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THERMOCHEMICAL DECONTAMINATION OF PAPER WIPER WASTES THROUGH COMBINED CARBONIZATION AND CHLORINATION

Chlorination has been used for the thermochemical decontamination of radioactive waste to address the significant amount of waste in nuclear facilities. Control of chlorination conditions is essential to optimize decontamination efficiency, as these conditions significantly influence chemical and physical evolution of target waste. In this study, the feasibility of thermochemical decontamination for reducing the radioactivity of paper wiper waste was investigated. A two-step thermochemical process, comprising low-temperature carbonization and high-temperature chlorination, was suggested to improve the decontamination efficiency. Simulated paper wiper waste contaminated with Cs and Co was treated in a closed system filled with air at 250°C for carbonization as a pretreatment. Subsequently, the partial carbonization product was chlorinated at 700-900°C to remove Cs and Co. Decontamination efficiencies of more than 99% were obtained after the two-step thermochemical process.

Keywords: Radioactive waste; decontamination; carbonization; chlorination; cellulose

1. Introduction

Recently, thermochemical decontamination based on chlorination has been suggested for volumetric/gravimetric reduction of radioactive wastes generated from nuclear facilities [1-3]. During high-temperature treatment in ambient Cl₂, radioactive contaminants (e.g., Cs and Co) in waste are chemically converted to their chlorides. As chlorides have sufficient solubility in water or high vapor pressure at elevated temperature, they can be separated from the waste, thereby decreasing its radioactivity [1-3]. It was reported that contaminated concrete waste can be treated by chlorination with a Cs and Co decontamination efficiency of 90% [2]. Since gas-phase chlorination is highly sensitive to operating conditions, establishing optimized parameters for each specific type of waste is essential.

On the other hand, the geological disposal of organic waste remains a concern because of its long-term chemical instability in underground environment. It can generate mobile species, such as gases and water-soluble complexes, when exposed to groundwater [4-6]. The mobile species can carry radioactive isotopes to urban structures over a prolonged period. Thus, proper conditioning of organic waste is necessary for improved management.

In this study, the technical feasibility of chlorination-based thermochemical decontamination for organic waste treatment

was investigated. Paper wiper, mainly composed of cellulose, was chosen as the representative candidate for organic waste. Cellulose-based wastes (e.g., paper, cotton, wood) account for approximately 50 wt.% of the combustible waste (~31.3% of total dry active waste) stored in nuclear power plants in the Republic of Korea at 2012 [6]. A two-step thermochemical process comprising low-temperature carbonization as a pretreatment and high-temperature chlorination was designed to improve the decontamination efficiency.

2. Experimental

A commercial paper wiper (WypAll L25, Kimberly Clark) was selected as the test candidate. Simulated paper wiper waste was prepared by spiking a paper wiper with nonradioactive Cs and Co. An aqueous solution containing CsCl (98%, Sigma Aldrich) and CoCl₂·H₂O (98%, Sigma Aldrich) was used as the contamination source with target concentrations of 2000 ppm Cs and 1000 ppm Co. The solution (50 mL) was dropped onto two overlapped sheets of paper wiper and stored in a convection oven at 80°C for 7 days to stabilize Cs and Co.

The chlorination experiment was conducted in a laboratory tube furnace with a gas-flow system. A quartz tube was used

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to ensure sufficient chemical and thermal stability. The paper wiper sample was loaded into a tube using an Al_2O_3 boat. The furnace temperature was gradually increased to target values (700-1000°C) in ambient Ar. Subsequently, the chlorination reaction occurred at 700-1000°C for 2-6 h with an Ar/ Cl_2 mixed gas flow (total flow rate = 200 mL min^{-1}).

A Teflon-line autoclave (Model 4748A, Parr Instrument) was used for the low-temperature carbonization. For the hydrothermal carbonization, 100 mL deionized water and two overlapping sheets of paper wiper were placed in the autoclave. The autoclave was placed in a convection oven at 150-250°C for 10 h. A dry carbonization process without water was also tested. An identical autoclave containing the same amount of paper wiper was sealed with N_2 and air, respectively. The autoclave was heated at 250°C for 10 h.

