# Efficient long-term immobilization method of $Bi^0$-rGO iodine waste by cold sintering

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## 1. Introduction

Radioactive wastes produced at every stage of the nuclear fuel cycle is a key issue that must be managed safely and immobilizing radioactive wastes could be an innovative option to solve environmental problems. In particular, Iodine-129 is the main environmental concern requiring specific attention since it decays with a very long half-life of $1.57 \times 10^7$ years and a large amount of radioiodine is released during the reprocessing of spent fuels, needing to be treated and immobilized.

Unfortunately, very limited data is available on the chemical durability of bismuth-containing waste forms, which is of most interest for radioactive iodine long-term disposal. Notably, the standard immobilization methods such as vitrification and a lot of different studies on bonding materials such as cement and glasses have been investigated and designed for the immobilization and disposal of I-129. [1–7] However, these methods are not very effective in the long-term storage of $^{129}I$ because of low iodine waste loading capacities, long processing times, high energy consumption, and high processing temperature. Thus, the development of effective and suitable immobilization methods is essential for future nuclear options. Yang et al. [6] showed that the final waste form of $^{129}I$ ($BiI_3$) is subject to a considerable loss of iodine that could occur at the repository site. To deal with this issue, a simple post-sorption process was conducted by reacting $BiI_3$ with $Bi_2O_3$ to form a chemically stable phase ($Bi_5O_7I$). So far, few studies have been reported on the very low-temperature ($\leq 300$ ℃) sintering process of ceramic-based iodine waste forms.[8,9] This sintering process provides a high relative density ($\leq 98\%$) using a low temperature consolidation as a waste matrix without volatilization of loaded iodine.

Inspired by the above-mentioned immobilization method, we proposed a low temperature sintering for the immobilization of iodine waste and therefore we demonstrated that the loss of iodine from the sintered composite could be minimized at a very low temperature sintering. The obtained cold sintered samples are then investigated using an x-ray diffractometer (XRD) and scanning electron microscopy (SEM). Further studies on elemental leaching will also be investigated following the protocols of the standard Product Consistency Test (PCT) [10] to see the short-term leaching behavior of the cold sintered samples.

## 2. Methods and Results

In this section, the proposed experimental mechanisms from reference [8,9,11–13] are used for the cold sintering of I-Bi-rGO powder composites. (**Fig. 1**) The sintering experimental conditions are discussed below.

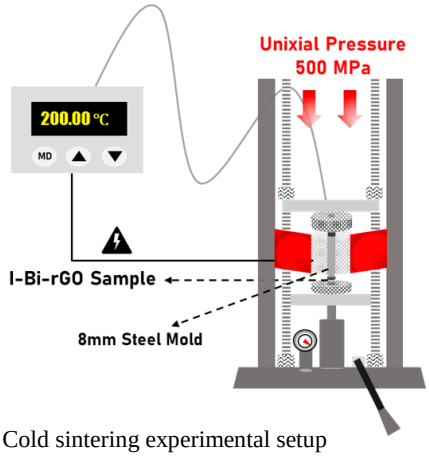


Fig. 1. Cold sintering experimental setup

### *2.1 Sintering methodology for I-$Bi^0$-rGO*

Before sintering, appropriate amounts of extra pure deionized water (20 wt.% of the mixed powder) were added to the mixture of $Bi_2O_3$ and I-$Bi^0$-rGO powders, and were ground into a homogenous mixture using a pestle and mortar After that, 0.4g of the mixed powder composites was placed into a cylindrical steel mold with an internal diameter of 8 mm and pressed with a uniaxial pressure of 500 MPa. With the uniaxial pressure sustained, the mold was then heated at a temperature of 200℃ with a rate of 10℃/min and held for 20 mins. After spontaneous cooling of the sintered pellet, the pressure was then released and finally, the sample was removed from the mold for characterization.

