

Research Article

Uranium Decontamination from Waste Soils by Chlorination with $ZrCl_4$ in LiCl-KCl Eutectic Salt

Junhyuk Jang¹, Tack-Jin Kim,² and Sungbin Park³

¹Pyroprocess Technology Division, Korea Atomic Energy Research Institute, Daejeon 34057, Republic of Korea

²Integrated Radwaste Control Team, Korea Atomic Energy Research Institute, Daejeon 34057, Republic of Korea

³Decommissioning Waste Management Team, Korea Atomic Energy Research Institute, Daejeon 34057, Republic of Korea

Correspondence should be addressed to Junhyuk Jang; jangjunhyuk@kaeri.re.kr

Received 25 March 2021; Revised 2 June 2021; Accepted 20 June 2021; Published 28 June 2021

Academic Editor: Peter Ivanov

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The dissolution behavior of U, contained in the soils, was examined through chlorination with $ZrCl_4$ to reduce the U concentration to clearance levels. Natural soils, composed of Si, Al, and approximately 2 ppm U, acted as surrogates for the contaminated soils. A salt mixture of LiCl-KCl-ZrCl₄ was prepared in an Al_2O_3 crucible at 500°C, and SiO_2 or natural soils were loaded for the chemical reactions. The reaction of SiO_2 and Al_2O_3 with $ZrCl_4$ was monitored by cyclic voltammetry, and no obvious change was observed. The results showed that SiO_2 and Al_2O_3 were stable against $ZrCl_4$. The reaction of natural soils with $ZrCl_4$ indicated that the U content decreased from 2 to 1.2 ppm, while ~0.4 ppm U appeared in the salt. Thus, the U, in the soils, dissolved into the salt by chlorination with $ZrCl_4$. Therefore, based on these results, a new method to remediate U-contaminated soil wastes by chlorination with $ZrCl_4$, followed by electrorefining of U, is suggested.

1. Introduction

Technologies that contribute to the effective decommissioning and/or dismantling of nuclear power plants are essential, especially considering that many power plants are close to the end of their design life. The dismantling of nuclear facilities produces a significant amount of radioactive waste; one such major waste is radiation-contaminated soil [1]. It is thus necessary to develop suitable technology for decontaminating the soil for disposal. Simultaneous improvement in the volume reduction of waste will significantly reduce the disposal costs and result in the efficient utilization of depository space [2].

Two research reactors and a U conversion facility have been decommissioned in Korea, generating a significant amount of radioactive soil, which is currently in temporary storage. Figure 1 shows the categories for the radioactive wastes established by Korea Institute of Nuclear Safety [3]. The majority of these soils show very low-level radioactivity, i.e., 60 Bq/g (the clearance level for U is 1 Bq/g, and thus, very low-level wastes are those that show radioactivity below

100 Bq/g). However, this number is still 60-fold greater than the permissible radioactivity for clearance. Despite the extremely low levels of radioactivity, these soils are considered as radioactive waste and therefore cannot be disposed normally. Thus, decontamination of the soils, to a level below that of deregulation, is essential.

In the aforementioned stored soils, the main contaminating radionuclide is U, and thus, the radioactivity must be reduced below 1 Bq/g for deregulation and safe disposal [3]. Contaminated soils are generally remediated by washing techniques, such as wet screening, and chemical treatments with various organic and inorganic acids, bases, salts, and chelating agents [1, 4]. However, these chemical treatments produce secondary waste, thereby reducing the decontamination efficiency. Thus, a technique that can remediate the soils, without generating secondary radioactive waste, must be developed.

The key technique for the reduction of secondary radioactive wastes is the selective dissolution of uranium oxide, which is the main contaminant. Herein, we introduce the selective dissolution of U via a chlorination of UO_2 with

