

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

Lab Seminar  
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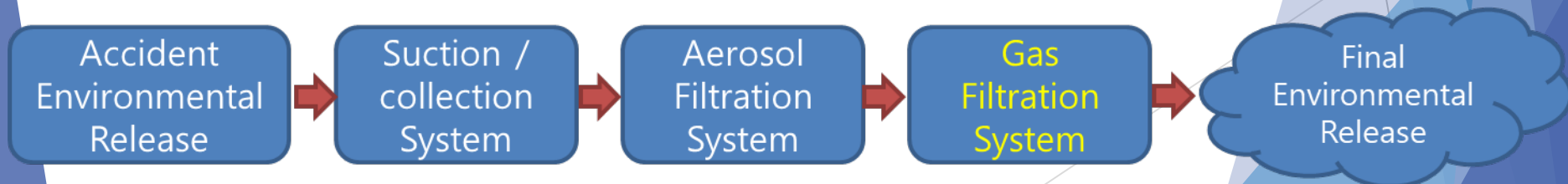
- I. **Purpose and Objective**
- II. Literature Review
- III. Current Work
- IV. Summary

# I. Background

- ▶ After accident in Fukushima, many countries (including Korea) began to pass laws to use 100 TBq of cesium-137 release as a part of the probabilistic risk criterion
  - ▶ Core damage frequency  $< 10^{-5}$  (or  $10^{-6}$ ) / reactor year (RY)
  - ▶ Large release frequency  $< 10^{-6}$  (or  $10^{-7}$ ) / RY
  - ▶ Frequency with greater than 100 TBq Cs-137 release  $< 10^{-6}$  / RY
- ▶ Problem:
  - ▶ Bypass accidents - specifically steam generator tube rupture (SGTR) and interfacing-systems loss-of-coolant accidents (ISLOCA)
    - ▶ An unmitigated individual event is usually in order of  $10^{-6}$ ~ $10^{-7}$  / RY, so if frequencies of all these events are added, it may be difficult for current nuclear power plants to meet the new regulation
- ▶ Solution:
  - ▶ Reduce accident frequency
  - ▶ Reduce accident consequence

# I. Purpose and Objective

- ▶ KAIST NENS severe accident group is developing new technologies to effectively 1) capture and 2) treat environmental radioactive releases from unmitigated steam generator tube rupture (SGTR) accidents
- ▶ My objective: develop a **cost-effective** filtration system to filter/treat the radioactive gaseous iodine
  - ▶ A part of a comprehensive environmental dispersion mitigation system for nuclear severe accidents
  - ▶ May be used for wider range of accidents/purposes in filtering gaseous iodine



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## II. About Iodine in Severe Accidents

- ▶ Iodine contribute the most to the radioactivity released into the environment, if a severe accident with environmental releases occurs
- ▶ Releases of iodine into containment during severe accident
  - ▶ In the primary coolant, most of the iodine will likely be transported in a form of CsI and may be released into the containment in that form initially
  - ▶ Iodine ions predominate in aqueous solutions except under oxidizing conditions
  - ▶ Iodine ions may become re-vaporized and be released as elemental iodine at higher temperature

## II. About Iodine in Severe Accidents

- ▶ Environmental releases of iodine in unmitigated SGTR
  - ▶ From NRC RG 1.183 “Alternative radiological source terms for evaluating design basis accidents at nuclear power reactors,” iodine releases from the steam generators to the environment should be assumed to be 97% elemental iodine, 3% organic iodide (i.e. gaseous form)
- ▶ In general, iodine may be removed through
  - ▶ Wet scrubbing
  - ▶ Solid sorbents

## II. Wet Scrubbing

- ▶ Gaseous iodine compounds are collected into a liquid solvent using high concentration of reactants
  - ▶ Water with sodium thiosulfate widely used as additives
  - ▶ Alkaline scrub (NaOH), Mercurex ( $\text{Hg}(\text{NO}_3)_2 + \text{HNO}_3$ ), Iodox ( $\text{HNO}_3$ )
    - ▶ Remove through chemical reaction
- ▶ Advantages
  - ▶ Both organic and elemental iodine can be removed with high efficiency
  - ▶ Can effectively cool the incoming gases and aerosols
- ▶ Disadvantages
  - ▶ Relatively complex process design
  - ▶ High maintenance costs
  - ▶ Corrosion of solvent container due to highly corrosive scrubbing solutions
  - ▶ Additional processing is needed prior to permanent disposal



