

IPRC 2018

International Pyroprocessing Research Conference 2018



Tokai-mura iVil, Ibaraki, Japan

October 24-26, 2018

**Sponsored by Atomic Energy Society of Japan,
Supported by Molten Salt Committee, The Electrochemical Society of Japan**



Preface

The IPRC, International Pyroprocessing Research Conference, was born in Idaho Falls, USA on 2006. Then grew up through 2nd IPRC at Jeju, Korea (2008), 3rd at Dimitrovgrad, Russia (2010), 4th at Fontana, USA (2012), 5th at Idaho Falls, USA (2014) and 6th at Jeju, Korea (2016).

Here we think the word "pyroprocess" does not mean unique specific process. As indicated by the prefix, "pyro" ("fire" in Greek), all process technologies contain high temperature steps can be called as pyroprocess. In contemporary, dry process using low temperature ionic liquid also belongs to pyroprocess.

Hence, the conference covers variety of the topics such as, overview and strategy, head-end process, oxide reduction, electrochemical and chemical separation, product treatment, waste management and molten salt reactor. Common science like basic researches, analytical techniques, safety and safeguards are also included in the topics.

The conference will be held in Tokai-mura, where is a historical center of nuclear research in Japan. Many research facilities and commercial reactors are located. The city is also surrounded by the beautiful natures like Pacific Ocean and paddy fields, and known by various natural foods such as dry vegetables and sea foods.

We expect many researchers will join this conference for making presentations and having fruitful discussions, resulting in big progress of pyroprocess technology for the world.

Tadafumi Koyama
Executive General Chair

Executive Committee

Chair: Tadafumi Koyama (Central Research Institute of Electric Power Industry, Japan)

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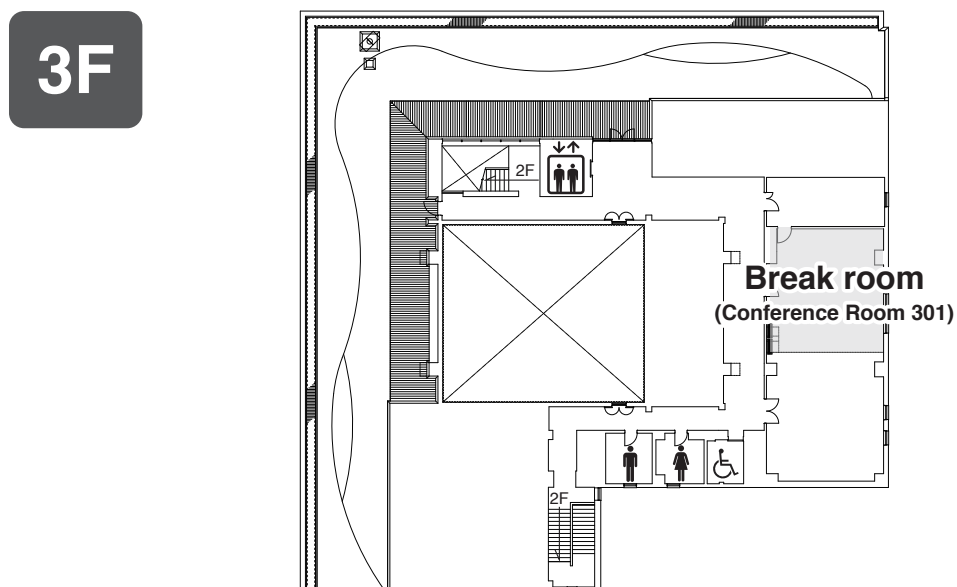
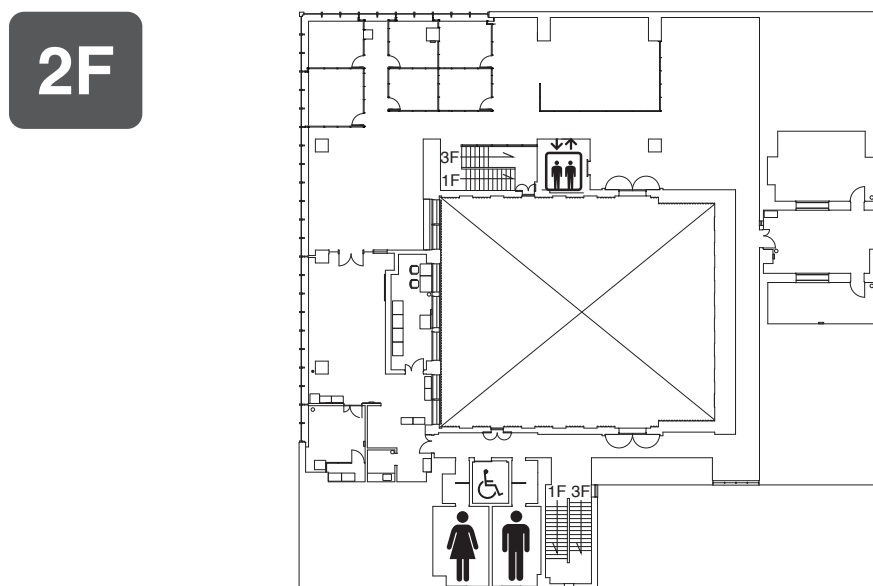
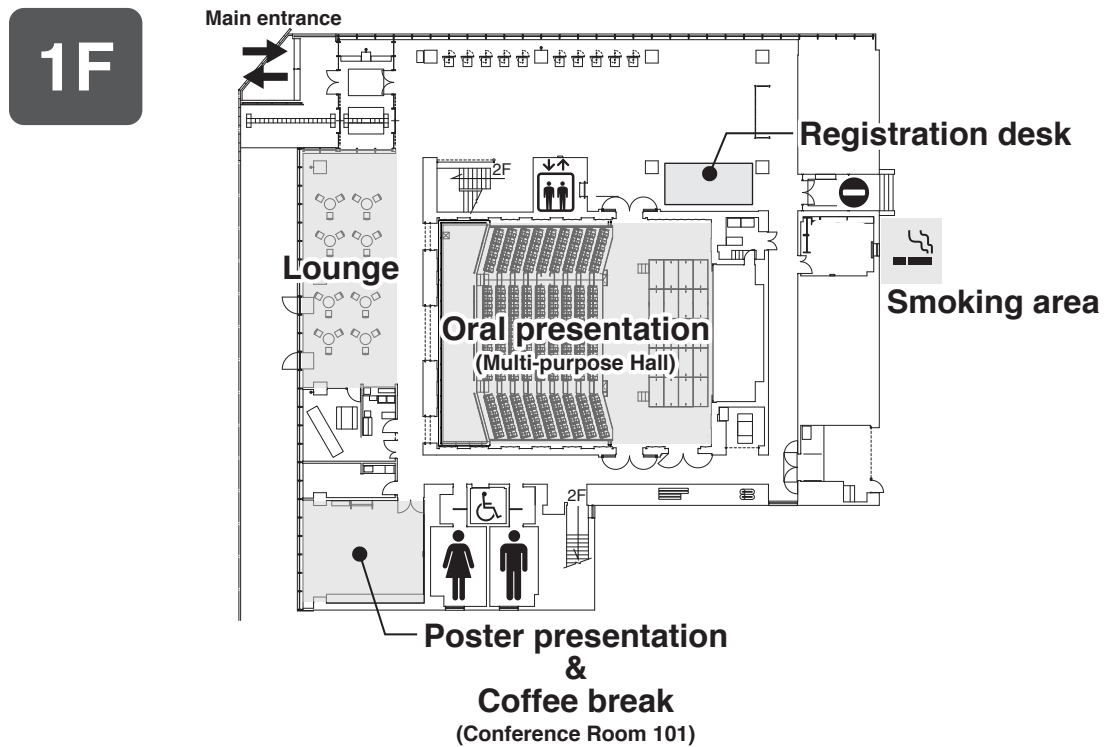
Yoshiharu Sakamura (Central Research Institute of Electric Power Industry, Japan)

Yasuhiro Tsubata (Japan Atomic Energy Agency)

Daisuke Watanabe (Hitachi Ltd., Japan)

	10/24 (Wed.)	10/25 (Thu.)	10/26 (Fri.)
9:00	Registration		
	Welcome and Opening Remarks	Oral presentation	Oral presentation
10:00	Oral presentation		
		Break	Break
11:00	Break	Oral presentation	Oral presentation
	Oral presentation		
12:00	Lunch	Lunch	Lunch
13:00	Oral presentation	Oral presentation	Oral presentation
14:00			
	Break	Break	Break
15:00	Oral presentation	Oral presentation	Oral presentation
16:00			
			Closing Comments
17:00			
	Poster Session		
18:00			
19:00		Banquet	
20:00			

Floor plan



Wednesday October 24, 2018

09:00 **Registration**

09:30 **Welcome and Opening Remarks**

Session 1: Overview and Strategy

Chair: Tadafumi Koyama

09:45	Electrochemical Processing R&D
[O1]	M. Williamson ANL
10:10	Pyroprocessing of ZrN-based Nitride Fuels
[O2]	H. Hayashi, T. Sato JAEA
10:35	Development of Pyroprocessing Technologies Providing Highly Flexible Nuclear Fuel Cycle Scenarios
[O3]	M. Iizuka ¹ , T. Murakami ¹ , T. Nohira ² , K. Tada ³ ¹ CRIEPI, ² Kyoto University, ³ JAEA

11:00 **Break**

Chair: Mark Williamson

11:15	Pyroprocessing Technologies Dedicated to Nuclear Fuel Cycle in Thorium-based Molten Salt Reactor
[O4]	Q.N. Li Shanghai Institute of Applied Physics, CAS
11:40	Applications of Pyroprocessing Methods to Molten Chloride Salt Reactors
[O5]	M. Simpson University of Utah

12:05 **Lunch**

Chair: Qingnuan Li

13:05	The Role of Pyroprocessing in the Development of Molten Salt Reactors
[06]	G.L. Fredrickson INL
13:30	Academic Research Paths on Pyroprocessing Technology in the United States with Respect to Other Nations
[07]	S. Phongikaroon Virginia Commonwealth University
13:55	Pyrochemical Operations and Development at Lawrence Livermore National Laboratory
[08]	D. Rappleye ¹ , P. Okabe ² , C. Zhang ² , M. Simpson ² ¹ Lawrence Livermore National Laboratory, ² University of Utah
14:20	Overview of Electrorefining Experiments with Irradiated Metallic Fuel METAPHIX in Molten LiCl-KCl on Solid Reactive and Inert Cathodes
[09]	P. Soucek ¹ , T. Murakami ² , K. Uruga ² , A. Rodrigues ¹ , M. Iizuka ² , J.-P. Glatz ¹ ¹ EC, JRC Karlsruhe, ² CRIEPI

14:45 **Break**

Session 2: Electrochemical and chemical separation

Chair: Pavel Soucek

15:05	Recovery of Residual U/TRUs in LiCl-KCl Molten Salt by Means of Reaction with Rare Earth Metals
[O10]	D. Yoon, J. Jang, J. Shim, S. Paek, S. Lee KAERI
15:30	Development of a Liquid Ga Electrode for Pyroprocessing
[O11]	T. Murakami, M. Iizuka CRIEPI

