Removal of ^{14}C in aqueous phase using isotope exchange reaction

Seokhoon Yang [a] and Wooyong Um [a,b*]
[a] *Division of Advanced Nuclear Engineering, POSTECH, 77 Cheongam- ro, Nam-gu, Pohang, Republic of Korea*
[b] *Division of Environmental Science & Engineering, POSTECH, 77, Cheongam-ro, Nam-gu, Pohang, Republic of Korea*
[*] *Corresponding author: wooyongum@postech.ac.kr*

1. Introduction

The radioactive carbon, ^{14}C, is a β-emitting radionuclide and it is produced both naturally and anthropogenically. In the nuclear reactor, ^{14}C can be formed during the nuclear reactions, such as $^{14}N(n, p)^{14}C$, $^{13}C(n, \gamma)^{14}C$, and $^{17}O(n, \alpha)^{14}C$.

In the CANDU reactors, the mechanism of ^{14}C production is the neutron activation of ^{17}O of the moderator (D_2O) by following reaction, $^{17}O(n, \alpha)^{14}C$. To remove ^{14}C species, Ion-exchange resins (IERs) have been used. However, the ^{14}C-loaded spent resin can be regarded as intermediate-level radioactive waste that could not be disposed of like a low-level waste [1].

In our previous study, we performed Fenton-like treatment and PMS-AOPs for the reduction of ^{14}C spent resin. However, in that process, because ^{14}C and ^{12}C may exist together, the efficient way of recovering ^{14}C has been important and challenging.

In this study, we used ^{13}C, a stable isotope that has similar physicochemical properties to ^{14}C, and conducted ^{13}C exchange experiment on calcite using an isotope exchange reaction. ^{14}C in solution can replace ^{12}C in calcite.

$$Ca^{12}CO_{3(s)} + {}^{14}CO_3{}^{2-}{}_{(aq)} \rightleftharpoons Ca^{14}CO_{3(s)} + {}^{12}CO_3{}^{2-}{}_{(aq)} \quad (1)$$

When the ^{14}C is added to the pre-equilibrated solution with calcite, excessive ^{14}C will drive rapid isotopic exchange kinetics [2]. In that process, ^{14}C in solution can replace stable C isotope in carbonate species.

Therefore, from this research result, we can remove ^{14}C from the ^{14}C contaminated solution waste, but also apply the exchanged ^{14}C for medical or industrial purpose.

2. Methods and Materials

2.1 Preparation of pre-saturated solution with calcite for isotope exchange experiment.

To prepare the saturated solution, we mixed equal volumes of 2.5mM Na_2CO_3 and N_2 purged 0.05mM $CaCl_2$ solutions. The pH of this solution was adjusted by addition of 1M NaOH. This solution was equilibrated with calcite powder (Sigma-Aldrich) to make the pre-equilibrated solution with respect to calcite. To prevent the effects of external $CO_2(g)$, the headspace was filled with N_2 gas and sealed with a rubber stopper, and stored inside a glove box after complete mixing for 7days in the glove box

2.2 Isotope exchange experiment

For the isotope exchange experiment, 50µl of 0.4M $Na^{13}HCO_3$ was spiked into the pre-equilibrated solution and shaken for 7days in the glove box for isotopic exchange reaction. The calcite with exchanged ^{13}C was separated by centrifugation and freeze-dried for further characterization.

The $^{13}C/^{12}C$ ratio ($\delta^{13}C$) was analyzed by Stable Isotope Ratio Mass Spectrometer System with Elemental Analyzer (Vision-EA, Isoprime, UK) and $\delta^{13}C$(‰) values were calculated using eq. 2

$$\delta^{13}C(‰) = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000 \quad (2)$$

where R corresponds to the $^{13}C/^{12}C$ ratio, and standard is Pee Dee Belemnite(PDB).

3. Results and Discussions

The results of ^{13}C exchange experiments with various amounts of calcite and pHs are shown in Fig. 1

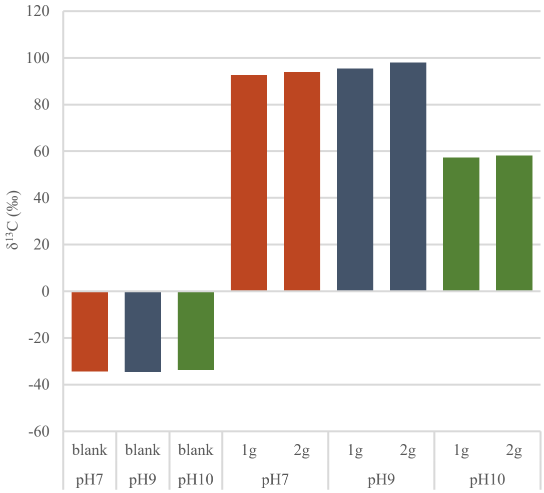

Fig. 1. $\delta^{13}C$(‰) with various pHs and amount of calcite (1g and 2g) in pre-equilibrated solution with respect to calcite. Blank is for 1g of calcite with no spiked ^{13}C.