## II. Solid Sorbents

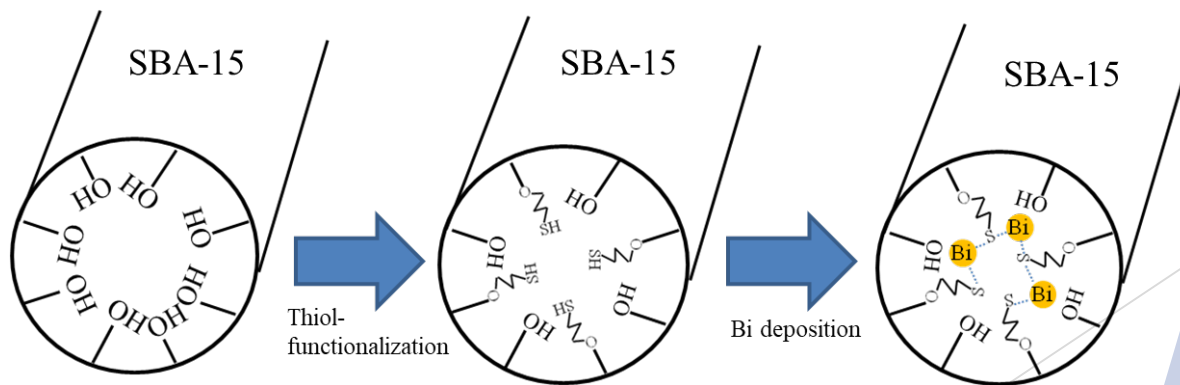
- ▶ Gaseous iodine compounds are collected using solid sorbents
- ▶ Charcoal, macroreticular resin, metal-incorporated zeolites
  - ▶ Physisorption and chemisorption
- ▶ Advantages:
  - ▶ Relatively simple system with few moving parts
  - ▶ No use of corrosive media
  - ▶ Relatively low maintenance costs
  - ▶ No additional processes required to separate iodine compounds
- ▶ Disadvantages:
  - ▶ Poorer performance at high temperature, especially for activated-carbon and macroreticular resin
  - ▶ Most metal zeolites are inefficient in absorbing iodine except silver

## II. Current Standard of Materials

- ▶ Charcoal and silver zeolites - current standard of materials for designing dry iodine filters
- ▶ Disadvantages of charcoal
  - ▶ Poorer performance at high temperature
  - ▶ Must ensure relative humidity of air is controlled
  - ▶ Low ignition temperature of TEDA (tri-ethylene-di-amine)
- ▶ Disadvantages of silver zeolites
  - ▶ High cost of silver: \$211~255 per pound (USGS, Mineral Commodity Summaries, 2019)
  - ▶ For iodine capture, not just chemisorption with silver but also physisorption through zeolites - not thermally stable
  - ▶ Toxicity of silver (strictly regulated by EPA)

## II. Bismuth-based solid adsorbent

- ▶ Dr. Yang has researched for new effective iodine adsorbent using bismuth to capture iodine released during spent fuel reprocessing
  - ▶ Large affinity for iodine
  - ▶ Cheaper: \$4.15~5.30 per pound (USGS, Mineral Commodity Summaries, 2019)
  - ▶ No or little physisorption: increase thermal stability
  - ▶ Less toxic compared with other heavy metals (e.g. silver)
  - ▶ Tested high removal efficiencies compared with AgX
- ▶ Thiol-functionalization of SBA-15 surfaces, followed by Bi deposition and reduction