15:55	Actinide Separation over Lanthanides via Aluminium/Gallium Cathode Based Electrolysis in LiCl-KCl Eutectic
[O12]	W. Shi, Y. Liu, K. Liu, Z. Chai Institute of High Energy Physics, CAS
16:20	Zirconium(IV) Electrochemical Behavior and Electrorefining in Molten Fluoride Salts
[O13]	E. Mendes ¹ , D. Quaranta ¹ , L. Massot ² , M. Gibilaro ² , J. Serp ¹ ¹ CEA Marcoule, ² LGC, Toulouse University
16:45	Electrochemical Evaluation of Some Amide-type Ionic Liquids Irradiated with Gamma-ray
[O14]	Y. Katayama, K. Yoshii, N. Tachikawa Keio University

17:10 **Poster Session**

18:30 **Adjourn**

Thursday October 25, 2018

Session 2 (Continued): Electrochemical and chemical separation

Chair: Hirokazu Hayashi

09:20	Experimental Study on Electrorefining of High-content-Zr TRU Metal Fuel
[O15]	T. Omori, H. Nakamura, Y. Tsuboi, K. Arie Toshiba Energy Systems & Solutions Corporation
09:45	Electrochemical Behavior of Alkali/Alkaline-Earths on Liquid Bi in LiCl-KCl Eutectic System
[O16]	M. Woods, S. Phongikaroon Virginia Commonwealth University
10:10	Separation of Rare Earth, Thorium Fluoride Using Precipitation-distillation Coupled Method in FLiNaK Melts
[O17]	H.Y. Fu, Y. Luo, J.X. Geng, Y. Yang, Q. Dou, Q.N. Li Shanghai Institute of Applied Physics, CAS

10:35 **Break**

Chair: Tae-Hong Park

10:50	Bi-Ce and Bi-Hf Alloy Formation in LiCl-KCl for Intermetallic Density Based Group Separation of Actinides and Lanthanides
[O18]	S. Sohn ¹ , J. Park ¹ , S. Jeong ² , J. Hur ² , I.S. Hwang ² ¹ Ulsan National Institute of Science and Technology ² Seoul National University
11:15	Application of Electrochemical Technology in TMSR
[O19]	W. Huang ^{1,2} , F. Jiang ^{1,2} , H. Peng ^{1,2} , T. Zhu ^{1,2} , C. She ^{1,2} , D. Han ^{1,2,3} , X. Wang ^{1,2,3} , Q. Xu ^{1,2,3} , Y. Gong ^{1,2} , Q. Li ^{1,2} ¹ Shanghai Institute of Applied Physics, CAS ² Key Laboratory of Nuclear Radiation and Nuclear Energy Technology, CAS ³ University of Chinese Academy of Sciences

11:40	Processing of Fuel Debris Using Molten Salts -Dissolution Behavior of Zirconium Compounds to the Molten Fluorides-
[O20]	T. Sato ¹ , H. Matsuura ¹ , N. Sato ²
	¹ Tokyo City University, ² Tohoku University

12:05 **Lunch**

Chair: Weiqun Shi

13:05	A Particularly Simple NH ₄ Cl-based Method for the Dissolution of UO ₂ and Rare Earth Oxides in LiCl-KCl Melt under Air Atmosphere
[O21]	Y.L. Liu, L.X. Luo, Z.F. Chai, W.Q. Shi
	Institute of High Energy Physics, CAS
13:30	Study of Reactions of Niobium Compounds with F ₂ by Thermogravimetric and Differential Thermal Analyses and X-ray Diffraction Analysis
[O22]	D. Watanabe, D. Akiyama, N. Sato
	Tohoku University
13:55	Development of Corrosion Measurement Methods for Electrorefining and Oxide Reduction Salts
[O23]	D. Horvath, O. Dale, P. Bagri, M. Simpson
	University of Utah
14:20	The Effect of Temperature, Concentration, Electrode Gap, and Electrode Depth on Solution Resistance of GdCl ₃ -LiCl-KCl System
[O24]	H.B. Andrews, S. Phongikaroon
	Virginia Commonwealth University

14:45 **Break**

Session 3: Analytical Technique

Chair: Supathorn Phongikaroon

15:05	Electrochemical On-line Monitoring of Uranium and Lanthanide Ions in LiCl-KCl Melt
[O25]	S.-E. Bae ^{1,2} , S. Choi ¹ , J.-H. Kim ¹ , Y.-H. Cho ¹ , J.-Y. Kim ^{1,2} , T.-H. Park ^{1,2}
	¹ KAERI, ² University of Science and Technology

15:30	Application of Normal Pulse Voltammetry for Bi-analyte Concentration Measurements in Molten LiCl-KCl Eutectic
[O26]	C. Zhang ¹ , D. Rappleye ² , J. Wallace ¹ , M. Simpson ¹ ¹ University of Utah, ² Lawrence Livermore National Laboratory
15:55	Optimization Fitting Method for Measuring Exchange Current Density in a Molten Salt System
[O27]	J. Zhang, S. Guo Virginia Tech
16:20	Spectroscopic, Electrochemical, and Computational Studies of Samarium Cations in LiCl-KCl
[O28]	T.-H. Park ^{1,2} , S.-E. Bae ^{1,2} , T.S. Jung ³ , K. Kwak ³ , S. Choi ¹ , N.-R. Lee ¹ , Y.-H. Cho ¹ , J.-Y. Kim ^{1,2} ¹ KAERI, ² University of Science and Technology, ³ Korea University

16:45 **Adjourn**

18:30 **Banquet**
-20:30

Friday October 26, 2018

Session 4: Safeguards

Chair: Eric Mendes

09:20	Multielectrode Array Voltammetry Sensor for Long-Duration Salt Monitoring
[O29]	N. Hoyt, J. Willit, M. Williamson ANL
09:45	A Triple Bubbler Sensor for Determining Density and Depth in Molten Salts
[O30]	A.N. Williams ¹ , A. Shigrekar ² , G.G. Galbreth ¹ , J. Sanders ¹ ¹ INL, ² University of Idaho
10:10	Determining Molten Salt Mass with a Radioactive Tracer Method
[O31]	L. Cao ¹ , D. Hardtmayer ¹ , K. Herminghuysen ¹ , S. White ¹ , A. Kauffman ¹ , J. Sanders ² , S. Li ² ¹ The Ohio State University, ² INL

10:35 **Break**

Session 5: Oxide Reduction, Product Treatment and Waste Management

Chair: Chang Hwa Lee

10:50	Study of Li ₂ O Entrainment for Reduced Uranium Product from Direct Electrolytic Reduction
[O32]	A. Burak, M. Simpson University of Utah
11:15	Preparation of γ-Uranium-molybdenum Alloys by Electrochemical Reduction of Solid Oxides in LiCl Molten Salt
[O33]	Y.-K. Zhong, Y.-L. Liu, W.-Q. Shi Institute of High Energy Physics, CAS

11:40	Mechanism of UN + CdCl ₂ Interaction in LiCl-KCl Molten Eutectic
[O34]	A. Potapov, K. Karimov, V. Shishkin, Y. Zaykov Institute of High Temperature Electrochemistry

12:05 **Lunch**

Chair: Alexei Potapov

13:05	Gas-Solid Chlorination of Metals with Impurities for Pyrochemical Pretreatment
[O35]	P. Okabe ¹ , D. Rappleye ² , M. Newton ¹ , C. Inman ³ , M. Simpson ¹ ¹ University of Utah, ² LLNL, ³ Massachusetts Institute of Technology
13:30	Application of Kinetic Model to Evaluate Behavior of Zeolite Column Systems for Spent Salt Treatment
[O36]	K. Uozumi, K. Inagaki CRIEPI
13:55	Development of Fuel Debris Treatment Technology by the Fluorination Method
[O37]	K. Endo ¹ , K. Hoshino ¹ , A. Sasahira ¹ , T. Fukasawa ¹ , T. Chikazawa ² , A. Kirishima ³ , N. Sato ³ ¹ Hitachi-GE Nuclear Energy, Ltd, ² Mitsubishi Materials Corporation, ³ Tohoku University
14:20	Casting Process Improvement for Reducing the Loss in the Metallic Fuel Fabrication Using the Pyroprocessed Materials
[O38]	J.Y. Park, S.W. Kuk, K.H. Kim, S.J. Oh, K.C. Jeong, Y.M. Ko KAERI

14:45 **Break**

Session 6: Molten Salt Reactor

Chair: Michael F. Simpson

15:05	Study on Fluoride Volatility and Low Pressure Distillation Technology at TMSR
[O39]	Q. Dou ^{1,2} , L. Sun ^{1,2} , H. Fu ^{1,2} , J. Zhou ^{1,2} , Q. Li ^{1,2} ¹ Shanghai Institute of Applied Physics, CAS ² Key Laboratory of Nuclear Radiation and Nuclear Energy Technology, CAS
15:30	Study on Vaporization Phenomena of Cesium and Iodine Dissolved in Molten LiF-NaF-KF Salt
[O40]	Y. Sekiguchi ¹ , T. Kato ² , K. Uozumi ² , K. Kawamura ³ , T. Terai ¹ ¹ The University of Tokyo, ² CRIEPI, ³ Tokyo Institute of Technology
15:55	Proof-of-concept for In-pile Electrochemical Corrosion Studies of Molten Fluoride Fuel Salt
[O41]	K.G. Kottrup ¹ , P.R. Hania ¹ , E. D'Agata ² , P. Soucek ³ , O. Benes ³ , R.J.M. Konings ³ , H.J. Uitslag-Doolaard ¹ ¹ NRG, ² EC, JRC Petten, ³ EC, JRC Karlsruhe
16:20	Safety of the Chemical Plant of the Molten Salt Fast Reactor Concept in the Frame of the SAMOFAR H2020 Project
[O42]	P. Soucek ¹ , S. Delpech ² , E. Lopez Honorato ³ , A. Marchix ⁴ , E. Merle ⁵ ¹ EC, JRC Karlsruhe, ² IPNO-IN2P3-CNRS Orsay, ³ CINVESTAV Mexico, ⁴ CEA, Centre de Saclay, ⁵ LPSC - IN2P3-CNRS/UJF/Grenoble INP

16:45 **Closing Comments**

16:55 **Adjourn**

Posters

- [P1] UCl_3 Production Using Electrochemical and Chemical Reactions with Zinc Chlorides
C.H. Lee, T.-J. Kim, D. Yoon, S.-J. Lee
KAERI
- [P2] Effect of Tungsten Electrode on U Recovery in LiCl-KCl Molten Salts
C.H. Lee, S.-J. Lee, J.-M. Hur
KAERI
- [P3] Investigation of Current-Potential Relation of Anode-Liquid Cathode Module for LCC Electrorefining
G.-Y. Kim, S. Paek, J. Jang, C.H. Lee, S.-J. Lee
KAERI
- [P4] The Development and Testing of an Oxide Reduction Voltammetry Sensor at Idaho National Laboratory
A.N. Williams, G. Cao, J. Sanders
INL
- [P5] Electrochemical Studies of Molten MgCl_2 -KCl-NaCl Salts to Measure Hydroxide Impurities and Study Effect of Mg Addition
S. Choi, N.E. Orbona, P. Okabe, C.T. Inman, M.F. Simpson
University of Utah
- [P6] Measurement of Gibbs Free Energy of Formation of GdCd_6
S. Akashi, H. Shibata, T. Sato, H. Hayashi
JAEA