The amount of organic components in the paper wiper was determined using an elemental analyzer (EA, FlashEA 1112 for C, H, and N; Flash 2000 series for O, Thermo Fisher Scientific). The crystal structure of the paper wiper before and after heat treatment was analyzed using X-ray diffraction (XRD, D2 Phase, Bruker). Thermogravimetric (TG) analysis (SDT Q600, TA Instruments) was performed under an Ar atmosphere. Scanning electron microscopy (SEM, S4800, Hitachi) was used to observe the morphology of the paper wiper. The compositions of Cs and Co were analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, iCAP 7400 Duo, Thermo Fisher Scientific).

3. Results and discussion

Prior to the thermochemical decontamination experiment, the properties of the paper wiper were identified. The atomic ratio of C:H:O in the paper wiper was approximately 6.00:10.49:4.99, which corresponds to the nominal composition of cellulose ($(\text{C}_6\text{H}_{10}\text{O}_5)_n$). The XRD pattern of the paper wiper (Fig. 1a) shows the distinctive diffraction peaks corresponding to cellulose. Fig. 1b shows the TG behavior of the paper wiper under an Ar atmosphere. The small weight loss (7.1%) during the initial stage of heating (<150°C) was ascribed to the evaporation of adsorbed water (arrow I). The weight of the sample drastically reduced by 65.2% at temperatures above 290°C, indicating the thermal decomposition of cellulose. The weight loss slowed above 405°C (arrow II), and the final weight at 900°C was approximately 17.8% of the initial value. Fig. 1c is a SEM image of the paper wiper. Long continuous cellulose fibers aggregated in the paper wiper.

The chlorination of contaminants (Cs and Co) in paper wiper requires high thermal energy for the formation and evaporation of their chlorides [1-3]. Direct chlorination occurred at 900°C under a Cl_2 atmosphere. Upon chlorination, the thermal decomposition (i.e., pyrolysis) of the paper wiper is expected to leave a solid carbonaceous compound because of the sufficient thermal energy supply. The weight of the paper wiper greatly decreased to 17.1% after chlorination, leaving a black solid