<Concept of synthesizing Bi deposited SBA-15>

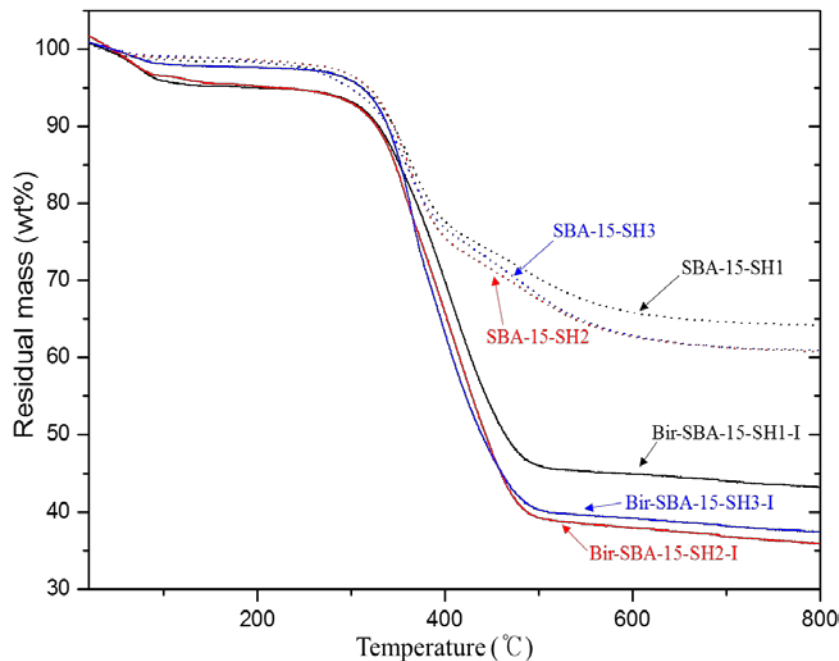
## II. Bismuth-embedded SBA-15: Problems

1. It takes long time to synthesize the small amount of samples (2~3g final product and over 7 days per cycle).
  - ▶ Not guaranteed similar iodine capture capacity if same synthesizing steps are followed with increase in the amount
2. Is it really cost effective?
  - ▶ AgX - 626,600 KRW/100g or about **6,300 KRW per gram** (Sigma Aldrich, May 2019)
  - ▶ Synthesizing Bi-SBA-15 following Dr. Yang's synthesis steps, over **10,000 KRW/g** required in materials cost only!
    - ▶ Cost driver: MPTMS, ethanol,  $\text{BiCl}_3$
    - ▶ Over 10,000 KRW/g even using cheaper chemical companies such as Samchun rather than famous ones such as Merck/Sigma-Aldrich for basic chemicals such as HCl,  $\text{BiCl}_3$ , MeOH, and EtOH

## II. Bismuth-embedded SBA-15: Problems

### 3. Efficiency decreases at higher temperature

- ▶ As expected, when the temperature increases, the capture efficiency decreases (below figure shows that indirectly), starting around 100 °C and especially after 300 °C
- ▶ Thus it may not be suitable for iodine released during severe accident



- Curves for the samples prior to iodine capture are presented with a dashed line
- Curves for bismuth-embedded SBA-15 after iodine capture are shown with a solid line

<Obtained data using thermogravimetric (TGA) analysis by Dr. Yang for various Bi-SBA samples>

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### III. Bismuth SBA-15 synthesis experiment

- ▶ Bi-SBA-15 synthesis optimization (reducing time and cost)
  - ▶ Time: more than 7 days -> 5 days
  - ▶ Amount: increased around 4 times the amount of the final product without loss of efficiency

A1	Bir-SBA-15-SH2 synthesis	Start Time	Duration
	1 Make 1.9M HCL (837g:163g distilled water: Junsei HCl)		0
	2 Dissolve <b>4g of P123</b> into <b>125g of 1.9 HCl</b> Solution for 1h	5/7/2018 9:00 AM	1:30
	3 Add 27 mmol of TEOS and stir at 40C for 3h ( <b>6ml</b> )	5/7/2018 10:30 AM	3:00
	4 Add 14 mmol of MPTMS and stir at 40C for 20h ( <b>2.6 ml</b> )	5/7/2018 1:30 PM	20:00
	5 Pour resultant mixture into a PTFE bottle, seal tightly, and keep it at 120C for 24h	5/8/2018 9:30 AM	24:00
	6 Filter the mixture to recover a solid product	5/9/2018 9:30 AM	0:45
	7 Dry the solid product at 40C for 24h	5/9/2018 10:15 AM	24:30
	8 Remove surfactants within the solid by refluxing with ethanol for 24h (1g per 100mL)	5/10/2018 10:45 AM	24:45
	9 Filter the mixture to recover a solid product	5/11/2018 11:30 AM	0:15
	10 Dry the product at 40C for 24h to get SBA-15-SH	5/11/2018 11:45 AM	24:15
	End Time	5/12/2018 12:00 PM	
B	SBA-15-S-Bi synthesis		
	1 Create bismuth solution by dissolving BiCl3 into boiling MeOH at a ratio of 2.5g:100mL at 80C for 1.5h of refluxing	5/12/2018 10:00 AM	1:45
	2 Take clear bismuth solution without BiOCl precipitate	5/12/2018 11:45 AM	0:15
	3 Impregnate dried SBA-15-SH with bismuth solution at a ratio of 1g:100mL for 6h at 40C	5/12/2018 12:00 PM	6:15
	4 Take the precipitate only (yellow-turned sample)	5/12/2018 6:15 PM	0:15
	5 Dry the precipitate at 40C for 24h	5/12/2018 6:30 PM	24:00
	6 Thermally treat the samples at 250C for 6h in 4% H2/Ar atmosphere to break P123	5/13/2018 6:30 PM	7:15
	End Time	5/14/2018 1:45 AM	