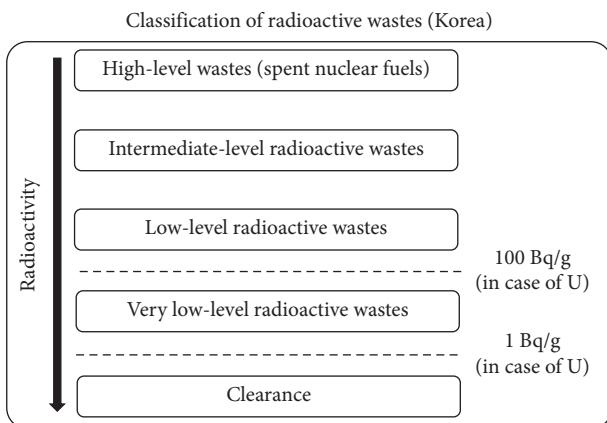
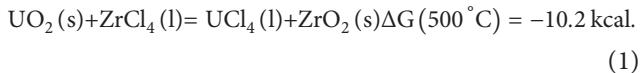


FIGURE 1: Radioactive-waste classifications, established by the Korea institute of nuclear safety [3].

$ZrCl_4$ in $LiCl-KCl$ molten salt (equation (1); UO_2 is assumed a crystal structure of U):



In this study, we examined the dissolution behavior of U, contained in soils, through chlorination with $ZrCl_4$. Natural soils were used as surrogates for the contaminated soils showing extremely low-level radioactivity. The reactivity of SiO_2 and Al_2O_3 (which are the major components in soils) with $ZrCl_4$ was evaluated to estimate the dissolution behavior of the main soil products. The change in the concentration of U in the natural soils was examined, before and after the chlorination with $ZrCl_4$. A salt mixture— $LiCl-KCl-ZrCl_4$ —was prepared in an Al_2O_3 crucible at $500^\circ C$, and SiO_2 or natural soils were immersed in it to induce a chlorination, which was monitored via cyclic voltammetry (CV). The natural soils were characterized, before and after the chemical reaction, to evaluate the amount of UO_2 dissolved. Based on these experimental results, herein, a possible method for the remediation of radiation-contaminated soils is suggested.

2. Materials and Methods

$LiCl-KCl$ eutectic salt (Alfa Aesar, A Johnson Matthey Company, purity > 99.9%) was dried at $500^\circ C$, under vacuum, before use. $ZrCl_4$ (Alfa Aesar, A Johnson Matthey Company, purity > 99.5%) was dissolved into the molten $LiCl-KCl$ for the preparation of $LiCl-KCl-ZrCl_4$. SiO_2 (Sigma-Aldrich, purity > 99.5%, ~325 mesh) and natural soils were used for the chlorination. The natural soils, used as the surrogate material for U-contaminated soils, were collected near the dismantled nuclear facility. The soils were sieved by 70 mesh, indicating that the particle sizes were less than $210 \mu\text{m}$.

160 g of $LiCl-KCl$ were loaded into an Al_2O_3 crucible (diameter: 70 mm and height: 55 mm), which was then heated to $500^\circ C$. 9.2 g of $ZrCl_4$ was added into the molten $LiCl-KCl$, and temperature was maintained for 4.3 h.

50 g of SiO_2 was added into $LiCl-KCl-ZrCl_4$, in the Al_2O_3 crucible, at $500^\circ C$, and the temperature was maintained for 4 h. The consumption of $ZrCl_4$ was monitored from the peak intensity for oxidation/reduction of Zr^{4+} via CV (Bio-Logic, SP-300 potentiostat/galvanostat) during the chlorination of SiO_2 and Al_2O_3 with $ZrCl_4$. The cell configuration is shown in Figure 2. A W wire (diameter: 1 mm, Nilaco Corp., Japan) and glassy carbon (diameter: 3 mm, Alfa Aesar, USA) were immersed into the salt to be used as a working electrode and counter electrode, respectively. An Ag wire inserted into $LiCl-KCl$ -1 mol% $AgCl$ loaded in a Pyrex tube was used as a reference electrode. The distance between working and counter electrode was 25 mm. The CV was measured at a potential from 0 to -1.6 V in a scan rate of 100 mV/s. A detailed description of measurement was already described in a previous report [5].

The $LiCl-KCl-ZrCl_4$ mixture was heated to $500^\circ C$, and 50 g of natural soils were placed in the crucible for the chlorination of natural soils with $ZrCl_4$. The temperature of the mixture was maintained for over 20 h, and then it was gradually cooled to room temperature. The soils were then water washed to remove the adhered salt and mix homogeneously. And then the soils were vacuum dried for characterization.