- [P7] Material Balance Evaluation in Pyro-reprocessing of ADS Nitride Fuel
H. Tateno, T. Sato, Y. Tsubata, H. Hayashi
JAEA
- [P8] Estimation of the Composition of MA Nitride Fuel Irradiated in ADS
Y. Tsubata, T. Sugawara, H. Hayashi
JAEA
- [P9] Nitridation of Dysprosium and Gadolinium Dissolved in Liquid Cadmium
T. Sato, H. Hayashi
JAEA
- [P10] LLFP Recovery from Simulated Vitrified Radioactive Wastes by Reductive Decomposition of Glass Structure in Molten Salt
S. Kanamura¹, T. Omori¹, M. Kaneko¹, T. Nohira², Y. Sakamura³
¹ Toshiba Energy Systems & Solutions Corp., ² Kyoto University, ³ CRIEPI
- [P11] Redox Behaviors of Selenium and Tellurium in Molten Chlorides
Y. Sakamura, T. Murakami, K. Uozumi
CRIEPI
- [P12] Electrochemical Properties of Gadolinium on Liquid Gallium Electrode in LiCl-KCl Eutectic
M. Lin¹, B. Li^{1,2}, K. Liu², J. Pang², L. Yuan², Y. Liu²
¹ University of Science and Technology of China
² Institute of High Energy Physics, CAS

Abstracts

2018 International Pyroprocessing Research Conference
Tokai-mura, Ibaraki, Japan, October 24 - 26, 2018

Electrochemical Processing R&D

M.A. Williamson, J.L. Willit, M. Rose, A. Merwin, N. Hoyt, M.M. Tylka,
P. Motsegood, J. Figueroa, R. Blaskovitz and L. Maggos
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Argonne, IL, 60439 USA

ABSTRACT

Electrochemical processing is central to a closed nuclear fuel cycle for a metal-fueled fast neutron spectrum reactor. With the development of the electrolytic reduction process, used fuel from the GEN III and III+ light water reactors (LWR) can be converted from oxide to metallic form, which can be treated by electrorefining to recover the actinides for use in a GEN IV system. However, electrorefining used LWR fuel presents challenges to process design due to the large quantity of uranium to be recovered. At the back-end of the fuel cycle, it is essential to maximize actinide recovery from fission product laden waste salt and minimize the amount of waste salt discharged, in an engineered waste form, to a geologic repository. This paper will describe Argonne's approach to electrochemical flowsheet development along with technical results from research activities addressing the chemistry of the electroreduction and back-end waste salt treatment processes.

KEYWORDS

electrochemical processing, pyroprocessing, nuclear fuel recycling, actinide recovery

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Pyroprocessing of ZrN-based nitride fuels

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ABSTRACT

Transmutation of long-lived radioactive nuclides including minor actinides (MA: Np, Am, Cm) is effective to reduce the burden of high level radioactive wastes and using repositories efficiently. Uranium-free nitride fuel has been chosen as the first candidate fuel for MA transmutation using accelerator-driven system (ADS) in Japan Atomic Energy Agency (JAEA) under the double strata fuel cycle concept. To improve the transmutation ratio of MA, reprocessing of spent MA fuel and reusing the recovered MA is necessary. Our target is to transmute 99 % of MA arisen from commercial power reactor fuel cycle, with which the period until the radiotoxicity drops below that of natural uranium can be shorten from about 5000 years to about 300 years. Each reprocessing process is required to recover 99.9% of MA to meet the target [1]. Typical composition of the solid solution type (MA,Pu,Zr)N fuel is considered as 30 wt.% of MA nitride, 20 wt.% of Pu nitride, and 50 wt.% of ZrN (dilution material to adjust the power density). Pyroprocessing has been proposed to adopt for reprocessing of the spent MA nitride fuel.

This paper summarizes the status of our study on pyroprocessing of ZrN-based nitride fuels. Electrorefining of the ZrN-based nitride fuels is considered as a promising method. However, experimental results show that selective electrochemical dissolution of actinides into a molten salt bath is hard to be achieved, though anodic dissolution potential of ZrN is about 1V higher than those of AnN. Therefore, a significant amount of Zr is dissolved into molten salts and recovered into liquid Cd cathode by the electrorefining [2]. Formation of intermetallic compounds (*i.e.* ZrCd₂), on the surface of Cd [3] will affect the performance of selective recovery of actinides. On the other hand, selective dissolution of actinide elements into molten salts has been reported for pyrochemical dissolution of ZrN-based actinide nitrides powder samples using CdCl₂ as a chlorinating reagent [4]. Pyrochemical dissolution followed by selective recovery of actinides into liquid Cd phase is considered as an option for reprocessing of ZrN-based nitride fuels. Meanwhile, actinides recovered in Cd phase is to be converted to nitrides by nitridation-distillation combined process [2]. In this process, contamination of Zr is considered to be acceptable because Zr dissolved in Cd phase can be converted to ZrN [5].

References. [1] H. Hayashi et al., Proc. 13th OECD/NEA IEMPT, NEA/NSC/R(2015)2, 370–377 (2015). [2] State-of-the-Art Report on the Progress of Nuclear Fuel Cycle Chemistry, OECD/NEA No.7267, 165-169 (2018). [3] T. Murakami, T. Kato, J. Electrochem. Soc. 155, E90-E95 (2008). [4] T. Sato et al. , Proc. 12th OECD/NEA IEMPT, NEA/NSC/DOC(2013)3, 199-208 (2013). [5]T. Sato *et al.* NuMat2016.

KEYWORDS

Minor Actinides, Transmutation, Nitride fuel, Uranium-free, Inert matrix

Development of pyroprocessing technologies providing highly flexible nuclear fuel cycle scenarios

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ABSTRACT

The pyroprocessing technology has a lot of excellent features as an advanced nuclear fuel cycle technology such as

- No radiation damage in the solvents used in the pyroprocessing
- Recovery of all actinides (including minor actinides (MAs): Np, Am, Cm) without additional steps
- Economic advantage at smaller-scale (favorable for technology introduction, learning and innovation)

By adopting the pyroprocessing together with the metal fueled fast reactor which has hard neutron spectrum providing high MA burning efficiency, a MA recovery and transmutation system shown in Fig. 1 can be established, which flexibly accommodates various possible scenarios for the fast reactor introduction and Pu/MAs management with the largest reduction effects on nuclear waste toxicity.

To develop and evaluate the performance of this system, researches from three important viewpoints are currently in progress: (1) design of fast reactor core partially loaded with MA-containing metal fuel, (2) demonstration of MAs recovery from various products in entire fuel cycle by pyroprocessing technology, and (3) elucidation of transformation performance during multiple recycling of MAs in the proposed system.

In the field of pyroprocessing, emphasis is put on development of liquid Ga electrode in pursuit of higher separation performance between the actinides and rare earths fission products (FPs). The liquid Ga electrode also contributes to the glass-bonded sodalite waste volume reduction by removal of rare earths FPs from spent electrorefiner salt. Another challenge is recovery of halogen FPs (I and Br) from the anode used in the electrolysis of spent chloride melt. Results of these studies are finally integrated into the design of equipment concept and the pyroprocessing flow sheet.

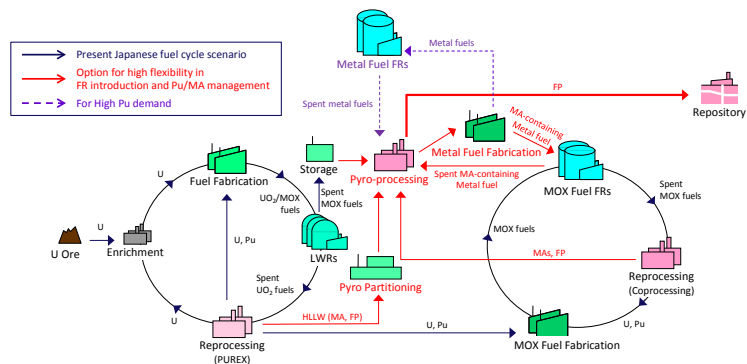


Fig. 1 Concept of highly flexible nuclear fuel cycle system

This work is being conducted as the nuclear system research and development program under the contract with MEXT Japan.

KEYWORDS

Fast reactor fuel cycle, Partitioning and transmutation, actinide/rare earth separation, waste treatment

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Pyroprocessing technologies dedicated to nuclear fuel cycle in Thorium-based Molten Salt Reactor

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ABSTRACT

Molten Salt Reactor (MSR) is one of the six nuclear energy systems recommended by Generation IV International Forum. The unique feature of MSR comes from the use of liquid fuel by dissolving actinide fluorides in carrier salt (mainly the eutectic salt comprising of ${}^7\text{LiF}$ and BeF_2), which continuously circulates inside the primary circuit. Such design makes it possible to charge/discharge fuels on line without shutting down the reactor, which is particularly well adapted to the thorium-uranium fuel cycle. The fuel exits as liquid fluoride salt in MSR, which has poor solubility in water and is suitable to be a medium for pyrochemical process. So pyroprocessing technologies is judged to be the only technologies suitable for Thorium-based Molten Salt Reactor (TMSR). A flow sheet for the nuclear fuel cycle in TMSR was designed. The targets of the flow sheet include: 1) to separate and recycle the most valuable UF_4 and carrier salts on-line as soon as possible using pyroprocessing techniques; 2) to separate ${}^{233}\text{U}$ (decay from ${}^{233}\text{Pa}$) and Th from the residue after cooling for several months for recycling at a suitable time. The fluoride volatility method (separation of U) and low-pressure distillation (separation of ${}^7\text{LiF}$ and BeF_2) are the crucial techniques in the above-mentioned flow sheet. Our work focuses on the above two methods as well as for electrochemical separation because of its versatile applications. Our updated results on these three techniques and molten salt reactor will be presented

KEYWORDS

MSR, Thorium, Pyroprocessing, flow sheet

Applications of Pyroprocessing Methods to Molten Chloride Salt Reactors

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ABSTRACT

The emergence of molten salt reactors (MSRs) as a leading Gen-IV nuclear reactor candidate is an exciting opportunity to apply knowledge gained from decades of research into metallic and oxide fuel pyroprocessing research. A number of different salt systems are currently being proposed for commercial MSRs, including chloride and fluoride salt mixtures. Pyroprocessing researchers need to become engaged with the MSR community to share understanding of molten salt reactors, which are more closely characterized as chemical reactors than nuclear reactors in the traditional paradigm. This presentation primarily targets the opportunity to apply lessons learned from electrorefining in eutectic LiCl-KCl to safeguarding, waste processing, and actinide recovery for NaCl-based MSR salt systems. High UCl₃ or UCl₄ concentrations in the salt will present challenges for electrochemically measuring or separating minor actinides from the salt. Recent studies in optimization of electrochemical measurement of minor components in LiCl-KCl-UCl₃ may point to a strategy for measuring and safeguarding PuCl₃ in molten salts containing much higher UCl₃ concentrations. Optimization of electrode geometries and the normal pulse voltammetry method enabled the measurement of down to 1 wt% GdCl₃ in salt mixtures containing up to 10 wt% UCl₃. Average relative error of the minor component concentration was only 2.7%. Long term operation of MSRs is expected to be limited by concentration of soluble fission products. This will drive the need to process and dispose of waste salt. Salt processing and waste form production developed for pyroprocessing electrorefiners can conceivably be adapted for MSR salt. Actinides can be galvanically reduced and separated from the waste salt. This has been demonstrated to be highly efficient with LiCl-KCl-UCl₃ salt mixtures using a Gd metal counter electrode. Waste salt can be contacted with H-exchanged zeolite Y to achieve fission product ion exchange into the zeolite with dechlorination via HCl generation. Dechlorination is critical in order to recycle Cl-36 and eliminate it from the high-level waste stream and repositories. Anhydrous HCl produced in this ion exchange process can be used to synthesize UCl₃ for the current reactor as well as generate startup fuel for an expanding fleet of MSR reactors.