Start Time	Duration	No.	Crucible mass:
9/3/2018 09:00	1:30	1A	Dissolve <b>12g of P123</b> into <b>375ml of 1.9 HCl</b> Solution
9/3/2018 10:30	3:30	2A	Add 81 mmol of TEOS and stir at 40C ( <b>18ml</b> )
9/3/2018 14:00	17:00	3A	Add 42 mmol of MPTMS and stir at 40C ( <b>7.8 ml</b> )
9/4/2018 07:00	17:15	4A	Pour resultant mixture into a PTFE bottle, seal tightly, and keep it at 120C
9/5/2018 00:15	1:45	5A	Filter the mixture to recover a solid product using vacuum pump and filtration equipment
9/5/2018 02:00	16:15	6A	Dry the solid product at 50C
9/5/2018 18:15	0:15	7A	Make the dried product into powder
9/5/2018 18:30	14:25	8A	Remove surfactants within the solid by refluxing with ethanol ( <b>1.5L</b> )
9/6/2018 08:55	1:05	9A	Let the refluxed mixture to settle
9/6/2018 10:00	1:15	10A	Filter the mixture to recover a solid product using vacuum pump and filtration equipment
9/6/2018 11:15	9:00	11A	Dry the product at 50C to get SBA-15-SH
9/6/2018 11:25	0:10	12A	Create bismuth solution by dissolving BiCl3 into boiling MeOH at a ratio of 2.5g:100mL at 80C (reflux) <b>for at least 500mL</b>
9/6/2018 20:15	0:10	13A	Make the dried product from Step 11 into powder
9/6/2018 20:25	6:30	14A	Impregnate dried SBA-15-SH with clear bismuth solution without precipitate at a ratio of 1g:100mL <b>or about 400-450mL</b>
9/7/2018 02:55	0:30	15A	Filter the precipitate only (yellow-turned sample)
9/7/2018 03:25	9:05	16A	Dry the precipitate at 50C
9/7/2018 12:30	8:15	17A	Turn on the cooling for tube furnace, and thermally treat the samples at 250C in 4% H2/Ar atmosphere for 6h to break P123
9/7/2018 20:45			End A-cycle

### III. Bismuth SBA-15 synthesis experiment

► Bi-SBA-15 synthesis optimization (reducing time and cost)

► Cost: reduced by 1/4 and to less than cost of AgX (6,266 KRW/g)

Price	CAS	Chemical	Company	Amount	Unit	Note
8600	7647-01-0	Hydrochloric acid	Junsei	1	L	GR
170700	9003-11-6	PEG-PPG-PEG, Pluronic P-123	Aldrich	1	L	average Mn ~5800
83900	78-10-4	Tetraethyl Orthosilicate (TEOS)	Aldrich	500	mL	reagent grade 98%
143800	4420-74-0	MPTMS	Aldrich	100	g	95%
11400	67-56-1	Methanol	동양화학	3.8	L	EP
35700	64-17-5	Ethanol	OCI	3.8	L	EP
90000	7787-60-2	Bismuth (III) Chloride	Samchun	500	g	GR, >98%
626600	N/A	Silver-exchanged zeolite, granular	Aldrich	100	g	+20 mesh

Dr. Yang's Steps (~2.5g)		KRW per g	11,698
Chemical	KRW	Note	
HCl	175	Requires 125 mL	
P123	683	Requires 4g	
TEOS	1007	Requires 6mL	
MPTMS	3739	Requires 2.6mL	
EtOH	20042	Requires 3g of intermediate material: 800 mL, around 8-10g at this step (i.e. 2.4L)	
MeOH	900	Requires 300mL	
BiCl <sub>3</sub>	2700	Requires 15g (5g BiCl <sub>3</sub> : 100mL MeOH)	