In the blank samples, the $\delta^{13}C$ values are -33.82‰ to -34.01 ‰ and there was no difference by the pH change. However, with ^{13}C to the pre-equilibrated solutions, the $\delta^{13}C$ values were changed after 7days from -33.823‰ to +98.03‰ at pH 9, indicating that ^{13}C was exchanged on calcite. At pH 10, the $\delta^{13}C$ value showed less than other pH conditions. Considering that the solubility of calcite decreases as the pH increases and pKa of calcite is 8.5 [3], in the solubility equilibrium at pH 8.5, the dissolution and the formation rate are equal, while at pH below 8.5, the dissolution reaction is more dominant than the formation of calcite. However, above pH 8.5, the formation of calcite reaction is more dominant that the dissolution reaction. Therefore, we could expect the isotope exchange reactions will occur more at around pH 8.5. In Fig. 1, $\delta^{13}C$ values were highest at pH 9 and followed pH 7 and pH 10.

Increasing the amount of calcite is also expected to increase the number of reaction sites where ^{13}C can be exchanged more. However, there was no significant difference compared to the $\delta^{13}C$ values of 1g calcite (20g/L) and 2g calcite (40g/L). This is inferred that the added amount of calcite was already exceeded the solubility of calcite at pH 10, thus, the dissolution reaction did not occur well.

Also, the added amounts of calcite could reduce the extent of isotope disequilibrium, resulting in less concentration of ^{13}C. However, there were no significant differences between 1g calcite and 2g calcite used. Therefore, under this condition, the dissolution /formation reaction is playing more important role in isotope exchange ractions.

There was no difference in the XRD pattern, but noticeable increase of intensity was found as the pH increased (Fig. 2). This can attribute to the different solubility of calcite (i.e., relatively lower solubility at higher pH). In addition, it can be inferred that there was no formation or precipitation of other solids, and ^{13}C and concentrated by the dissolution/formation reaction of calcite.

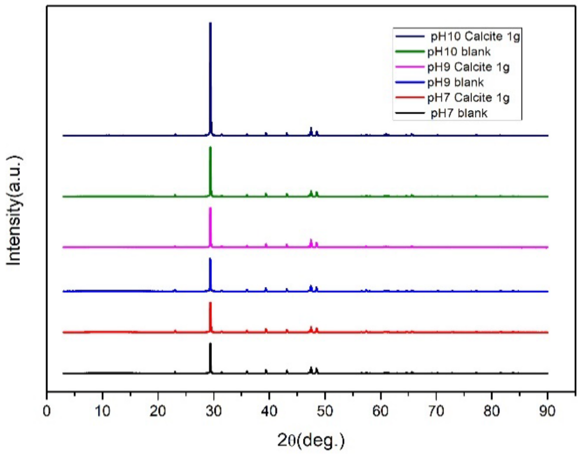

Fig.2. Effect of pH on XRD patterns of ^{13}C exchanged calcite. Blank is 1g of calcite with no ^{13}C added

4. Conclusion

In this study, we could exchange the ^{13}C onto the calcite using the isotope exchange reaction without any changes in the mineral structure of calcite. The isotope exchange reaction has occurred the most at pH 9, but the least at pH 10. Considering the solubility and pKa values of calcite, the dissolution/formation reaction of calcite is more important to control the isotope exchange reaction.

ACKNOWLEDGEMENT

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIP: Ministry of Science, ICT and Future Planning) (No. NRF-2019M2A7A1001811).

REFERENCES

[1] M. Aamir Hafez, Junsung Jeon, Seokju Hong, Neil Hyatt, Jong Heo and Wooyong Um, Fenton-like treatment for reduction of simulated carbon-14 spent resin, Journal of Environmental Chemical Engineering, Vol.9, 2021

[2] Garnier, J.M, Retardation of dissoluved radiocarbon through a carbonated matrix, Geochemica et Cosmochimica Acta, Vol.49, pp. 683-693, 1985

[3] Langmuir, D., Carbonate chemistry, Aqueous Environmental Geochemistry, Prentice-Hall, New Jersey, pp. 193-230, 1997.