### *2.2. Leaching test*

The product consistency test (PCT) test was studied in accordance with the American Society of Testing Materials (ASTM C1285 Protocol)[10] to verify the stability of the sintered samples. In brief, 1g of a crushed, sieved (150 μm) powdered sample was dispersed in 10 ml of ASTM-type I water and contained in a tightly sealed autoclave. The samples were placed in an oven at 90 ± 1℃ for 7 days, after which the sample was spontaneously cooled to ambient conditions. Eq. (1) was used to calculate the normalized leaching rate ($NLR_i$) of the ith element.

$$NLR_i = \frac{C_i}{t \times f_i \times S/V} \quad (1)$$

where $NLR_i$ is the Normalized leaching rate (g/m$^2$/day) of component I, $C_i$ is the Concentration of component I (g/L) leached into water after a reaction time of t, $f_i$ is the weight fraction of the ith element in the starting sample and $S/V$ (m$^2$/L) is the Specific Surface Area of the powdered waste form (1 g).

## 3. Result and Discussion

The XRD pattern of I-Bi$^0$-rGO after additiveless cold sintered (Fig. 2a) displays a similar XRD pattern to the preadsorbed I-Bi$^0$-rGO, implying that the structural proprieties of the material remained intact after sintering. However, after mixing with $Bi_2O_3$ powder and $H_2O$ at weight ratio of 14: 6: 5 for the sintering process at 200℃ as shown in Fig.2b, the iodine-bearing phase shifted from $BiI_3$ to a more stable compound BiOI (PDF NO. 00-010-0445) and some other peaks such as $Bi_5O_7I$ (PDF NO. 01-075-1467) and α-$Bi_2O_3$ (PDF NO. 01-071-0465) were also detected.

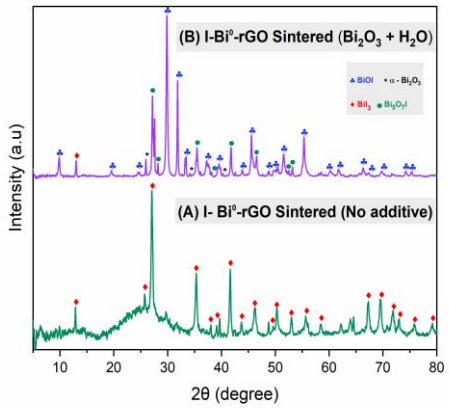


Fig. 2. PXRD patterns of (a) I-Bi$^0$-rGO Sintered without any additive and (b) Cold sintered I-Bi$^0$-rGO mixed with $Bi_2O_3$ powder and $H_2O$ at weight ratio of 14: 6: 5.

**Fig. 3** shows SEM images of the (a-b) fracture surfaces of the sample and (c) cold-sintered sample. **Fig. 3(a-b)** reveals the fracture surfaces of the cold sintered sample which achieved a well densified and homogenized sintering without any visible porosity in the waste form. In **Fig. 3c**, it can be seen that the addition of $Bi_2O_3$ and $H_2O$ has a great effect on the microstructure of cold sintered Bi$^0$-rGO composites.

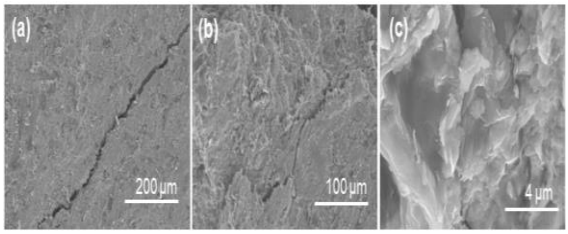


Fig. 3 (a & b) fractured surfaces and (c) 200℃ cold sintered I-Bi$^0$-rGO mixed with $Bi_2O_3$ powder and $H_2O$ at weight ratio of 14: 6: 5.

## 4. Conclusions

This study provides a new approach to an ultra-low temperature sintering of I-129 waste forms. The optimum conditions were found to be: a temperature of 200 °C, a holding time of 20 min, and a pressure of 500 MPa. Further research is to be performed to evaluate the chemical durability of the waste forms to better understand the leaching behavior of the sintered samples.

## Acknowledgments

This study is supported by the National Research Foundation of Korea (NRF-2021M2D2A1A02043946) and the KAI-NEET, KAIST.

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