Optimized Steps (~10g)		KRW per g	2,744
Chemical	KRW	Note	
HCl	561	Requires 375mL of 1.9M HCl, assumed 400 mL	
P123	2219	Requires 12g, assumed 13g	
TEOS	3356	Requires 18mL, assumed 20mL	
MPTMS	11504	Requires 7.8mL, assumed 8mL	
EtOH	4697	Requires >1.6L, assumed 1.9L	
MeOH	1500	Requires at maximum 500 mL	
BiCl <sub>3</sub>	3600	Requires 12.5g, assumed 15g	

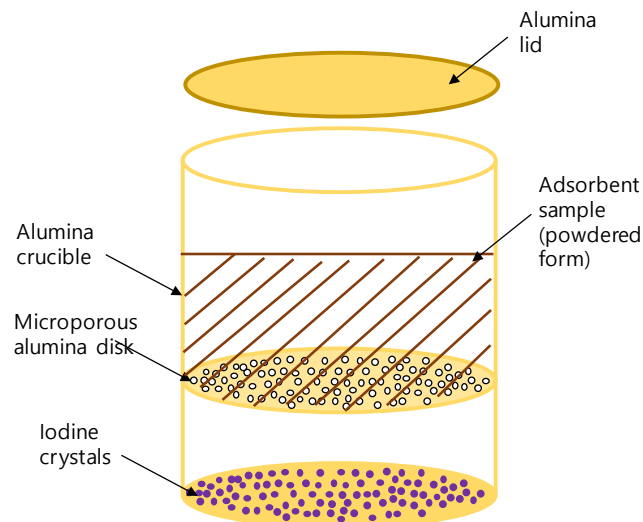


### III. Bismuth SBA-15 closed experiment

- ▶ Testing to make sure the iodine adsorption capacity did not decrease following the newly optimized procedure



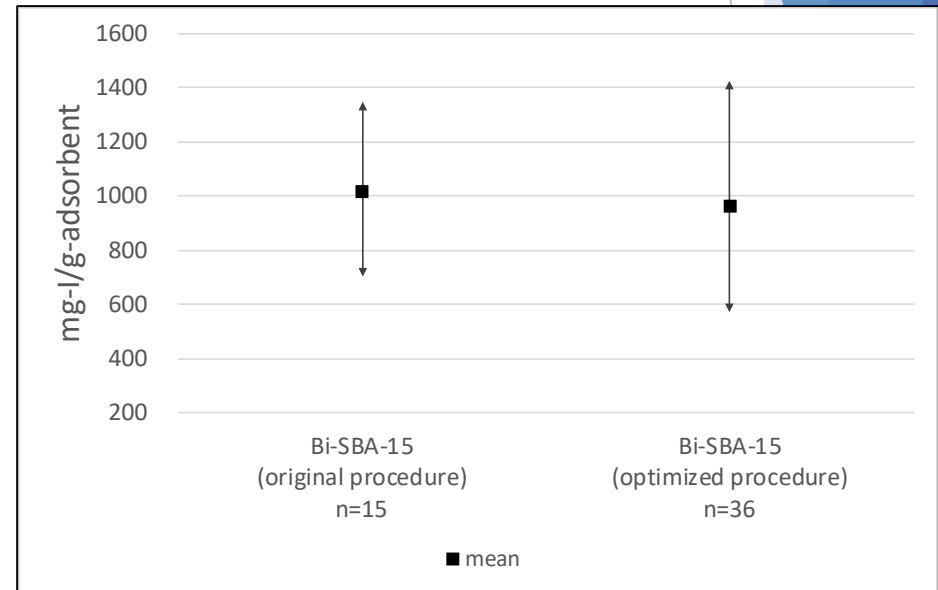
<Final product: bismuth-embedded SBA-15>



<Experimental setup for the closed iodine capture experiment>

$$C = \frac{m_{abs,I}}{m_{s,i}} = \frac{m_{s,f} - m_{s,i} + m_{s,loss}}{m_{s,i}}$$

