

## Low Temperature Sintering For the Immobilization of Bi<sup>0</sup>-rGO Iodine Wastes

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### 1. Introduction

The safe and responsible disposal of radioactive waste resulting from the nuclear fuel cycle has been a significant concern for the nuclear industry for many years. [1]. To ensure the safety of the environment and prevent potential health risks, it is essential to remove radioactive iodine, particularly <sup>129</sup>I, from off-gas streams in reprocessing facilities before releasing them. This is because radioactive iodine is highly volatile and has a long half-life of 1.57 x 10<sup>7</sup> years, which means it can persist in the environment for an extended period [2,3].

Cement and glasses have been investigated as options for immobilizing I-129, but their long-term storage effectiveness is limited by several factors, including low iodine waste loading capacities, extended processing times, high energy consumption, and elevated processing temperatures [4–6]. In contrast, there have been limited studies on low-temperature sintering of ceramic-based iodine waste forms (<300 °C) [7,8]. This sintering process is an emerging approach avoiding the use of high temperatures, which can cause the release of radioactive species into the environment as in conventional sintering methods.

In this study, we synthesized a new sorbent, Bi<sup>0</sup>-rGO, and investigated its ability to absorb iodine gas. We also employed low temperature sintering to immobilize iodine waste, and evaluated the performance of the sintered pellets using characterization methods including PXRD and SEM. To determine the effectiveness of the pellets, we will carry out short-term leaching experiments using PCT protocols [9].

### 2. Methods and Results

#### 2.1 Iodine capture experiment

Iodine capture experiments were studied under static air conditions at 200 °C for several times, and the iodine capture capacity was calculated by weighing the sample before and after exposure to iodine gas at various time intervals using Eq. (1).

$$q_e(\text{mg/g}) = \frac{\Delta m}{m_s} \times 1000 \quad (1)$$

where  $\Delta m$  (g) and  $m_s$  (g) are the mass gain and the initial mass of sorbent, respectively, and  $q_e$  (mg/g) represents the iodine capture capacity of sorbent.

A blank control was also performed to confirm that the mass increase was due to iodine capture and not oxidation through air reaction.

#### 2.2 Sintering conditions for I-Bi<sup>0</sup>-rGO

Two samples were prepared: (1) additive-free I-Bi<sup>0</sup>-rGO (CS BiI<sub>3</sub>) and (2) I-Bi<sup>0</sup>-rGO mixed with Bi<sub>2</sub>O<sub>3</sub> powder and distilled water (CS BiOI) for thermal annealing at 300 °C for 12 h. Both samples were pressed with a uniaxial pressure of 500 MPa in an 8 mm cylindrical steel mold and sintered at 300 °C for 20 min. The sintered samples were removed from the mold for characterization.

### 3. Result and Discussion

Due to high-pressure sintering, the CS BiI<sub>3</sub> sample (**Fig. 1**) exhibited a reduction in crystallite size as evidenced by peak broadening in the PXRD pattern, although there were no notable shifts in XRD peak positions. The BiI<sub>3</sub> phase in the CS BiOI sample shifted to BiOI through a chemical reaction between Bi<sub>2</sub>O<sub>3</sub> and BiI<sub>3</sub>.

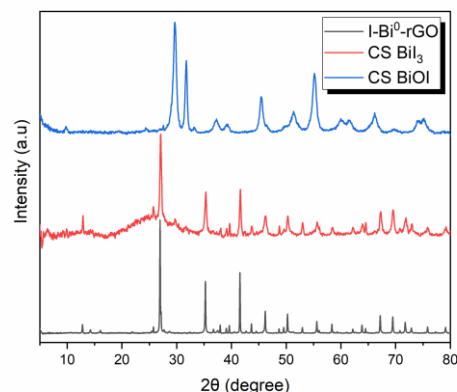


Fig. 1. PXRD patterns of I-Bi<sup>0</sup>-rGO, CS BiI<sub>3</sub>, and CS BiOI.

The formation of distinct platelet-shaped crystals due to the combination of additives and thermal annealing procedures can be observed in the fracture surface micrographs of CS BiOI [10], as depicted in **Fig. 2**.