The crystal structures of the samples were studied by X-ray diffraction (XRD), using a multipurpose attachment X-ray diffractometer (Bruker Corp. D8 ADVANCE, USA) with an X-ray tube producing $Cu K\alpha$ radiation. The morphology and chemical composition were observed via scanning electron microscopy (SEM) (Hitachi Ltd. S-8010, Japan), in conjunction with energy dispersive X-ray spectroscopy (EDS) (Horiba Ltd. EX-250 X-max, Japan). The soil compositions, before and after the reaction, were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Fisher Scientific, iCAP Qc). The uncertainty in the ICP measurements was within the range, 1–10%, depending on the element.

The change in the Gibbs free energy, with the reaction of various oxides and $ZrCl_4$, was calculated by using the HSC Chemistry v.9 (Outotec Oyj, Finland) software [6], as a function of temperature from $0^\circ C$ to $700^\circ C$.

3. Results

To estimate the reaction trend of soils against $ZrCl_4$, we characterized the composition of natural soils collected near the dismantled nuclear facility. Figure 3 shows the crystal structure of the soils. A pattern for illite, which consists of Si, Al, K, and OH, is mainly observed. OH was attributed to the adhered water on the soils because the samples were analyzed without drying. A pattern for SiO_2 is also provided here. The chemical composition, observed by SEM-EDS, confirmed that the main components of the soils were Si and Al, as shown in Table 1. Fe was present in minor concentrations.

Considering the composition of soils, thermodynamic reactivity of various oxides containing Si, Al, Fe, and U was estimated against $ZrCl_4$. Figure 4 shows the changes in the Gibbs free energy for the reactions as a function of the

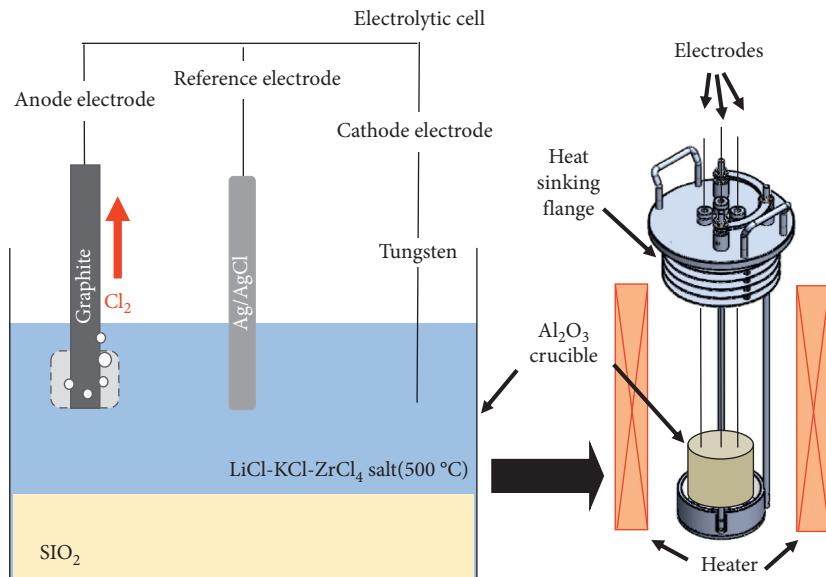


FIGURE 2: Cell configuration for the chlorination.