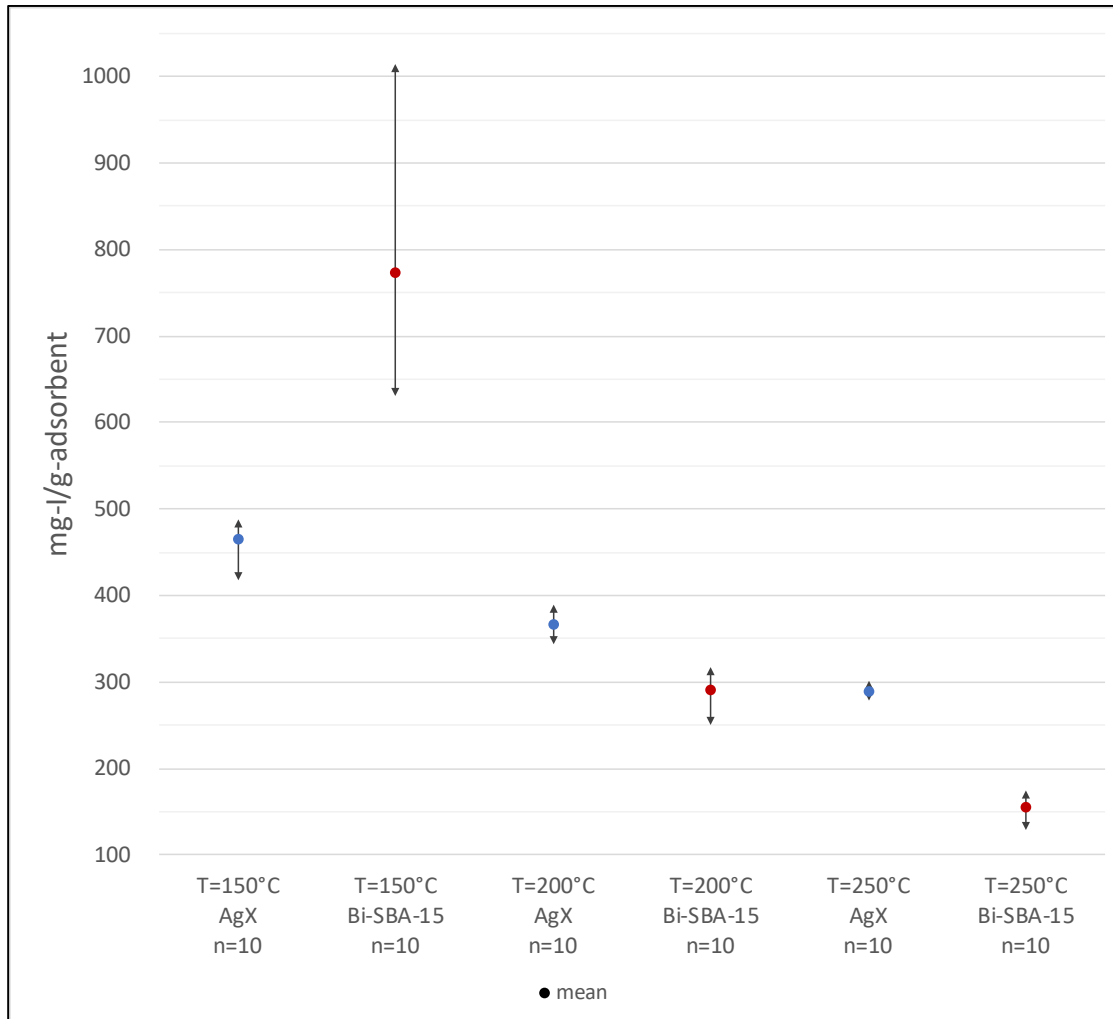
<Equation used to calculate the iodine capturing capacity of the sorbent>



<Experimental results for the iodine adsorption capacity of Bi-SBA-15 at 150°C following the original procedure and newly optimized procedure >

### III. Bismuth SBA-15 closed experiment

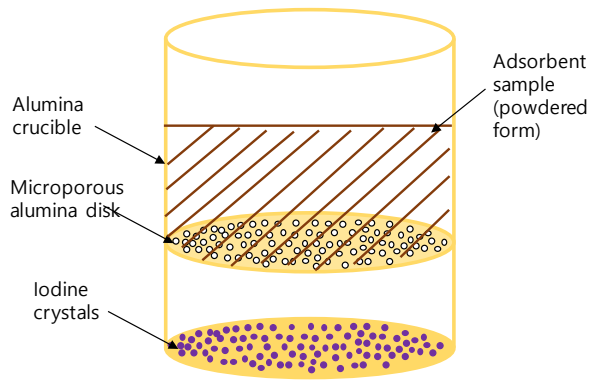
- ▶ Comparison of iodine adsorption capacity for Bi-SBA-15 and AgX at 150, 200, and 250 ° C (accounting for re-evaporation)