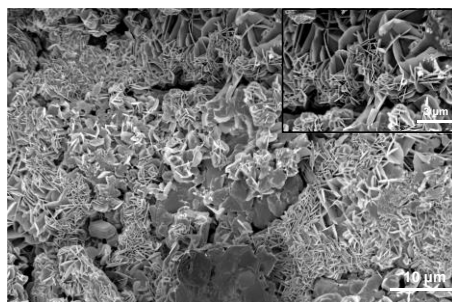


Fig. 2. SEM image of fractured surfaces of CS BiOI at 300 °C.

#### 4. Conclusions

In this study, we proposed a low-temperature sintering method for the stable and long-term disposal of  $^{129}\text{I}$  waste by synthesizing  $\text{Bi}^0\text{-rGO}$  composite materials using a solvothermal route. To immobilize the iodine waste form,  $\text{BiI}_3$  was converted into a more chemically durable  $\text{BiOI}$  through a simple thermal annealing process. However, further research is necessary to comprehensively evaluate the long-term iodine behavior of  $\text{Bi}^0\text{-rGO}$  under various leaching conditions in a deep groundwater environment.

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#### REFERENCES

- [1] S.U. Nandanwar, K. Coldsnow, V. Utgikar, P. Sabharwall, D. Eric Aston, Capture of harmful radioactive contaminants from off-gas stream using porous solid sorbents for clean environment – A review, *Chem. Eng. J.* 306 (2016) 369–381. <https://doi.org/10.1016/j.cej.2016.07.073>.
- [2] Q. Jiang, H. Huang, Y. Tang, Y. Zhang, C. Zhong, Highly Porous Covalent Triazine Frameworks for Reversible Iodine Capture and Efficient Removal of Dye, *Ind. Eng. Chem. Res.* 57 (2018) 15114–15121. <https://doi.org/10.1021/acs.iecr.8b02866>.
- [3] J.H. Yang, Y.J. Cho, J.M. Shin, M.S. Yim, Bismuth-embedded SBA-15 mesoporous silica for radioactive iodine capture and stable storage, *J. Nucl. Mater.* 465 (2015) 556–564. <https://doi.org/10.1016/j.jnucmat.2015.06.043>.
- [4] L. Campayo, S. Le Gallet, D. Perret, E. Courtois, C. Cau Dit Coumes, Y. Grin, F. Bernard, Relevance of the choice of spark plasma sintering parameters in obtaining a suitable microstructure for iodine-bearing apatite designed for the conditioning of I-129, *J. Nucl. Mater.* 457 (2015) 63–71. <https://doi.org/10.1016/J.JNUCMAT.2014.10.026>.
- [5] L. Campayo, A. Grandjean, A. Coulon, R. Delorme, D. Vantelon, D. Laurencin, Incorporation of iodates into hydroxyapatites: A new approach for the confinement of radioactive iodine, *J. Mater. Chem.* 21 (2011) 17609–17611. <https://doi.org/10.1039/c1jm14157k>.
- [6] U. Donald, I.W. (Atomic Weapons Establishment, Aldermaston, U. Metcalfe, V.L. (Atomic Weapons Establishment, Aldermaston, U. Taylor, R.N.J. (Atomic Weapons Establishment, Aldermaston, Review The immobilization of high level radioactive wastes using ceramics and glasses, *J. Mater. Sci.* 2 (1997) 5851–5887.
- [7] M. ul Hassan, H.J. Ryu, Cold sintering and durability of iodate-substituted calcium hydroxyapatite (IO-HAp) for the immobilization of radioiodine, *J. Nucl. Mater.* 514 (2019) 84–89. <https://doi.org/10.1016/j.jnucmat.2018.11.024>.
- [8] M. ul Hassan, S. Venkatesan, H.J. Ryu, Non-volatile immobilization of iodine by the cold-sintering of iodosalite, *J. Hazard. Mater.* 386 (2020) 121646. <https://doi.org/10.1016/j.jhazmat.2019.121646>.
- [9] G. Products, B. Glass, C. Attack, G. Manufacture, P.E. Spectrometry, I.W. Forms, S.I. Chromatography, Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses and Multiphase Glass Ceramics: The Product Consistency Test (PCT) 1, (2005) 1–22. <https://doi.org/10.1520/C1285-21>. Copyright.
- [10] J.L. Krumhansl, T.M. Nenoff, Hydrocalcite-like layered bismuth-iodine-oxides as waste forms, *Appl. Geochemistry.* 26 (2011) 57–64. <https://doi.org/10.1016/J.APGEOCHEM.2010.11.003>.