KEYWORDS

Molten salt reactors, electrochemistry, safeguards, separations, zeolite, waste processing

2018 International Pyroprocessing Research Conference
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The Role of Pyroprocessing in the Development of Molten Salt Reactors

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ABSTRACT

The field of pyroprocessing has an important role to play in the development of molten salt reactors (MSRs). Contemporary pyroprocessing research has focused on safeguarding, reprocessing, and waste management technologies as applied to the treatment of spent metallic and oxide fuels. These same three families of technologies are needed by MSRs, but the specific requirements and challenges for implementation are quite different. This presentation outlines some of the different MSR concepts being proposed in the United States and describes some of the areas where the pyroprocessing research community can contribute.

KEYWORDS

Pyroprocessing, Molten Salt Reactor, Fluoride Salt, Chloride Salt, Uranium-Thorium Fuel Cycle, Protactinium Management, Corrosion

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**Academic Research Paths on Pyroprocessing Technology in the United States
with Respect to Other Nations**

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ABSTRACT

Used nuclear fuel (UNF) from the Experimental Breeder Reactor-II can be treated through a process known as pyroprocessing or electrochemical technology. This unique process utilized an electrolyzer to electrochemically oxidize uranium at the anode while simultaneously reduce and deposit uranium metal at the cathode. Other actinides and fission products are oxidized to form chlorides in the electrolyte, which consists primarily of eutectic LiCl-KCl. The overall goal is to recover useful actinides from UNF while separating and stabilizing radioactive fission products into durable high level waste forms which can be placed into long-term storage. This study presents progress and statistics on academic research and development (R&D) areas (e.g., oxide fuel treatment and reduction, chemical and physical processes of molten salt, electrochemical separation, safeguards and materials detection, etc.) of different countries from 2016 to present. The data sets have been obtained from available open public sources and web-based domains. The results will be presented and discussed on the U.S. R&D through collaborative efforts between universities and national laboratories with respect to other nations such as South Korea, Japan, Russia, and China.

KEYWORDS

Pyroprocessing, Chemical process, safeguards, waste processing, oxide reduction

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Pyrochemical Operations and Development at Lawrence Livermore National Laboratory

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ABSTRACT

Lawrence Livermore National Laboratory (LLNL) currently employs a variety of pyrochemical processes to produce actinide metals for programmatic needs while exploring modifications to improve operations and to expand capabilities. Processes currently employed at LLNL include direct oxide reduction, molten salt extraction, electrorefining (ER) and casting. Additionally, LLNL maintains an in-house salt preparation line. Current process feedback available to operators in these processes is limited to temperature and cell potential in ER. LLNL is currently developing electrochemical probes to provide feedback during processing to increase understanding and control of process conditions. These techniques are currently being tested in non-radioactive surrogate systems and designed to be adapted to current process equipment. LLNL is also exploring an alternative route to purifying actinides utilizing the volatility of chloride salts. This presentation discusses the work at LLNL on pyroprocessing at a high level, highlighting key results.

KEYWORDS

Pyroprocessing, Electrochemistry, Actinide

Overview of electrorefining experiments with irradiated metallic fuel METAPHIX in molten LiCl-KCl on solid reactive and inert cathodes

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ABSTRACT

A pyrochemical electrorefining process for recovery of actinides from spent metallic fuel is being investigated in Joint Research Centre Karlsruhe (JRC-Karlsruhe, European Commission) in collaboration with Central Research Institute of Electric Power Industry (CRIEPI, Japan). The peculiarity of this process resides in using solid reactive aluminium cathodes and/or solid inert cathodes for a grouped selective deposition of all actinides, which are previously anodically dissolved from the fuel. An eutectic LiCl-KCl melt serves as an electrolyte at temperatures in a range of 450-500°C. At first, the process has been studied and optimised using ternary U-Pu-Zr based alloys, in some cases containing up to 5 wt.% of selected minor actinides and lanthanides. Excellent selectivity of the actinides over lanthanides has been shown, as well as sufficient efficiency and very high capacity of solid aluminium to take up actinides.

The present work summarises demonstration experiments carried out with irradiated metallic fuels METAPHIX-1, initially composed of U₆₇-Pu₁₉-Zr₁₀-MA₂-RE₂ (wt.%, MA = Np, Am, Cm, RE = Nd, Ce, Gd, Y) and irradiated to a burn-up of ~2.5 at.%, and METAPHIX-2, initially composed of U₇₁-Pu₁₉-Zr₁₀ alloy and irradiated to ~7 at.%. The fuel was fabricated in JRC-Karlsruhe and irradiated in the PHENIX reactor in France. The experiments were focused on evaluation of selectivity of actinides over lanthanides during the electrorefining process in an electrolyte containing different concentrations of dissolved lanthanides up to 6.5 wt.%, simulating the later and final stages of the process. A comparison of usability of the solid reactive aluminium and solid inert cathodes for homogeneous recovery of all actinides was studied, as well as the effect of zirconium co-dissolution from the fuel on the process efficiency and on the structure of the deposits. In addition, the transport properties of An into solid Al were evaluated.

The results showed an excellent selectivity using aluminium cathodes, as a very efficient separation between actinides and lanthanides was achieved at all studied concentrations of lanthanides. The separation factors of the lanthanides vs. U were in a range of 10³-10⁴ and the deposits had relative content of actinides typically > 99%. On the other hand, homogeneous recovery of all actinides was possible only using the aluminium cathodes. On the solid inert cathodes, only uranium was deposited even at high cathodic current densities > 30 mA/cm², although the content of Pu in the melt was twice as high as U.

In addition, the portion of actinides, which can be recovered from the fuel without co-dissolution of Zr was investigated applying a constant anodic current density. E.g., at -28 mA/cm², 87.3% of actinides were dissolved without oxidation of Zr. During the ensuing non-selective runs, Zr was allowed to co-oxidise from the fuel. Somewhat lower current efficiencies and higher contents of the salt in the deposits on the used solid Al cathodes were found, however only a very low content of Zr was co-deposited with the actinides and it affected neither the macroscopic structure of the deposits nor the selectivity. Moreover, no Zr was found to be dissolved in the melt, which can likely be explained by rather fast reduction of the formed Zr ions by the actinides from the fuel.

KEYWORDS

Pyrochemical separation process, electrorefining, metallic nuclear fuel, homogeneous recovery of actinides, reactive aluminium electrode, solid inert electrode, molten LiCl-KCl salt

Recovery of Residual U/TRUs in LiCl-KCl Molten Salt by Means of Reaction with Rare Earth Metals

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ABSTRACT

The recovery of uranium (U) and transuranic (TRU) elements from a multicomponent salt system is an important process at the pyroprocessing stage in terms of recycling TRU materials through the fast reactors as well as minimizing cumbersome treatments in the nuclear waste stream. LiCl-KCl- UCl_3 - RECl_3 salt systems were prepared as a surrogate salt system after electrowinning. Here, U was selectively recovered by introducing rare earth (RE) metals, proceeding by chemical reactions with Gibbs free energy differences and the galvanic interactions between U and RE metals. Lanthanum (La), cerium (Ce), and yttrium (Y) metals were used in different loading methods and reacted with UCl_3 in the salt. The results revealed that three RE metals were available to recover U elements from the multicomponent salt system. It was confirmed that the U concentration in the remaining salt was below 50 ppm. In addition to the recovery of U, separation of the residual TRU elements from the salt was of interest; consequently, a couple of surrogate materials were tested [dysprosium chloride (DyCl_3) and magnesium chloride (MgCl_2)] considering the similar Gibbs free energies to that of TRUs. Experiments were performed in LiCl-KCl- UCl_3 - MgCl_2 and LiCl-KCl- UCl_3 - DyCl_3 , respectively, to recover U and Dy/Mg into a receiving crucible. The resulting data set shows that U was fully recovered while Dy was barely recovered from the salt by the reaction with Y metal. Although Dy has a similar Gibbs free energy to that of the TRU elements, its reduction potential is more negative, which presumably affected the galvanic reaction between Y and Dy. The recovered U in the receiving crucible was obtained by distillation of the salt at 1,323 K under a pressure of less than 0.1 Torr, indicating that U product was recovered as a powdery formation. In consideration of the input amount of U, 88 % of U was practically recovered. In the case where Mg was used as a surrogate material, MgCl_2 concentration was slowly decreased by the reaction with Y metal in the salt. Once U element was entirely removed from the salt, the recovery rate of Mg increased; however, the reaction time was not long enough to recover the entire quantity of Mg from the salt system. The calculated ratios between U and RE recovered in the receiving crucible were of a value greater than six. The data established in the present work should prove useful to develop a methodology to separate U/TRU elements in a multi-element salt system. Detailed results and data sets will be further presented and discussed.

KEYWORDS

Pyroprocessing, Residual Actinide Recovery, LiCl-KCl

Development of a liquid Ga electrode for pyroprocessing

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ABSTRACT

As one of the promising methods to process spent nuclear fuels, pyroprocessing utilizing chemical and electrochemical reactions in molten salts at 773 K has been developed from laboratory to engineering scale. Recently, the authors reported a notable feature of a liquid Ga electrode that separation factors (SF) of U, Pu and Am over lanthanides at the liquid Ga electrode (~12 g of Ga) were higher than that at the conventional liquid Cd electrode [1]. The high separation efficiency of the liquid Ga electrode enables us to propose a pyroprocessing highly flexibly applicable to various kinds of nuclear fuels in composition and to high level liquid wastes.

To explore the practicality of the liquid Ga electrode in LiCl-KCl melt, the followings were investigated in this paper: As a crucible to hold the liquid Ga and an electrical lead of the liquid Ga electrode, alumina and tungsten were confirmed to be suitable materials, respectively, as they showed no reaction with liquid Ga at 773 K. Polarization curves for Ce deposition in liquid Ga were measured without and with stirring the liquid Ga phase or the melt, which showed that the smaller over-potential was observed at each given cathodic current by stirring the liquid Ga phase at the higher rpm, while the polarization curves with stirring the melt were almost the same as without stirring (Fig. 1). This suggested that the rate determining step of Ce recovery in liquid Ga would be the diffusion of the Ce deposited on the surface into the bulk of the liquid Ga. Based on the aforementioned results, an electrolyzer equipping an engineering scale liquid Ga electrode (~2 kg of Ga) was designed and fabricated. Engineering scale tests of Ce (a simulant for actinides) recovery using the liquid Ga electrode are planned in ~7 kg of LiCl-KCl melt.