<Experimental  
Results for Closed  
Iodine Capture  
Experiment using  
AgX and Bi-SBA-15>

### III. Bismuth SBA-15 open experiment

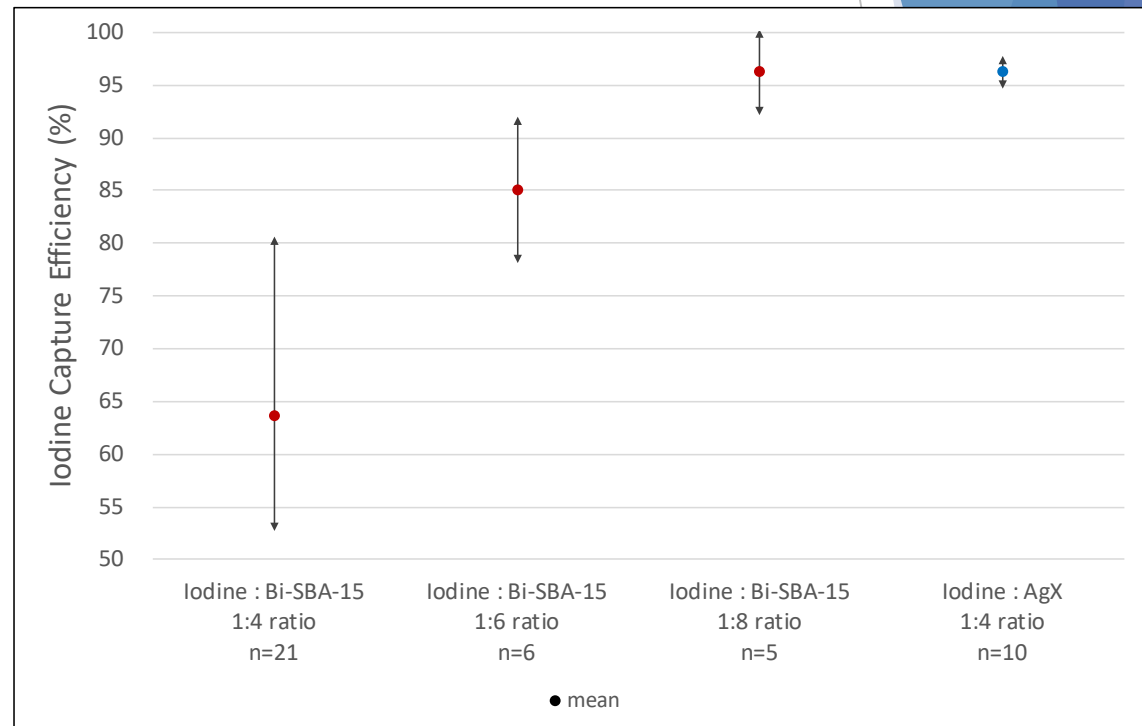
- ▶ Open iodine capture experiment using Bi-SBA-15 and AgX for iodine capture efficiency



<Experimental setup for the open iodine capture experiment>

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

<Equation used to calculate the iodine adsorption efficiency for open experiment>



<Iodine Capture Efficiency of Bi-SBA-15 and AgX in Open Iodine Capture Experiment at 250°C>

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## IV. Summary

- ▶ Was able to further optimize Bi-SBA-15 synthesis by reducing cost (both monetary and temporal) while maintaining iodine adsorption capacity
  - ▶ Time: 7+ days -> 5 days
  - ▶ Material cost: 10,000+ KRW/g -> 2,700 KRW/g
    - ▶ AgX: 6,300 KRW/g
- ▶ Even at 250°C where the iodine adsorption capacity is decreased significantly compared with 150°C, only about twice the mass of AgX was required to get similar average value on the iodine capture efficiency
  - ▶ However, it may be ideal to have additional systems to cool the incoming iodine gas before the required filtration

## IV. Future Work

- ▶ Find out how much the material's ability is hindered if it is degraded (exposed to wet, hot condition before iodine arrives at the filtration system)
- ▶ Perform iodine capture experiments for organic iodides

**END**