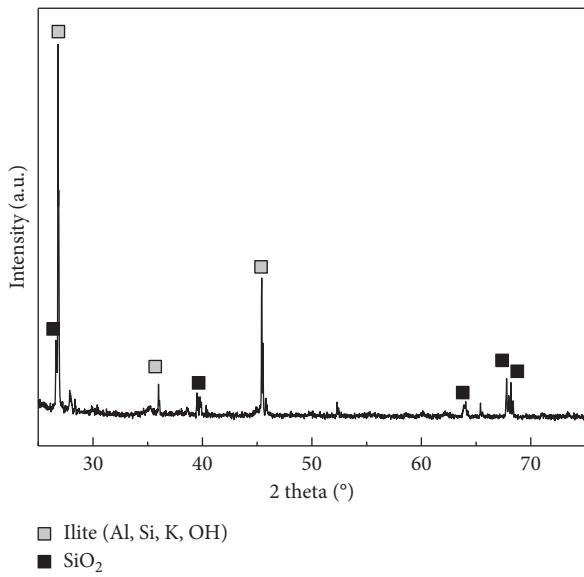
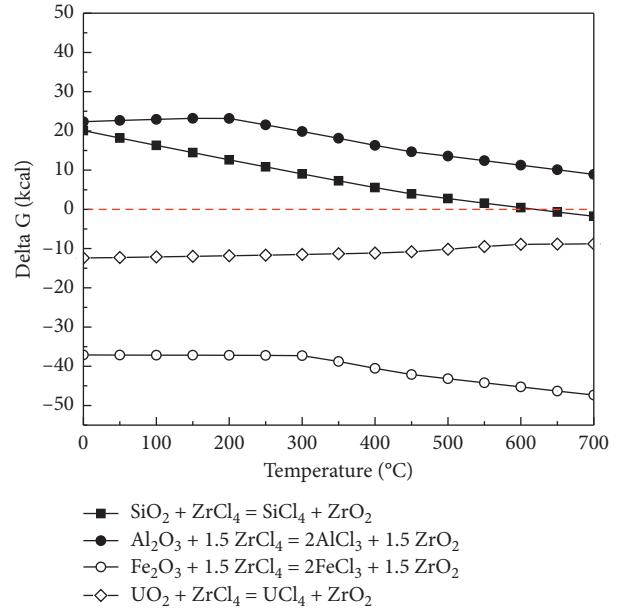


FIGURE 3: XRD pattern of the natural soils.

TABLE 1: Chemical composition of the natural soils, observed via SEM-EDS.

Element	Weight (%)	Atomic (%)
C K	8.51	13.33
O K	53.86	63.32
Mg K	1.00	0.78
Al K	10.21	7.12
Si K	18.02	12.07
K K	2.75	1.33
Ca K	1.24	0.58
Fe K	4.39	1.48
Total	100.00	—

FIGURE 4: Gibbs's free energy changes for chlorination with ZrCl₄ as a function of temperature.

temperature, calculated using HSC Chemistry v. 9. The major components, SiO₂ and Al₂O₃, were estimated to be stable against ZrCl₄, showing positive values for the changes in the free energy at temperatures below 600°C. However, the changes in the free energy became smaller with increasing temperature, showing negative values for SiO₂ at temperatures above 600°C. Furthermore, UO₂ was estimated to react with ZrCl₄, showing negative free energy changes. In this study, we assumed that the crystal structure of uranium oxide was UO₂, as we could not define the crystal structure due to its small contents. The results suggest that UO₂ can be

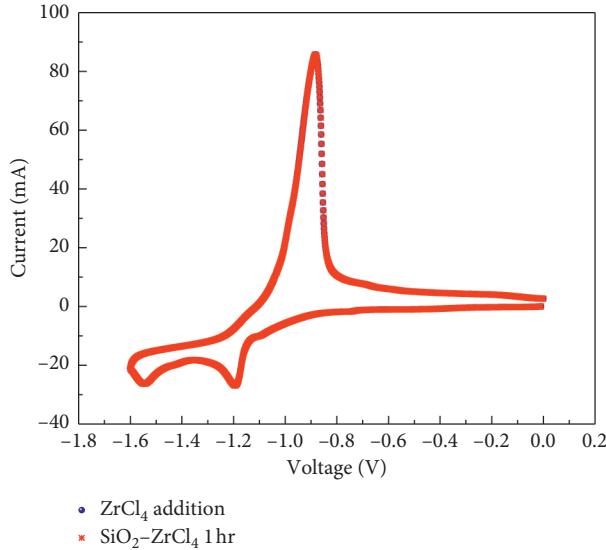


FIGURE 5: CV pattern of the salt mixture, before and after the reaction of SiO_2 and Al_2O_3 with ZrCl_4 .

selectively dissolved into LiCl-KCl salt by reaction with ZrCl_4 , without affecting the major components of soils. The minor component, Fe_2O_3 , is also estimated to dissolve into the salt by reaction with ZrCl_4 . Therefore, Fe can be separated from U using by the considerable difference in the potential for deposition on the cathode electrode (Fe is approximately -0.7 V [7] and U is approximately -1.5 V [8]) as described in Section 4.

