluronic P123 (Sigma-Aldrich, Mw = 5,800) is dissolved in 375ml of 1.9M HCl solution for about 2~3 hours at 40°C. Then, 18ml of tetraethylorthosilicate (TEOS, Sigma-Aldrich, 95%) was added into the micellar solution and was stirred at 40°C for 3~4 hours. Afterward, 8ml of MPTMS (Sigma-Aldrich) was added and the mixture was kept stirring at 40°C for 12+ hours. This resulted in sol-gel reaction of the mixture. The resultant white mixture was poured into a PTFE bottle, and it was kept it for 15+ hours at 120°C. This hydrothermally treated mixture was filtered using vacuum pump to recover a solid product, which was then dried at 60°C inside furnace for 15+ hours.

There were still surfactants within this solid product to be removed through solvent extraction. The solid product was refluxed for 12+ hours in 1.5L of ethanol. The original procedure from [Yang, Jae Hwan, et al, 2015] recommended ratio of 3g of the solid sample reflux with 800mL of ethanol for 24 hours (i.e. somewhere between 6~8 L of ethanol to be used for refluxing, if following the procedure from this section). However, it was enough to use 1.5 L of ethanol in total when 1) the solid product was powdered before the reflux and 2) magnetic stirrer was used to stir the mixture during the refluxing. These two steps were used to facilitate the solvent extraction successfully with reduced cost from reducing the amount of ethanol to less than one-fourth.

Then the refluxed material was filtered again to recover the resulting solid product, which was powdered again to increase the surface area of the SBA-15 per

given mass. The recovered product was then dried for 8+ hours at 60°C.

For bismuth adsorption, the thiol-functionalized SBA-15 was submerged into 400+ml of bismuth solution for 6+ hours at 60°C. The bismuth solution was prepared by refluxing 12.5g BiCl<sub>3</sub> to 500mL methanol for 2 hours (the original procedure recommended ratio of 5g BiCl<sub>3</sub>: 100mL methanol). This step resulted in 1) the insoluble bismuth oxychloride and 2) the bismuth solution. Only the clear bismuth solution was used to impregnate the SBA-15 (i.e. insoluble bismuth oxychloride was filtered beforehand). After the impregnation was completed, the yellow-turned solid sample was filtered and was dried at 60°C for 8+ hours. Since iodine adsorption is significantly affected by bismuth oxidation rate [Yang, Jae Hwan, et al, 2015], the yellow Bi-SBA-15 was thermally treated at 250°C for 6 hours in 3.9% H<sub>2</sub>/Ar reducing atmosphere, yielding the end product to be used for the iodine adsorption.

However, this optimization of the procedure (reducing time and monetary cost from the original procedure) to produce Bi-SBA-15 did not yield in loss of gaseous iodine adsorption efficiency. This is shown in Figure 1, which was performed as closed experiment at 150°C with long reaction time (over 6 hours) with very high iodine concentration (2g of iodine per 0.2g of Bi-SBA-15) [Yang, Jae Hwan, et al, 2015]. The equation used to calculate the iodine capturing capacity of the sorbent was found using the Eq. 1.

$$C = \frac{m_{s,f} - m_{s,i}}{m_{s,i}} \quad (1)$$

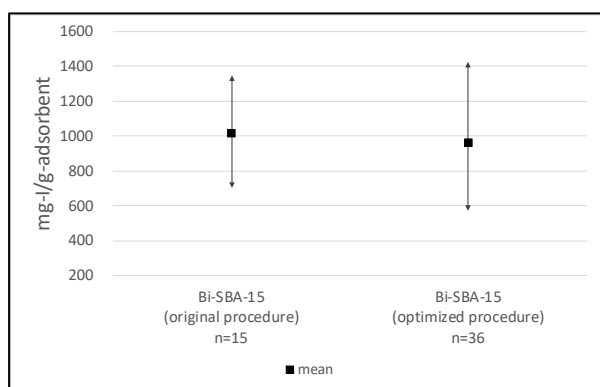


Figure 1. Comparison of the iodine adsorption capacity for original procedure and improved procedure

Through trial and error, 1) the amount of final product was increased while maintaining similar filtration efficiency; 2) the overall synthesis time was reduced; and 3) the monetary cost was reduced (reduced use of ethanol and BiCl<sub>3</sub>, which are two biggest cost-drivers in the material cost of synthesizing Bi-SBA-15). This resulted in the synthesis of the Bi-SBA-15 used in the iodine capture experiment in rest of this paper.

### 3. Open Iodine Adsorption Experiments at Various Temperatures

In the actual filtration system, the Bi-SBA-15 must capture the iodine flowing through the filtration system (i.e. not in a closed system but in an open system). If the iodine filtration system is at the end of the overall filtration system (which may include pool scrubbing), the flow rate may become comparable to the natural flow by the time it reaches the end. This is since the captured radioactive materials would first flow through the suction system and the aerosol filtration system (including pool scrubber, which would reduce temperature and speed, in theory) [Ullah, Sana, et al. 2018]. Passing these intermediate sub-systems would allow the radioactive material to lose energy and thus result in decrease in the speed of the gaseous iodine.

