

Mechanochemical Reaction for Cs Removal from Cs-Loaded Illite

Sung-Wook Kim*, Ilgook Kim, In-Ho Yoon, Min Ku Jeon
Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon 340571
*Corresponding author: swkim818@kaeri.re.kr

1. Introduction

Illite is a non-expandable clay mineral, whose composition is $K_{0.8-0.9}(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2$. Cs removal from the illite is challenging because Cs^+ ions are strongly trapped in interlayer and frayed edge sites of its layered structure [1]. In our recent study, it was demonstrated that high-temperature molten chloride salt treatment could effectively extract Cs^+ ions from the Cs-loaded illite [2]. More than 99% of Cs^+ ions were removed after the thermal treatment in NaCl-MgCl₂-CaCl₂ ternary system at 850°C [2]. It was revealed that vigorous cation incorporation (mainly, Mg^{2+} ions) from the molten chloride medium into the two-dimensional illite structure induced structural rearrangement to three-dimensional structure (indialite, $Mg_2Al_4Si_5O_{18}$) and this results in releasing Cs^+ ions and K^+ ions from the clay into the molten chloride medium (Fig. 1) [2].

Despite the high Cs removal efficiency of the molten chloride treatment, its practical application is difficult because of complicated process equipment, high energy cost and generation of large amount of secondary wastes composed of the chloride salts. In this study, we proposed solid-state mechanochemical process for the Cs removal at room temperature. When sufficiency mechanical energy is supplied, the chemical reaction (i.e., mechanochemical reaction) between solid-state materials can occur to form reaction products [3]. As a preliminary feasibility test, mixtures of the Cs-loaded illite and MgCl₂ (solid-state) were treated by a planetary ball-mill machine delivering high-energy to supply the mechanical energy for the chemical reaction. Such ball-milling process is thought to be simple, cost-effective, and scalable.

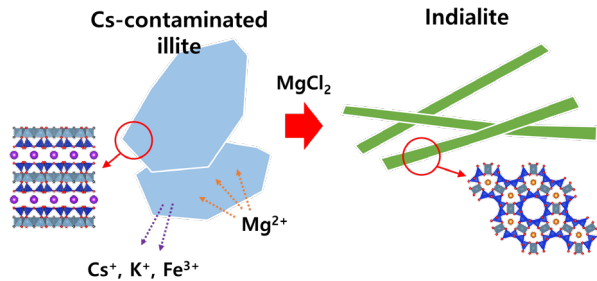


Fig. 1. Structural evolution and Cs removal of illite by cation incorporation from molten chloride

2. Methods and Results

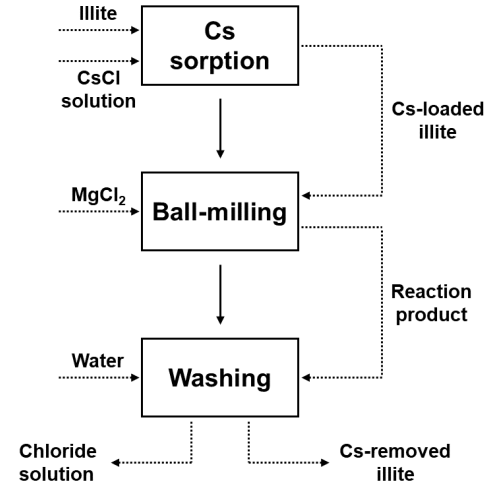


Fig. 2. Experimental procedure for mechanochemical Cs removal process from Cs-loaded illite

Fig. 2 briefly shows the experimental procedure of this study. Illite was aged in a CsCl solution (3mM) for few days to prepare the Cs-loaded illite. The Cs-loaded illite was mixed with MgCl₂ and the mixture was ball-milled (using a ZrO₂ jar and ZrO₂ balls) at 400 RPM for 8 h to ignite the chemical reaction for the Cs removal, i.e., Mg^{2+} ion incorporation and the simultaneous Cs^+ ion extraction. The mixing ratio is given in Table I. After the ball-milling, the reaction product was washed with deionized water to get rid of water-soluble chloride phases (including CsCl). Inductively coupled plasma (ICP) spectroscopy was carried out to evaluate the Cs removal efficiency as given in Table II.

Table I: Mixing ratio of Cs-loaded illite and MgCl₂ for ball-milling process

Sample	Cs-loaded illite (g)	MgCl ₂ (g)
1	1.5	0
2	1.5	1.5
3	1.5	4.5

It should be noted that weight of the recovered samples is larger than that of the pristine Cs-loaded illite (1.5 g). Significant amount of Zr was found in the ball-milled samples as shown in Table II. The weight gain of each samples is quite comparable to that of ZrO₂

amount calculated from the Zr concentration. This indicates that ZrO₂ fine particles came off the jar and the balls during the ball-milling to be mixed with the reaction products. In this respect, the concentrations of Cs, Mg, and K were re-evaluated as given in Table III.

Table II: Composition analysis results of reaction products after ball-milling

Sample	Pristine	1	2	3
Recovered (g)	-	2.57	1.71	1.62
Cs (ppm)	751	487	247	345
Mg (ppm)	270	-	4075	1605
K (ppm)	28970	18930	12034	20742
Zr (ppm)	95	302653	88012	49005

Table III: Compensated composition analysis results of reaction products after ball-milling (without Zr)

Sample	Pristine	1	2	3
Cs (ppm)	751	834	282	372
Mg (ppm)	270	-	4657	1736
K (ppm)	28970	32434	13750	22492

It is clearly seen that adding MgCl₂ is effective to remove Cs from the Cs-loaded illite as shown in Table III. With the removal of Cs, the incorporation of the Mg²⁺ ions and the extraction of K⁺ ions were also observed, which is similar to the chemical reaction in the previous study done at high temperature using the molten chloride medium, as illustrated in Fig. 1 [2]. Thus, it is thought that the high-temperature Cs removal reaction also can occur at room temperature when the sufficiently high mechanical energy is supplied. The Cs removal efficiency, however, was not that high (~40-50%) compared to the previous study (>99%). No tendency on the mixing ratio of the Cs-loaded illite and MgCl₂ was identified in this condition.

3. Conclusions

In this study, the mechanochemical reaction between the Cs-loaded illite and MgCl₂ at room temperature was investigated for remediating the Cs-contaminated illite. The Cs content in the illite was reduced (~40-50%) after the mechanochemical reaction with MgCl₂. From the ICP study, it was thought that the overall reaction is identical to the high-temperature reaction between the

Cs-loaded illite and the molten MgCl₂. This suggests that the simple and cost-effective ball-milling technique can be considered as a technical option for the soil remediation. However, further investigation should be followed to overcome the several issues, such as low Cs removal efficiency and the Zr contamination of the reaction products as figured out in this study.

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