The chlorination of SiO_2 with ZrCl_4 was carried out in an Al_2O_3 crucible to confirm the stability of SiO_2 and Al_2O_3 because the thermodynamic estimation showed that the free energy changes became smaller as the temperature increased (Figure 4). SiO_2 was immersed into LiCl-KCl-5.4 wt% ZrCl_4 , which was loaded in the Al_2O_3 crucible at 500°C and maintained for 4 h. The reaction was monitored by the intensity decrease of Zr^{4+} peak in CV measurement. Figure 5 shows the CV pattern of the salt mixture, before and after the reaction test, showing oxidation/reduction peaks of Zr^{4+} at -0.9 and -1.2 V [9]. No obvious change was observed. The result confirms that SiO_2 and Al_2O_3 were stable against ZrCl_4 at the reaction temperature.

The reaction test of natural soils and ZrCl_4 was performed to examine the dissolution behavior of U. Natural soils were used as surrogates for the radioactive soil waste. As mentioned before, the primary aim of this study was to develop an effective soil-remediation method to reduce the radioactivity of radiation-contaminated soils to a level below the clearance level (Figure 1); therefore, the U in the natural soils was suitable as a surrogate in an extreme case. The concentration of U in the natural soils was characterized by ICP-MS, and it was found that approximately 2.0 ppm of U was contained in the natural soils.

50 g of natural soils were immersed into LiCl-KCl-5.4 wt% ZrCl_4 at 500°C and maintained for 20 h for sufficient reaction with ZrCl_4 . Figure 6 shows the soils before and after the reaction. The soils settled to the bottom of the crucible after the reaction (Figure 6(b)), showing clear separation of salt (top, bright yellow) and soils (bottom, gray). The bottom was

collected and water washed to remove adhered salt (Figure 6(c)). Table 2 shows the contents of U before and after the test in both soils and salt. The contents of U in the soils decreased from 2.0 to 1.2 ppm, while approximately 0.4 ppm U appeared in the salt. Even though the concentration of initial U in the soil was extremely small, 40% of U was dissolved by the reaction with ZrCl_4 .

4. Discussion

The results of the reaction between soils and ZrCl_4 in LiCl-KCl salt showed that the U, in radioactive soils, selectively dissolved into the salt mixture, leaving behind the major soil components— SiO_2 and Al_2O_3 —unaffected. In addition, the very low-level (below the clearance level) U, in natural soils, was successfully dissolved into the LiCl-KCl salts during the chlorination of the natural soils with the salt mixture, suggesting that the U in the contaminated soils can be removed for deregulation by utilizing the method described, in this paper. The U, dissolved in the LiCl-KCl salts, seems to behave similarly to that, in the pyroprocess, i.e., the U in salt can be recovered almost completely by electrolysis. The U recovery, utilizing the electrorefining technique, is one of the most important processes in pyroprocessing, which recycles the U and transuranic materials for fuel fabrication [10, 11]. It is confirmed that almost all of the U can be recovered, from the LiCl-KCl-UCl₃ mixture, by this process [12–14].

Therefore, herein, we suggest a new method to remediate the U-contaminated radioactive waste via chlorination with ZrCl_4 , followed by electrorefining of U. Figure 7 shows a schematic of the process. First, the U-contaminated soils are immersed in the LiCl-KCl-ZrCl₄ salt at 500°C for reaction with ZrCl_4 (equation (1)), to selectively dissolve the U into the salt mixture. Second, the U in the salt is recovered by electrorefining on the cathode. The selective recovery of only U from the soils can dramatically reduce the volume of the radioactive waste.



FIGURE 6: Soils (a) before and (b and c) after the chlorination.

TABLE 2: U contents in both soils and salts, before and after the reaction test.

Samples		U contents (ppm)
Initial	Soils	2.0
	Salts	N.D.*
After reaction	Soils	1.2
	Salts	0.4

*denotes detection limit: 0.1 mg/kg.