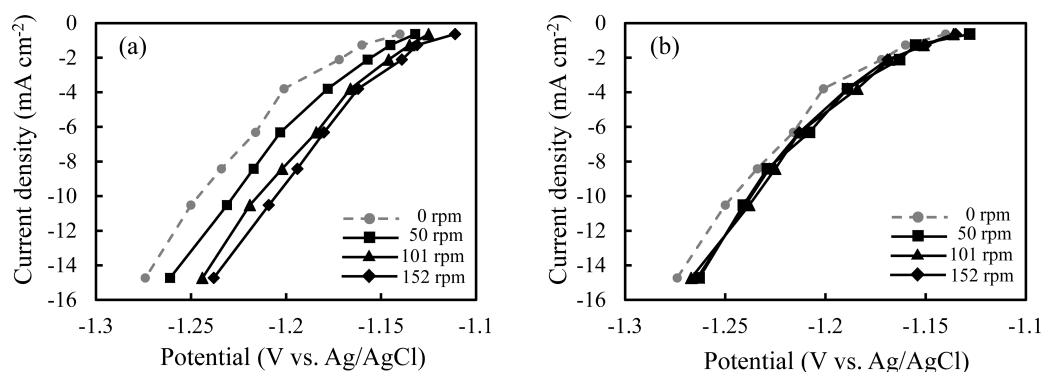


Fig. 1 Polarization curves of the liquid Ga electrode in LiCl-KCl-1mol%CeCl₃ melt at 723 K with stirring (a) the liquid Ga phase and (b) the melt.

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Reference [1] T. Murakami et al., J. Nucl. Radiochem. Sci., 16 (2016) 5-10.

KEYWORDS *Liquid Ga electrode, LiCl-KCl*

Actinide Separation over Lanthanides via Aluminium/Gallium Cathode Based Electrolysis in LiCl-KCl eutectic

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ABSTRACT

Pyrometallurgical process is one of the most attractive options for the reprocessing of advanced nuclear fuels and transmutation blankets which are well-known to possess high burn-up and high content of Pu and minor actinides. In a typical traditional pyrometallurgical process, predominant uranium is recovered onto a solid stainless steel cathode, whilst most remaining uranium, plutonium and minor actinides are deposited together at the liquid cadmium cathode. Nevertheless, one of the main drawbacks of this pyrochemical method is that significant amount (~6% wt) of rare earth elements remains in transuranium products. As reported by previous investigations, the deposition potential gap of actinides and lanthanides on a solid Al cathode are much larger than those on other active solid or liquid cathodes, and therefore the separation of actinides from lanthanides by using a solid Al electrode should be a good choice. Keeping this in mind, in this work, attempts of actinide separation over lanthanides by using active solid Al cathode and liquid Ga cathode as well as Al-Ga binary alloy cathode were conducted based on systematic electrochemical behavior investigations and correlated thermodynamic calculations toward representative elements in molten salt.

KEYWORDS

Actinides; Lanthanides; Electrolysis; Spent fuel; Pyrometallurgy

Zirconium(IV) electrochemical behavior and electrorefining in molten fluoride salts

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ABSTRACT

Zirconium is a strategic metal used in various activity sectors and particularly for nuclear applications because of its physicochemical properties: a low cross-section of neutron capture, excellent mechanical and corrosion resistance under extreme conditions (high temperature, aggressive media), . Thus 90% of the production of zirconium metal is used in the nuclear field, as zirconium alloy claddings, U–Zr fuel, and dissolvers used for spent fuel reprocessing. Zirconium metal is commonly obtained in the form of zirconium sponges produced by Kroll process that consists in a chemical reduction of zirconium chlorides into zirconium metal. On the other hand, spent zircaloy claddings represent a consequent amount of zirconium considered nowadays as a waste. There could be an economic interest to recycle the irradiated zircaloy claddings in order to valorize Zr for further reuse within nuclear applications.

One promising zircaloy recycling process consists in electrorefining in molten salt media. The use of chloride salts to operate such a process might be difficult mainly because of the several stable oxidation states of Zr coexisting in these media, whereas the use of fluoride systems should stabilize Zr oxidation state as Zr^{4+} .

A first step consists in investigating the feasibility of the electrochemical recovery of Zr metal in fluoride media. Thus, the present work focused on the electrochemical behavior study of zirconium in molten fluoride using transient electroanalytical techniques, e.g. cyclic voltammetry, square wave voltammetry, and chronopotentiometry. These different technics allowed to understand the zirconium reduction mechanism by determining the number of exchanged electrons and assessed the thermochemical properties of Zr in the salt (diffusion coefficient, etc.). Zirconium electrocrystallisation process was also investigated by chronoamperometry and cyclic voltammetry. This set of data is of first importance in order to estimate the further feasibility of the process.

KEYWORDS

Pyroprocessing, Recycling, Zirconium, molten fluorides

Electrochemical evaluation of some amide-type ionic liquids irradiated with gamma-ray

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ABSTRACT

Aprotic amide-type ionic liquids consisting of bis(trifluoromethylsulfonyl)amide (TFSA⁻) have some favorable properties, such as wide electrochemical potential window, acceptable ionic conductivity, less flammability, and less volatility. These characteristics are considered advantageous to electrochemical separation and recovery of the elements in high-level radioactive liquid waste (HLW). However, high radioactivity of various radioactive nuclides in HLW has been known to lead to radiolysis of the ionic liquids. In order to apply the ionic liquids to electrochemical separation and recovery technology, it is necessary to elucidate the electrochemical properties of the ionic liquids irradiated with radiation. In the present study, the electrochemical properties of some amide-type ionic liquids were evaluated after irradiation of gamma-ray from ⁶⁰Co at different absorbed doses.

The amide-type ionic liquids, BMITFSA (BMI⁺ = 1-butyl-3-methylimidazolium), BMPTFSA (BMP⁺ = 1-butyl-1-methylpyrrolidinium), and PP13TFSA (PP13⁺ = 1-propyl-1-methylpiperidinium), were sealed in glass ampules under vacuum and irradiated with gamma-ray of ⁶⁰Co at the absorbed dose from 0.5 to 2.0 MGy. The irradiated ionic liquids were handled in dry argon atmosphere and used for electrochemical measurements. Platinum was used as a working and counter electrode. Silver wire immersed in BMPTFSA containing 0.1 M AgCF₃SO₃ was used as a reference electrode. The protic cations of 1-methylimidazolium (HI⁺), 1-methylpyrrolidinium (MP⁺), and 1-methylpiperidinium (PP1⁺) were synthesized by the reactions of HTFSA with 1-methylimidazole, 1-methylpyrrolidine, and 1-methylpiperidine, respectively.

The colorless ionic liquids turned to the brown ones after irradiation with gamma-ray. Gas bubbles were observed when the glass ampules were opened, suggesting production of hydrogen gas as a decomposition product of the organic cation. Fig. 1 shows the linear sweep voltammograms of a platinum electrode in BMPTFSA before and after irradiation of gamma-ray (2 MGy). The cathodic current corresponding to reduction of the decomposition products was observed at the more negative potential than -1.5 V after irradiation. Since the similar cathodic current was observed in the linear sweep voltammogram of a platinum electrode in BMPTFSA containing MPTFSA, one of the possible decomposition products by irradiation of gamma-ray is considered the protic organic cation, in which a longer alkyl chain is replaced with hydrogen atom.

This work was funded by ImPACT Program of Council for Science, Technology and Innovation (Cabinet Office, Government of Japan).

KEYWORDS

Ionic liquids, Radiolysis, Electrochemical properties

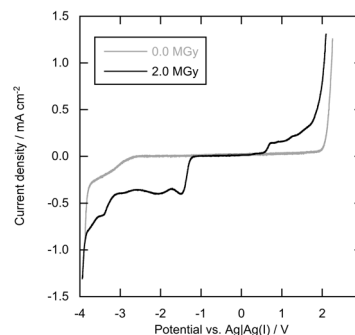


Fig. 1. Linear sweep voltammograms of a platinum electrode in BMPTFSA before and after irradiation of gamma-ray (2 MGy).

Experimental study on electrorefining of high-content-Zr TRU metal fuel

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ABSTRACT

Fast reactor (FR) is widely recognized to effectively burn transuranic elements (TRU) and contribute to reduction of the burden of the waste disposal due to its higher fission-to-neutron-capture ratio compared to light water reactors (LWRs). The most effective way to burn TRUs from LWR with minimum investment is FR cycle using uranium-free TRU fuel since it does not produce any additional TRU during irradiation. For uranium-free TRU fuel, the fuel composition would be 60wt% TRU and 40wt% Zr in case of Zr metal alloy fuel considering the melting point of fuel. In order to keep low Zr-ratio deposit at the cathode and low Zr concentration in salt during electrorefining, we have chosen Cd pool which fuel dissolved in as anode. This paper shows the electrorefining test results for high-content-Zr metal fuel.

In the experiment, LiCl-KCl eutectic salt, Cd, U and Zr (U:Zr is 60:40wt.%) with CdCl₂ for oxidant were set in a carbon steel crucible, and its temperature was elevated 500 degree C to form Cd pool with dissolved U and Zr. Then Cd cathode was set in the crucible and the electrorefining was conducted for three hours. The current densities were approx. 10mA/cm² for anode and 124mA/cm² for cathode.

Figure 1 shows applied current, measured anode potential and ampere-hour (AH) during electrorefining. Anode potential was kept at approx. -1.3V (vs Ag/AgCl) in order to dissolve only U. The total consumed electricity is 1.58AH. Figure 2 shows the U concentration in salt was kept almost constant and the Zr concentration in salt remained 0wt%. Figure 3 shows the deposited U at Cd cathode. The total amount of the deposit was 3097mg of U and 14.6mg of Zr. Zr contents in the deposit was less than 1 wt%. Electric efficiency was 66.1%. Thus, the feasibility of the electrorefining for high-content-Zr TRU metal fuel has been confirmed.

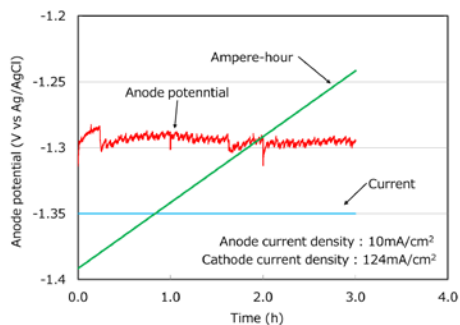


Fig.1 Current, anode potential and ampere-hour

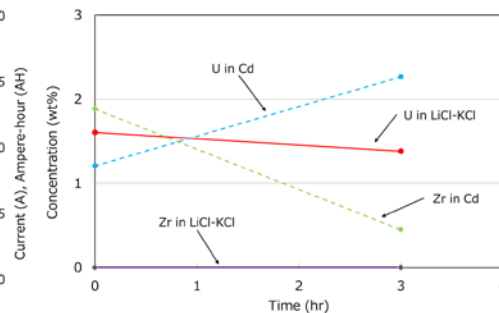


Fig.2 U, Zr concentrations in salt, Cd



Fig.3 Deposited U at Cd cathode

This work has been conducted as the nuclear system research and development program under the contract with MEXT and supported by Nuclear Safety Research Association in Japan.