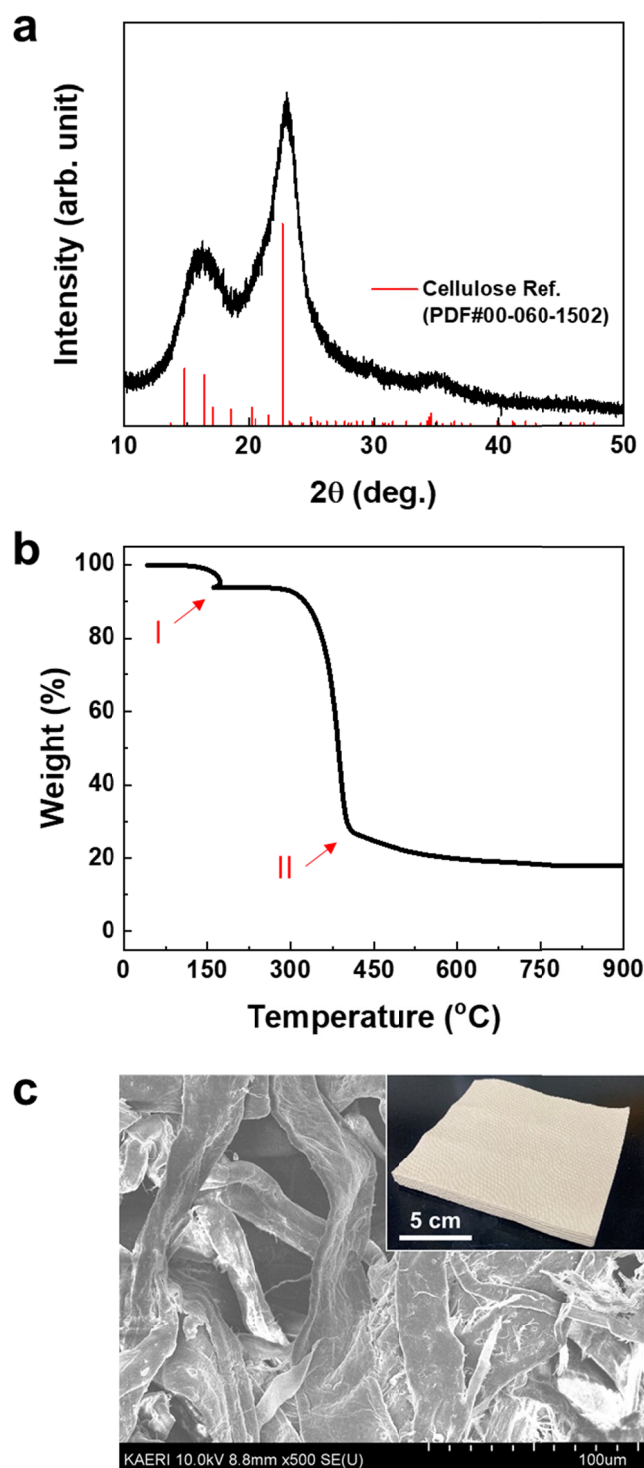


Fig. 1. (a) XRD pattern (with a reference pattern (PDF#00-060-1502)), (b) TG curve obtained in ambient Ar (room temperature to 900°C), and (c) SEM image (inset: photograph) of the paper wiper

product. This weight loss was comparable to that observed in the TG experiment (Fig. 1b), suggesting that the pyrolysis of cellulose occurred to form carbonaceous compounds during chlorination. The result of the thermochemical decontamination by chlorination are summarized in TABLE 1 (DC). The Cs and Co concentration in the contamination solution was identified to 2005.61 and 957.91 ppm, respectively. The decontamination efficiencies (DE), listed in TABLE 1, were calculated based on

these values. The results demonstrated the contaminant removal by chlorination. However, the decontamination efficiency was insufficient (~73/80% for Cs/Co). Hence, a modified chlorination process was designed to enhance the decontamination performance.

In this respect, we proposed a two-step thermochemical decontamination process through carbonization and chlorination. In the low-temperature (up to 250°C) carbonization, the paper wiper was partially decomposed into a solid carbonaceous compound. Subsequently, the carbonaceous compound obtained by carbonization was treated in ambient Cl₂ at a higher temperature (>700°C) for chlorination. During chlorination, the contaminants (Cs and Co) in the paper wiper were chlorinated, and the chloride products were separated from the carbonaceous compound by volatilization. Additional carbonization may occur during chlorination owing to residual organic species in the low-temperature carbonization product.

The hydrothermal carbonization of cellulose compounds has been extensively investigated for recycling organic waste into biofuel [7-10]. High-temperature pressurized water assists in the dehydration and depolymerization of cellulose to form solid carbonaceous compounds at lower temperatures than that in simple pyrolysis [9,10]. The low-temperature carbonization of the paper wiper was tested in a closed autoclave. First, a carbonization experiment was conducted with water, similar to previous studies [7-10]. The appearance of the paper wiper slightly changed after hydrothermal treatment at 150°C (Fig. 2a), indicating the insufficient reaction. At higher temperatures (200-250°C), the paper wiper darkened (Figs. 2b and 2c), denoting the hydrothermal carbonization of cellulose. Simultaneously, a considerable weight loss was observed. The weight loss increased at higher temperatures (28.92/62.07% at 200/250°C) because of the increase in the degree of cellulose decomposition. The carbonization of the paper wiper in the closed system occurred above 200°C, which is lower than the onset temperature (~290°C) of the ambient pressure pyrolysis in an open Ar-flowing system (Fig. 1b). This implies that subcritical water has a catalytic effect on cellulose decomposition. However, the use of water during carbonization generates large amounts of wastewater (Fig. 2d). Contaminants and organic byproducts can dissolve in water during the hydrothermal process. Therefore, a wastewater treatment process must be followed, which complicates the entire process.