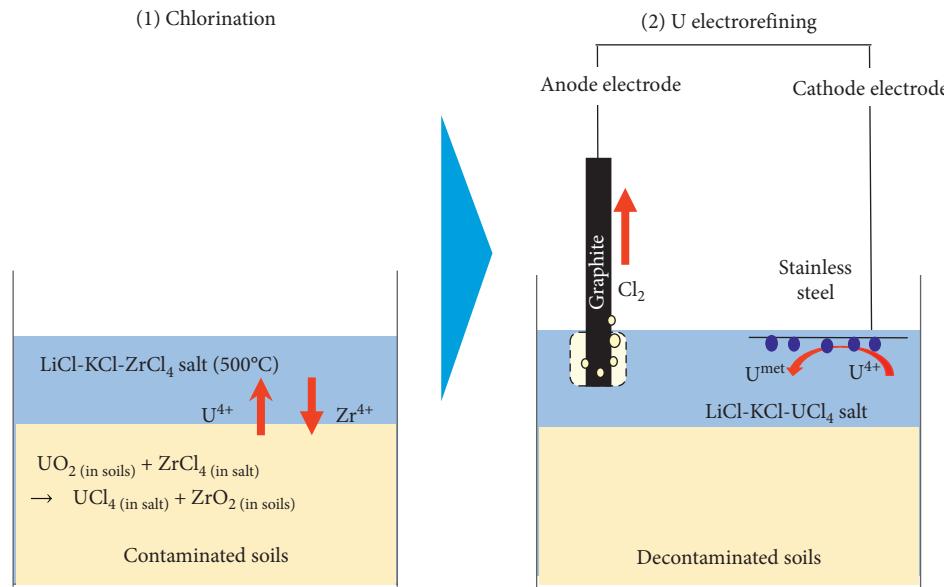
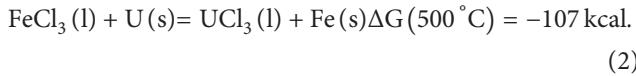


FIGURE 7: Schematics showing the method to remediate U-contaminated radioactive waste via chlorination with $ZrCl_4$, followed by electrorefining.

As shown in Table 1, ~4.4 wt% of Fe was contained in the soils, as a minor component, and possibly dissolved into the salt due to a reaction between Fe_2O_3 and $ZrCl_4$, as implied by the negative free energy changes (Figure 4). Therefore, Fe, dissolved into the LiCl-KCl salt, can be separated by Fe electrorefining, without U contamination, which is evident from the significant difference of equilibrium potential between Fe and U (the equilibrium potentials of Fe and U are approximately -0.7 V and -1.5 V , respectively [7, 8]). Moreover, the U possibly deposited on the cathode would dissolve again into the salt by the chlorination of U with $FeCl_3$ (equation (2)):



Even though K and Ca can dissolve from the soils into the salts (Table 1), they are quite small and stable and do not affect the electrorefining; KCl is one of the main components of the electrolytes; the standard potential of Ca, depositing on the cathode, is considerably low.

Thus, the proposed method, which consists of a chlorination of the contaminated soils with $ZrCl_4$ in LiCl-KCl salt followed by electrorefining, can remediate the U-contaminated soils, generating negligible secondary radioactive waste.

5. Conclusions

The dissolution behavior of U, contained in natural soils, with $ZrCl_4$ in LiCl-KCl salt was examined. The concentration of U in the soils was evaluated before and after the test. The following results were obtained:

- (i) SiO_2 and Al_2O_3 were estimated to be stable for the chlorination with $ZrCl_4$, while UO_2 was destabilized, as indicated by the thermodynamic calculations

- (ii) The chlorination test of SiO_2 and Al_2O_3 , which were the main component of soils, confirmed their stability against $ZrCl_4$ in LiCl-KCl
- (iii) The U in the natural soils was successfully dissolved into LiCl-KCl by chlorination with $ZrCl_4$, even though the initial U was extremely small

Based on these results of the laboratory test that 40% of U was dissolved from natural soils into LiCl-KCl salt by the chlorination with $ZrCl_4$, we suggest a new method to remediate the U-contaminated soils by chlorination and followed by U electrorefining. We believe that the U dissolved into the LiCl-KCl salt can be recovered by U electrorefining similarly to the pyroprocess. Further research studies of a bench scale are planned to figure out the feasibility of the proposed method.

Data Availability

The data used to support the findings of this study are included within the article.

Disclosure

The preliminary study on the chemical reaction of $ZrCl_4$ and soils was presented as a poster in 16th International Symposium on Novel and Nano Materials (ISNNM) (2020), Phoenix Jeju, Korea, PMP-P19.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

This work was supported by the Korea Atomic Energy Research Institute (KAERI) R&D program of the Korean Ministry of Science and ICT (MSIT) (Grant nos. 521210-21).

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