KEYWORDS

Pyroprocessing, Recycling, Actinide, High-content-Zr metal fuel

**Electrochemical Behavior of Alkali/Alkaline-Earths on Liquid Bi in LiCl-KCl
Eutectic System**

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ABSTRACT

The electrochemical reactions of Sr/Sr^{2+} , Cs/Cs^+ and Ba/Ba^{2+} on a liquid Bi cathode have been independently investigated in this study using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques. All experiments were conducted in LiCl-KCl eutectic salts with the element of interest (M) at concentrations of 0.5 wt% to 4 wt% and at operating temperatures of 723 K to 823 K in order to understand temperature and concentration effects on properties such as the exchange current density (i_0) and diffusion coefficient (D). For CV experiments, scan rates of 10 mV/s to 1000 mV/s were used to elucidate the dependence of the reaction on scan rate. From the CV experiments, the diffusion coefficient of M from the bulk salt into the bulk cathode was calculated from the cathodic peaks. Additionally, the charge transfer resistance was calculated via the slope of the current-potential within the small region of overpotential (< 5 mV) when the oxidation of the deposited mass of M started to occur. This measured charge transfer resistance was then used to calculate i_0 . The EIS experiments were performed near equilibrium potential with small overpotentials (< 10 mV) to initiate the M/M^{N+} reaction. This result allowed the charge transfer resistance to be measured and i_0 was calculated from these values. From these experiments, we were able to compare the diffusion behaviors and exchange current densities of different alkali/alkaline-earth elements. Overall, the reactions of the alkali/alkaline-earths with the Bi cathode were weak compared to lanthanide and actinide reactions on the Bi cathode from other studies and our own study conducted with Ce/Ce^{3+} . The electrochemical properties calculated from this study are useful in assessing liquid Bi as a possible cathode for pyroprocessing and for modeling systems of LiCl-KCl/Bi. More detailed analyses of the systems and trends of the properties with respect to temperature, concentration, and valency will be discussed.

KEYWORDS

Pyroprocessing, bismuth, alkali/alkaline-earths, LiCl-KCl, cyclic voltammetry, electrochemical impedance spectroscopy

Separation of rare earth, thorium fluoride using precipitation-distillation coupled method in FLiNaK melts

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Abstract

Molten Salt Reactor, a unique liquid fuel reactor among the advanced fourth generation reactors, has received much attention from the international nuclear community recently. However, the efficiency of MSRs relies, to a large extent, on high-temperature online treatment of the irradiated nuclear fuel. The distillation method is one of the key steps for the pyroprocessing treatment of molten-salt liquid fuel. Due to the significant volatile difference between the carrier salt and fission products, distillation is feasible to recover the valuable fluoride carrier salts from non-volatile fission products. In the present work, the precipitation-distillation coupled method was applied to improve the separation efficiency. At high temperature, CaO was confirmed to react with NdF_3 and form rare earth oxide Nd_2O_3 insoluble in FLiNaK molten salt. At 730 °C, the conversion rate for Nd was up to 95%. After the precipitation reaction, the evaporation rate and separation efficiency under low pressure distillation were compared with the preceding one. The decontamination factor of Nd was deduced to $(9.4 \pm 0.5) \times 10^4$ while the value was $(3.1 \pm 0.4) \times 10^4$ without adding CaO. And the evaporation rate also was improved after precipitation. The similar phenomena were observed in ThF_4 -FLiNaK melts. The combination of the precipitation and distillation treatment is proved to be an effective way to achieve the high throughput performance in the salt separation process.

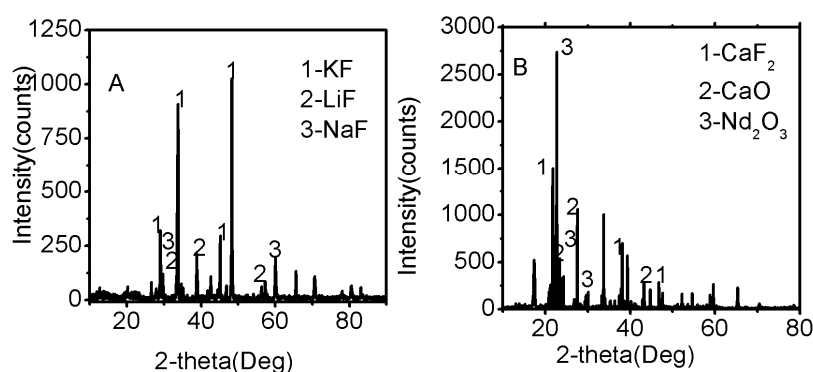


Fig. 1 XRD spectra of NdF_3 -FLiNaK distillation products: Receiver salts (A) ,
Remaining salts (B) at 930 °C, 5 Pa)

Keywords

Separation, Fluoride melts, Precipitation-distillation coupled method

Bi-Ce and Bi-Hf Alloy Formation in LiCl-KCl for Intermetallic Density Based Group Separation of Actinides and Lanthanides

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ABSTRACT

The innovative density-based separation has been developed based on the fact that bismuth intermetallic of actinides (An_xBi_y) have higher density than liquid bismuth that however has higher density than its intermetallic of Ln (Ln_xBi_y). It has been shown both theoretically and experimentally that actinides and lanthanides can be deposited onto a liquid Bi cathode to readily form intermetallics due to their low solubility limits at 500 °C. In addition, the density difference is shown to provide adequate separation forces, overcoming surface tension effect, by externally applying acceleration.

In order to investigate thermodynamic and kinetic characteristics of intermetallics, a series of cyclic voltammetry experiment have been carried out for the cations of Ce and Hf on a set of key cathode materials (tungsten and bismuth). Ce is chosen as a representative material for lanthanides whereas Hf are employed as surrogates for actinides due to their high Bi-intermetallic densities relative to pure liquid Bi as well as similar standard potential.

Powdery metal of Ce and Hf were dissolved to characterize the intermetallic formation in liquid Bi. After conducting the metal dissolution experiments, liquid Bi cell was solidified to reveal the vertical distributions. The ingot cross section was microscopically and crystallographically analyzed to investigate the stoichiometry of intermetallic phase and the vertical location of intermetallic particles in Bi.

Galvanostatic and potentiostatic electrolyses in LiCl-KCl/Bi have been conducted to reduce Ce and Hf ions in the eutectic salt so as to form their Bi-intermetallics in liquid Bi. Upon the completion of electrolysis, the vertical cross sections of solidified Bi cathode were analyzed to identify intermetallics phase and their spatial distribution in Bi to demonstrate density-based group separation behaviors of actinides and lanthanides, respectively.

From Ce experiments results, Ce could be dissolved into liquid Bi at low concentration of below approximately 3 wt. %. Then $CeBi_2$ intermetallic particles are found to locate at the top of Bi. However, $CeBi_2$ was widely distributed at the whole area in Bi cross section at the high Ce concentration over 12 wt. %. In case of Hf, all $HfBi$ intermetallic particles are found at the bottom of the Bi. The vertical distribution of intermetallic particles is confirmed to come from the density difference, not by solidification by conducting Ce dissolution experiments by two different solidification methods, i.e., quenching and annealing, to investigate its dependence shown in Bi cross section.

Electrodeposition experiments were resulted to show equivalent intermetallics formula and spatial distribution with the results of metal dissolution for Ce and Hf.

KEYWORDS

Pyroprocessing, spent nuclear fuel, actinides, lanthanides, liquid Bi, intermetallic compound, density-based group separation, electrochemistry

Application of electrochemical technology in TMSR

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ABSTRACT

The molten salt reactor (MSR) is the only liquid fuel reactor of six advanced reactors recommended by GIF (Generation IV International Forum), and is one of the best reactors for the implementation of the Th-U fuel cycle. Uranium separation is always the first step in the reported Thorium-based molten salt reactor (TMSR) fuel processing, and almost all of them are realized by fluoride volatility method (FVM). However, in the process of fluorination, the combined influence of fluoride salts and fluorine gas at high temperature has a serious corrosion to the material of reactor. So, it is necessary to develop some other technologies with potential application as alternative solutions.

Molten salt electrochemical technology is one of the most widely studied and successful pyroprocessing technologies in the world. It is suitable for treating various forms of spent fuel. In the reprocessing of TMSR fuel, electrochemical separation technology will play a role in the following areas:

(1) Direct electrolysis of U^{4+} from TMSR fuel salt. TMSR fuel salt is a good liquid electrolyte at high temperature and is suitable for direct electrochemical treatment. The composition of TMSR spent fuel is $LiF-BeF_2-UF_4-ThF_4-FPF_x$, and U^{4+} could be reduced to metal by two steps in $LiF-BeF_2$ molten salt ($U^{4+} \rightarrow U^{3+}$ and $U^{3+} \rightarrow U^0$), in which the reduction potential of latter is a little close to those of lanthanide ions and electrochemical window potential of $LiF-BeF_2$ (Be^{2+}/Be^0). As a result, it's difficult for direct electrolytic reduction and separation of U^{4+} in $LiF-BeF_2$.

(2) UO_2^{2+} reduction and separate by electrolysis. The reduction potential of UO_2^{2+} ions is far from Be^{2+}/Be^0 and those of fission products, and UO_2 products can be separated from molten salt by electro-reduction. Researches have shown that the electrode reaction of UO_2^{2+} in the chlorine salt system is a two-step reduction process: $UO_2^{2+} + e^- \rightarrow UO_2^+$, $UO_2^+ + e^- \rightarrow UO_2$. If UF_4 is converted to uranyl fluoride in the TMSR fuel salt, UO_2 product could be reduced by electrolysis and easily separated from the molten salt, which will greatly reduce the difficulty of the TMSR fuel reprocessing.

(3) Thorium recovery. After the recovery of uranium and $LiF-BeF_2$ carrier salt from TMSR fuel salt ($LiF-BeF_2-UF_4-ThF_4-FPF_x$), the residues are mainly thorium and fission products (FPs) in fluoride form. As a result, separation of thorium from FPs is the key issue in Th recovery. However, it should be noted that the reduction potential of $Th^{4+} \rightarrow Th$ is beyond the electrochemical window of $LiF-BeF_2$. It is therefore necessary to adopt a medium with wider electrochemical window, such as $LiCl-KCl$. The $LiCl-KCl$ melt is promising due to its wider electrochemical window, lower melting point and more positive reduction potential for Th^{4+}/Th^0 .

KEYWORDS

Molten salt electrochemistry, TMSR, fuel reprocessing, electrolysis separation, uranium, thorium

Processing of fuel debris using molten salts -Dissolution behavior of zirconium compounds to the molten fluorides-

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ABSTRACT

Fuel debris including nuclear fuel has been produced in the core meltdown accident at the Fukushima Daiichi nuclear power plant in 2011. In order to treat the fuel debris, a new treatment method having a wide flexibility is required. Since fuel debris has been undergone a specific generation process which is different from ordinary spent fuel, it is difficult to process by known method. In this research, we are studying pyroprocessing i.e. three procedures, selective fluorination, selective dissolution and molten salt electrolysis. We have focused on Zr which is targeted component of the fuel clad for the selective dissolution into molten salt. In order to elucidate the solubility behavior of Zr compounds into the molten salts, various compositions of eutectic FLiNaK and ZrF_4 have been coexisted at various temperatures. The upper and lower part of the sample once molten and cooled down in the furnace were scraped off and molded into pellets, and Zr contents were quantified by X-ray Fluorescence analysis. Figure 1 shows the results that ZrF_4 is dissolved and diffused into the FLiNaK at 800°C for 6 hours.