Thus, an opened iodine capture experiment was performed allowing the iodine to flow outside the crucible naturally through evaporation. In the open experiment, 0.25 or 0.50 [g] of iodine and X [g] of sorbent (i.e. 1x iodine to 4x, 6x, or 8x sorbent) was used per sample to test the capture efficiency when the iodine flows out naturally after evaporation. This allowed the iodine gas to escape the alumina crucible as soon as the iodine beads evaporated. The experimental temperature was set at 250°C for a conservative measure. It was based on a judgement that the gaseous iodine temperature would likely not go over 250°C by the time it reaches the gas filtration sub-system, which is at the end-point of the overall mitigation system. Since the iodine adsorption capability decreases at higher temperature, if the adsorbents can capture the iodine with high efficiency at 250°C, it would be able to capture the iodine at lower temperature.

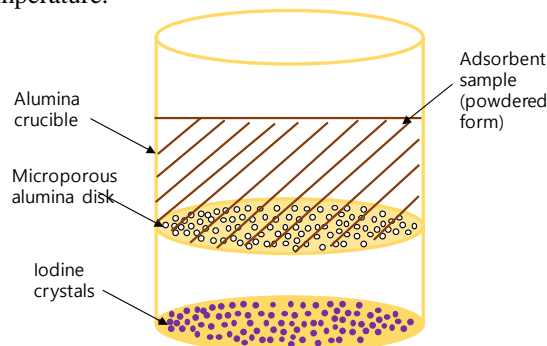


Figure 2. Experimental Setup for Open Iodine Capture Experiment

The iodine capture efficiency in the experiment was calculated using the following:

$$\eta = \frac{m_{I,abs}}{m_{I,o}} = \frac{m_f - m_{s,i} \times f}{m_{I,o}} \times 100\% \quad (2)$$

where  $\eta$  is iodine capture efficiency,  $m_{I,abs}$  and  $m_{I,o}$  are absorbed and initial mass of the iodine respectively,  $m_f$  is the final product mass measured,  $m_{s,i}$  is the initial mass of the sorbent, and  $f$  is the percent of the sorbent mass left during the control experiment without iodine (to account for mass change of the sorbent). Equation 2 was derived to account for the mass change of the sorbent itself during the experiment. Results of the open experiments are shown in Figure 3.

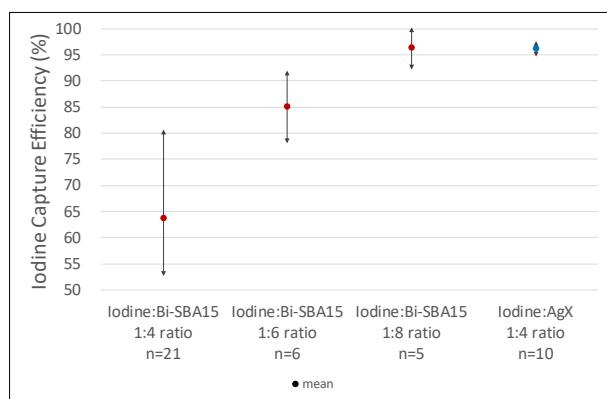


Figure 3. Iodine Capture Efficiency of Bi-SBA-15 and AgX in Open Iodine Capture Experiment

In an opened experiment where the iodine gas was allowed to move out of the crucible through natural flow, the average iodine adsorption efficiency for Bi-SBA-15 was 64, 85, and 96% for the mass used 4x, 6x, and 8x the mass of iodine, respectively. At 1:8 mass ratio of iodine to Bi-SBA-15, the sorbent showed iodine adsorption efficiency of above 90% (minimum experimental results showed 92%). As a comparison, only 4x the mass of iodine was required for AgX to capture iodine with an average of 96%. This experiment showed that at 250°C, more than twice the silver zeolite may be required if Bismuth-embedded SBA-15 is to be used for iodine adsorption during severe accident mitigation.

#### 4. Discussions

Although the amount of Bi-SBA-15 required to adsorb iodine was more than two times higher than the amount of AgX, the cost of Bi-SBA-15 should be much cheaper once it can be produced in mass production, as cost of bismuth is much cheaper than silver, which is one of main cost drivers for production of silver zeolites. The open experiment was held at 250°C, but if the radioactive gas flows at much lower temperature by the time it reaches the gaseous iodine filter (which may happen if the gas goes through various filtration sub-systems such as pool scrubbers and/or centrifugal filtration). Thus, depending on the design of the overall severe accident mitigation system, Bi-SBA-15 may be used as effective iodine adsorption material for the overall filtration system.

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