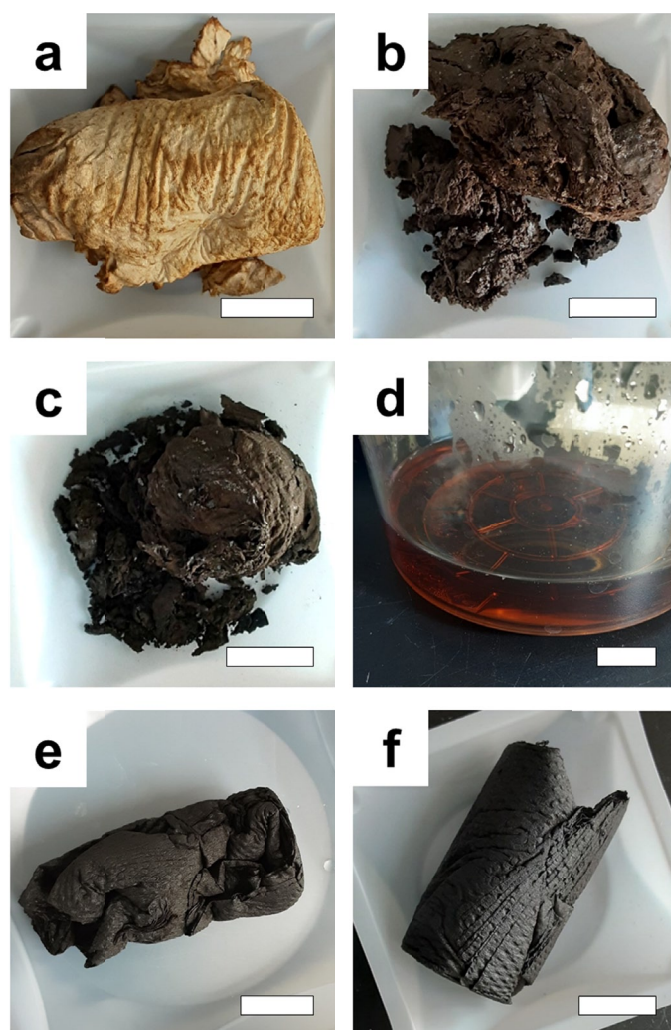


Fig. 2. (a-c) Paper wiper after the low-temperature carbonization at (a) 150, (b) 200, and (c) 250°C. (d) Waste water generated during the carbonization. (e, f) Paper wiper after the low-temperature carbonization at 250°C using an autoclave filled with (e) N₂ and (f) air (scale bar = 2 cm)

We examined the feasibility of a dry process without water in an identical autoclave system. The autoclave containing the paper wiper was sealed in N₂ and air atmosphere, respectively, and treated at 250°C. As shown in Figs. 2e and 2f, the paper wiper successfully decomposed to form a carbonaceous product even under dry conditions. The XRD pattern shown in Fig. 3a confirms the decomposition of cellulose during dry process. This suggests that a small amount of water vapor from surface

TABLE 1

Thermochemical decontamination results of the paper wiper by direct chlorination and the two-step process (DC: direct chlorination, TS: two-step process, DE: decontamination efficiency)

Sample	DC	TS1	TS2	TS3	TS4	TS5	TS6	TS7
Temperature (°C)	900	700	900	900	900	900	1000	1000
Time (h)	2	2	2	6	6	6	2	6
Cl ₂ flow (mL min ⁻¹)	2	2	2	2	1	10	2	2
Ar flow (mL min ⁻¹)	198	198	198	198	199	190	198	198
Weight loss (%)	81.0	42.2	54.5	51.1	56.6	51.9	55.3	54.9
DE of Cs (%)	72.65	97.68	97.31	99.42	99.46	99.69	99.76	99.87
DE of Co (%)	80.30	89.68	99.74	99.90	99.93	99.92	99.88	99.90