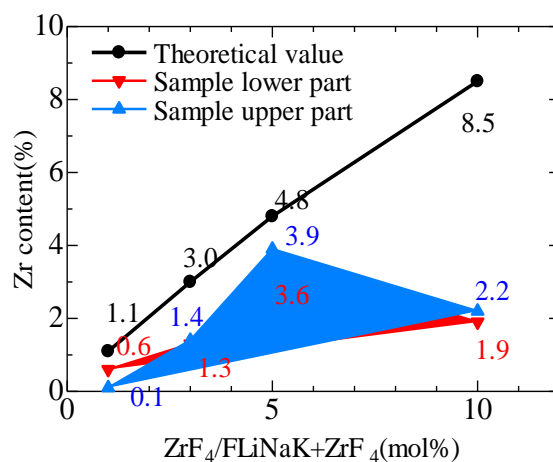


Fig. 1 Zr contents depending on initial composition of FLiNaK and ZrF_4 at 800°C for 6 hours.

KEYWORDS

Fuel debris, Fukushima daiichi nuclear plant, Molten salt, FLiNaK, Zirconium fluoride

A particularly simple NH_4Cl -based method for the dissolution of UO_2 and rare earth oxides in LiCl-KCl melt under air atmosphere

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ABSTRACT

Traditionally, the dissolution of UO_2 -based spent fuels in molten chlorides is difficult and usually conducted under strictly controlled environment. Herein, we report a particularly simple method utilizing NH_4Cl for the dissolution of UO_2 and rare earth oxides (RE_xO_y), which is of potential interest for the pyrochemical reprocessing of UO_2 -based spent fuels. In this work, NH_4Cl is conveniently introduced on the surface of LiCl-KCl melt. The results show that both of UO_2 and RE_xO_y can be successfully dissolved into LiCl-KCl melt in air atmosphere with the assistance of NH_4Cl . In addition, the dissolution mechanism is studied in detail by electrochemical and spectroscopic methods. For the dissolution of UO_2 , UO_2Cl_2 is finally formed with U_3O_8 and UO_3 as intermediates. In contrast, for the dissolution of RE_xO_y , RECl_3 is ultimately formed with production of main intermediate of $\text{RECl}_3\text{xNH}_4\text{Cl}$. The facile method proposed in this work has several advantages: (1) avoid the formation of precipitates during the dissolution process; (2) Do not produce highly volatile uranium chlorides; (3) No need to use corrosive chlorine gas. As a potential new option for the dissolution of UO_2 -based spent fuel with regard to pyrochemical reprocessing, further detailed elucidation on the dissolution behaviors of other actinides in LiCl-KCl melt and subsequent separation of actinides from fission products based on this method is much necessary.

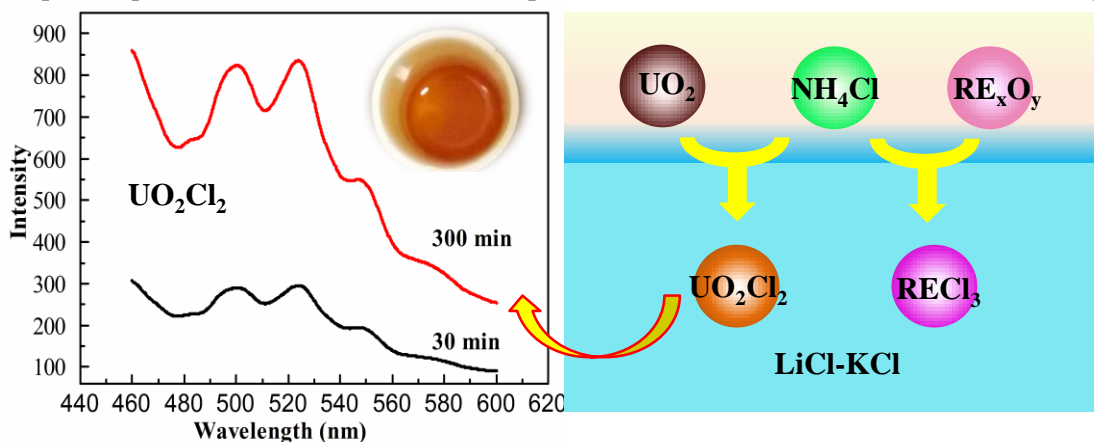


Fig. 1 Dissolution of UO_2 and RE_xO_y in LiCl-KCl melt.

KEYWORDS

Rare-earth oxides, UO_2 , NH_4Cl , Dissolution, Molten salt.

Study of reactions of niobium compounds with F₂ by thermogravimetric and differential thermal analyses and X-ray diffraction analysis

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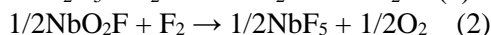
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ABSTRACT

The fluoride volatility method is one of the promising pyro-reprocessing method. In the fluoride volatility method, spent nuclear fuel is reacted with fluorination gas, and uranium is recovered as gaseous UF₆. Since fission products (FPs) are also fluorinated, fluorination and volatilization behavior of FPs is important for the fluoride volatility method. Niobium is one of the fission products, and its fluorination behavior is necessary because of highly volatile NbF₅ like UF₆. In this study, the fluorination and volatilization behavior including reaction temperature and path was investigated by thermogravimetric and differential thermal analyses (TG-DTA) and X-ray diffraction analysis (XRD).

TG-DTA curves of the reaction of niobium compounds with F₂ were obtained from room temperature to 500 °C with the Rigaku TG-DTA system (Thermoplus 2) set in a high purity argon atmosphere glove box. In order to prevent corrosion by F₂, nickel or nickel alloy was used in the TG-DTA system and the sample pan. The reaction products were identified by XRD analysis with the Rigaku Type MiniFlex600 diffractometer with a Ni filtered Cu K α irradiation (15 kV and 40 mA) equipped with a D/tex Ultra detector. The target compounds for fluorination were niobium metal, niobium oxides, which were as NbO, Nb₂O₃, NbO₂, and Nb₂O₅, and NbO₂F.

The TG-DTA curve of the reaction of Nb₂O₅ with fluorine was shown in Figure 1 as a representative of the fluorination experiments in this study. The mass change ratio (ΔM) started to decrease with two exothermic peaks above 300 °C, and ΔM reached to about -100 % at the end of the experiment. This indicates that Nb₂O₅ reacted with F₂ exothermically by two step reactions, and the niobium was volatilized completely. The product obtained by fluorination reaction after the first exothermic peak was identified as NbO₂F by XRD analysis. Furthermore, the fluorination experiment of NbO₂F was carried out, and it was clarified that NbO₂F was fluorinated to volatile product by single step reaction above 300 °C. Based on these results, the fluorination reaction of Nb₂O₅ would be described as reactions (1) and (2).



The fluorination and volatilization behavior of niobium compounds investigated in this study is applicable to evaluation of the niobium transfer phenomena in the fluoride volatility reprocessing process.

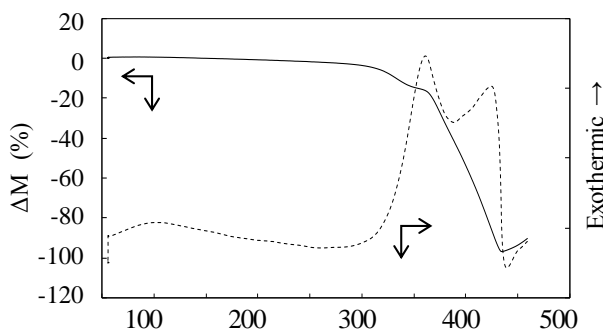


Figure 1 TG-DTA curve of the reaction of Nb₂O₅ with fluorine at a heating rate of 5 °C/min

KEYWORDS

Reprocessing, Fluoride volatility method, Fluorination, Fission product, Niobium

Development of Corrosion Measurement Methods for Electrefining and Oxide Reduction Salts

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ABSTRACT

Molten eutectic LiCl-KCl is used for electrefining spent metallic fuel, while molten LiCl-Li₂O (1 wt%) is used for oxide reduction of spent oxide fuel prior to electrefining. Steels are commonly used in currently operating electrefining and oxide reduction systems, but other metal alloys such as Inconel 600, Hastelloy C 276, and tantalum are also viable candidates for structural materials. The molten salts can contain oxidizing impurities formed from reactions with residual water and/or oxygen. The oxidation of metal alloys can lead to the contamination of the molten salt and/or degradation of vessel structures. Purity of product materials can also be lowered by these corrosion products. Corrosion inside molten salts has traditionally been studied through the use of coupons left in the salt for prolonged periods of time and then characterized after removal. With this approach, there is a large delay between a corrosion event and detection.

Instead of using coupons for mass loss corrosion measurements, electroanalytical techniques offer a more promising method to monitor metal corrosion in real time continuously. The corrosion of nickel within LiCl-KCl was monitored via open circuit potential measurements at various concentrations of moisture bubbling into the salt. It was observed the OCP increased when water was introduced to the system. By inferring from the Nernst equation, this increase in potential may be associated with an increased activity of oxidized species. When a rod of pure iron was exposed to 100 ppm H₂O at 200 ccm in molten LiCl-KCl at 773K; the OCP rose from -0.48 to -0.45 V (vs. 5mol% Ag/AgCl reference electrode), while the corrosion current as measured by the Tafel method also increased from 5×10^{-4} to 8×10^{-3} A.

In the oxide reduction system, oxygen gas is continuously formed at the anode and may lead to corrosion of metals in contact with the LiCl-Li₂O salt. Several alloys were monitored for corrosion caused by the presence of oxygen in LiCl-Li₂O using the zero resistance ammeter (ZRA). The Tafel method was also utilized as a means of obtaining corrosion potential and rate. The problem with the Tafel is the long duration of the scan, which makes it difficult for continuous corrosion monitoring. If there is a change in salt or surface composition then the measurement could have errors. An option for continuous monitoring of corrosion without applying overpotential (as in Tafel) is ZRA. This method involves shorting the working electrode (metal for corrosion) to an inert counter electrode (Pt plate) to measure both potential and current using a potentiostat. A baseline of current and potential was determined before the injection of oxygen. After the point of delivery, both current and potential were increased. The potential increased from an average starting potential of -0.9 to 0.7, -0.1, and -0.65 V vs Ni/NiO reference electrode (stainless steel 316, Inconel, tantalum, and C 276 respectively) when these alloys were exposed to pure oxygen at 47 ccm in LiCl-1wt%Li₂O at 923K. It can be concluded the impurities in ER and DER salts shall lead to increased corrosion rates.

KEYWORDS

Corrosion, Molten Salt, Electrefining and Oxide Reduction

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The Effect of Temperature, Concentration, Electrode Gap, and Electrode Depth on Solution Resistance of GdCl₃-LiCl-KCl System

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ABSTRACT

To model elemental compositions and distribution within the electrorefiner, benchtop scale electrochemical experiments are performed at universities and national labs to better understand material behavior. Within the electrochemical cell there is a small solution resistance to current between the cathode and anode. This results in a voltage drop, which can affect the results of the experiments. This voltage drop varies based upon concentration of the salt, the temperature, the distance between the anode and cathode, and the electrode depth.