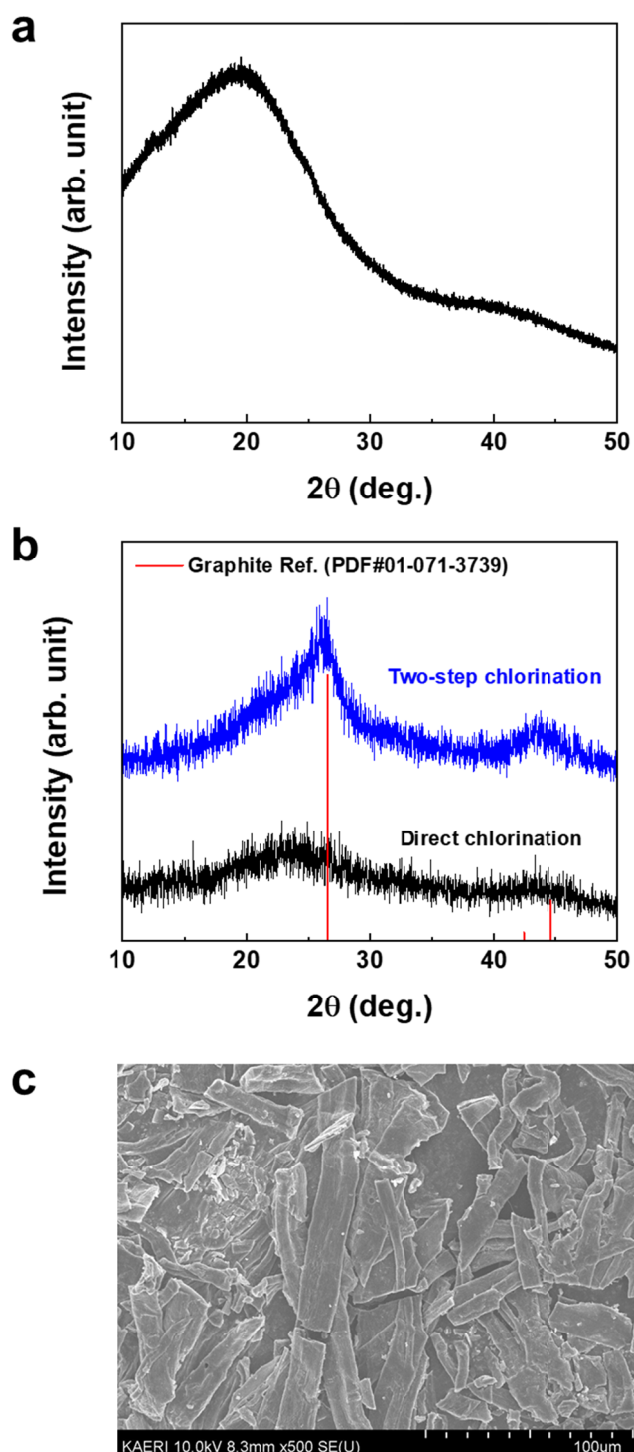


Fig. 3. XRD patterns of (a) the carbonization product in the air-filled case and (b) the paper wiper after (black) the direct chlorination and (blue) the two-step chlorination. (c) SEM image of the paper wiper after the two-step chlorination.

adsorption on pristine paper wiper is sufficient to promote the thermal decomposition of cellulose. The weight losses of the dry-processed products were comparable for both atmospheres (50.56/50.22% in N_2 /air), implying that small amounts of O_2 and water vapor in the air did not have a significant impact on cellulose decomposition. The C:H:O ratio of the dry process product was approximately 6.00:4.35:0.71, indicating that H and O in the paper wiper were removed during heat treatment.

Weight retentions of C, H, and O were 68.9, 5.2, and 21.6%, respectively, showing that the partial carbonization occurred under this condition. While the hydrothermal treatment achieved higher decomposition efficiency, the air-filled dry process using the autoclave was chosen as a better option because of its reasonable carbonization performance and simplicity.

High-temperature chlorination experiment was carried out using the partial carbonization product at 700–1000°C to identify the thermochemical decontamination efficiency of the two-step process. The simulated paper wiper contaminated by Cs and Co was treated at 250°C in an air-filled autoclave for the preparation of the carbonization product. TABLE 1 summarizes the chlorination experiments under various reaction conditions (TS1–TS7) in comparison with the direct-chlorination result (DC). The additional weight loss upon chlorination was approximately 50%, indicating that further thermal decomposition occurred owing to the residual H and O in the low-temperature carbonization product. The two-step process, even at 700°C (TS1), exhibited a higher decontamination efficiency than the direct chlorination process at 900°C (DC) at identical reaction time and Ar/ Cl_2 ratio. The decontamination efficiency of the two-step process increased to more than 99% at higher temperatures (>900°C) (TS2–TS7). The decontamination efficiencies increased as the reaction times were prolonged and the temperatures were increased; however, such differences were minimal. In addition, the Cl_2 flow rate has minimal impact (TS3–TS5). Notably, 0.5 vol.% Cl_2 in the gas flow was sufficient for the decontamination (TS4), which can be ascribed to the high reactivity of Cl_2 with Cs and Co at the elevated temperatures. This result demonstrates the superiority of the two-step process for thermochemical decontamination of paper wiper waste.

It is hypothesized that microstructural evolution significantly enhanced the decontamination performance of the two-step process. Fig. 3b compares the XRD patterns of paper wiper after direct chlorination and the two-step process. The XRD pattern of graphite was identified in the two-step process product, suggesting that partial carbonization facilitates the formation of an ordered structure during subsequent chlorination. This underscores the critical role of low-temperature pretreatment, as the resulting ordered matrix may provide efficient diffusion pathways for gaseous phases. Furthermore, the reduction of structural defects such as dangling bonds may weaken the chemical interaction between C and contaminants, promoting their release. As shown in Fig. 3c, the resulting discontinuous fibrous structure with smaller dimension increases the effective surface area, thereby further enhancing overall decontamination efficiency.

4. Conclusions

In this study, a two-step thermochemical process comprising low-temperature carbonization and high-temperature chlorination was investigated for decontaminating radioactive waste. The simulated paper wiper waste, contaminated with Cs

and Co, was processed in a closed vessel at 250°C for partial carbonization, and the carbonization product was subsequently treated in an ambient Cl₂ at high temperature (700-1000°C) to remove the contaminants. More than 99% of Cs and Co were removed after chlorination at above 900°C, demonstrating the ability of the two-step process to decontaminate paper wiper waste. The removal efficiency of the two-step process was higher than that of direct chlorination. The thermochemical processes investigated in this study could be widely applied to treat other combustible wastes, particularly cellulose-based compounds. This process generates carbonaceous compounds and chlorides as reaction products. Hence, in the next stage, the stabilization of the reaction products will be investigated to ensure their geological disposal feasibility.

Acknowledgments

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REFERENCES

- [1] M.K. Jeon, S.W. Kim, K.-Y. Lee, M.K. Oh, *J. Radioanal. Nucl. Chem.* **328**, 195 (2021).
- [2] M. Oh, M.K. Jeon, K. Lee, R.I. Foster, C.-H. Lee, *Prog. Nucl. Energy* **154**, 104458 (2022).
- [3] H.-C. Yang, H.-O. Park, K.-T. Park, S.-J. Kim, H.-J. Kim, H.-C. Eun, K. Lee, *Processes* **9**, 96 (2021)
- [4] L.R. Van Loon, M. A. Glaus, *J. Environ. Polym. Degr.* **5**, 97 (1997).
- [5] J. Small, M. Nykyri, M. Helin, U. Hovi, T. Sarlin, M. Itävaara, *Appl. Geochem.* **23**, 1383 (2008).
- [6] B. Park, C.-W. Kim, S.-H. Kim, J.Y. Kim, *Ann. Nucl. Energy* **42**, 89 (2012).
- [7] Z. Liu, A. Quek, S.K. Hoekman, R. Balasubramanian, *Fuel* **103**, 943 (2013).
- [8] H.B. Sharma, A.K. Sarmah, B. Dubey, *Renew. Sustain. Energy Rev.* **123**, 109761 (2020).
- [9] M. Sevilla, A.B. Fuytes, *Carbon* **47**, 2281 (2009).
- [10] J. Fan, M. De Bruyn, V.L. Budarin, M.J. Gronnow, P.S. Shuttleworth, S. Breeden, D.J. Macquarrie, J.H. Clark, *J. Am. Chem. Soc.* **135**, 11728 (2013).