For this study cyclic voltammetry was performed on GdCl₃-LiCl-KCl at various temperatures (723 – 798K), various sample concentrations (0.5, 1.0, 2.0, and 4.0 wt%), and three different electrode spacing configurations. Before each cyclic voltammogram the solution resistance of the electrochemical cell was measured using an electrochemical impedance spectroscopy (EIS) technique. In addition to exploring the effects of temperature, concentration, and interelectrode gap, the effect of the electrode depth on the solution resistance was investigated. By reducing the electrode depth incrementally and measuring the corresponding solution resistance for each electrode assembly a strong power function relationship between electrode surface area and solution resistance, $R_s (\Omega)$, was found in the form $R_s = C_R A^{-a}$, where C_R is the coefficient of resistance, A is the electrode surface area (cm²), and a is an exponential constant. Based on these experiments a model was developed to describe the relationship between electrode depth and solution resistance, allowing a stronger investigation of the other independent variables by applying these models to those experiments as well.

Concentration was found to have little to no effect on the solution resistance of the system. Meanwhile, increasing temperature showed a negative linear effect on the coefficient of resistance, C_R , found in the electrode depth model. This coefficient shows dependency on both temperature and the interelectrode gap. A decrease in C_R corresponded with a decrease in the interelectrode gap; however, due to the size limitations of these experiments, a model for the effect of the interelectrode gap was unable to be generated.

KEYWORDS

Pyroprocessing, Electrorefiner, GdCl₃, LiCl-KCl, Solution Resistance

Electrochemical On-line Monitoring of Uranium and Lanthanide Ions in LiCl-KCl Melt

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ABSTRACT

Since the uranium and nuclear elements are recovered during the pyrochemical process, it is critical to accurately determine the material flow of actinides and fission products in an electrolyte of molten salt during the process operation. Destructive analysis techniques are main tools to quantify nuclear materials with desirable measurement uncertainty for process monitoring and safeguards, but they often require tedious chemical separation procedures and radiometric or spectrometric measurements. On the other hand, the direct determination of the element concentration in the molten salt may monitor nuclear materials in real time and quickly present the meaningful safeguards information on whether the electrochemical process operates as declared. Previously, various electrochemical techniques, cyclic voltammetry (CV), chronoamperometry (CA), square wave voltammetry, and normal pulse voltammetry, were tested for the on-line monitoring of the pyrochemical process with a single element in the melt.

In this work, we have focused on developing a quantification method for the LiCl-KCl melt containing multi elements up to ~9 wt%, which likely resembles a real reaction medium in the pyroprocess. We established a CA method featuring the alternation of electrochemical deposition and dissolution, and demonstrated its capability to quantify individual metal ions present in LiCl-KCl melt containing multi components such as uranium, magnesium, and lanthanum as representatives for actinides and lanthanides. Magnesium was selected as a surrogate of plutonium because their standard redox potentials are similar. Moreover, we were able to accurately determine the concentration of uranium regardless of the composition of the solution.

KEYWORDS

Pyroprocessing, Electrochemistry, Uranium, Lanthanide, On-line Monitoring

Application of Normal Pulse Voltammetry for Bi-analyte Concentration Measurements in Molten LiCl-KCl Eutectic

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ABSTRACT

A challenge for pyroprocessing of spent nuclear fuel is to keep track of the actinides in the molten salt mixture to prevent proliferation. Recently, many publications on molten salt mixtures have either low UCl_3 concentration or single analyte show that electrochemical sensor could potentially monitor electrorefiner salt analytes in real time. However, the UCl_3 concentration during electrorefining operation is often between 5-10 wt%. The focus of this research is to develop an electrochemical method that is compatible with bi-analyte systems with up to 10 wt% UCl_3 . The electrochemical cell used in this research is shown in Fig. 1.

Two bi-analyte systems studied are U/Mg and U/Gd. Mg has similar reduction potential with Pu, therefore Mg is selected as a surrogate for Pu. Gd is used to represent rare earth metals due to their akin reduction potentials. The electrochemical method applied in this research is normal pulse voltammetry (NPV). NPV can prevent complications caused by U deposition in a melt contains high concentration of UCl_3 . Multiple optimizations were made to the NPV procedure to make it suitable for this application. The final concentration prediction average error values for UCl_3 (up to 10 wt %) and GdCl_3 (up to 3 wt%) are 1.6% and 2.70% respectively.

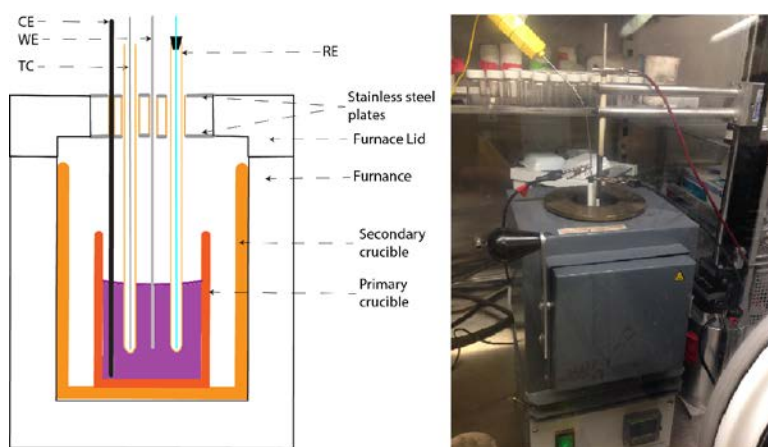


Fig. 1 Schematic diagram and photo of the electrochemical cell

KEYWORDS

International conference, Pyroprocessing, Recycling, Actinide, Electrorefining, Normal Pulse Voltammetry, Cyclic Voltammetry

Optimization Fitting Method for Measuring Exchange Current Density in a Molten Salt System

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Conventionally, the exchange current density of a redox reaction in an electrolyte is evaluated by analysis of electrochemical measurement data using methods of Tafel, linear polarization (LP) and electrochemical impedance spectroscopy (EIS). However, all those three methods are based on simplified electrode kinetic equations for which the mass transfer effects on the electrode reaction rate are neglected. In practice, the mass transfer effects cannot be completely avoided when the experiments are conducted in a static or flowing electrolyte. Therefore, the three conventional methods may introduce significant errors especially in the case of high electrode charge-transfer rate or/and low mass-transfer rate. In the present study, a method was developed to measure the exchange current density of the reduction reaction of fission products in molten salts. The method is based on applying an equation that integrates both reaction and mass transfer kinetics to fit the experimental data through optimization fitting procedures. Therefore, the mass transfer effects during experimental measurements are taken into account. The method was applied to study the exchange current density of redox reactions of La(III)/La and Gd(III)/Gd in a molten chloride salt and La(III)/La in a molten fluoride salt. The results proved that the new method could provide more reliable values than the three conventional methods. The study also identified the potential errors that are caused by the three methods. The Tafel method can lead to a much higher exchange current density while LP and EIS method normally underestimate the value, which depends on the experimental conditions.

Spectroscopic, Electrochemical, and Computational Studies of Samarium Cations in LiCl-KCl

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ABSTRACT

In molten salts including eutectic LiCl-KCl, samarium, europium, and ytterbium can form stable and soluble divalent ions besides trivalent ones whereas the other lanthanides exclusively exist as trivalent ones in the melt. Since Sm, one of the most abundant lanthanide elements in the fission products, causes a neutron poisoning effect, particular attention should be paid to the concentration of Sm in the nuclear fuel manufactured after pyroprocessing to avoid malfunction of an advanced nuclear reactor. The electrochemical and chemical behaviors of both divalent and trivalent Sm in the molten salt need to be well understood because Sm can be electrochemically deposited as alloys in reactive solid electrodes and liquid electrodes in the molten salt.

In this presentation, the oxidation state of Sm is controlled electrochemically. The reduction of Sm(III) in a LiCl-KCl eutectic produces stable Sm(II) in the melt, which can be confirmed using UV-Vis absorption and emission spectroscopic studies. The redox properties and diffusion coefficients of both divalent and trivalent Sm ions are determined using cyclic voltammetry. The intense and distinguished electronic absorption feature of Sm(II) dissimilar to that of the Sm(III) allows for the spectroelectrochemical monitoring of the redox reaction. A computational study interrogates the origins of the electronic transitions of the divalent Sm ion in the LiCl-KCl melt. In addition, the electrochemical behavior of Sm(III) in LiCl-KCl is investigated using various electrodes including rotation disk electrode (RDE) and microelectrode. The results can provide several electrochemical parameters including exchange current density.

KEYWORDS

Pyroprocessing, Lanthanide, Electrochemistry, Spectroscopy, Density Functional Theory

Multielectrode Array Voltammetry Sensor for Long-Duration Salt Monitoring

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ABSTRACT

Safeguards and process monitoring of molten salts in electrorefiners and oxide reduction equipment requires accurate quantitative measurements of actinide concentrations. The use of electroanalytical techniques such as voltammetry has been extensively investigated in recent years as they provide rapid real-time measurements for multiple species and are not affected by high radiation fields.

Researchers at Argonne National Laboratory have developed a multielectrode array sensor capable of providing concentration, redox potential, and salt level measurements and evaluated its use in pyroprocessing equipment. The sensor is composed of several bimodal electrodes arranged around a single counter electrode. All of the electrodes have specific lengths such that the differences in the immersed surface areas are known. By taking electroanalytical measurements on each electrode in a carefully designed sequence, the current per unit depth is measured to determine concentrations.

The sensor has been tested in an electrorefiner to demonstrate the practicability of its use for long-duration molten salt monitoring. Electrodes immersed in molten salt for more than six months showed no signs of degradation, provided proper electrochemical cleaning approaches were adopted. Fig. 1 shows the consistency of cyclic voltammograms taken during a 100-day measurement sequence. The response to the applied voltammetry waveforms is stable over time, resulting in overlapping curves. The peak cathodic currents associated with uranium and mischmetal chlorides in the salt are plotted in Fig. 2 and show low drift and random error over the entire test duration. The long-term stability of the measurements demonstrates the robustness of the multielectrode array for monitoring of molten salt species relevant to nuclear fuel reprocessing.

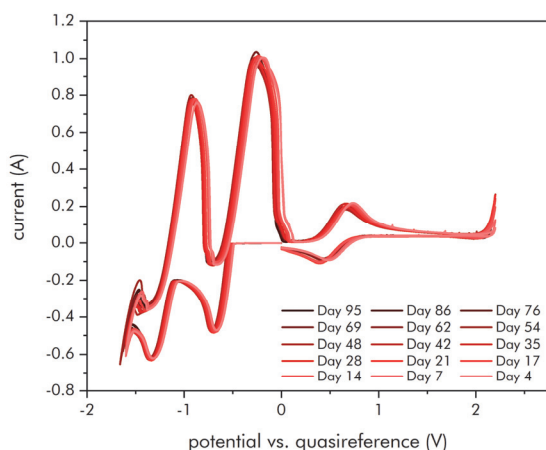


Fig. 1 Cyclic voltammograms taken throughout a 100 day measurement sequence

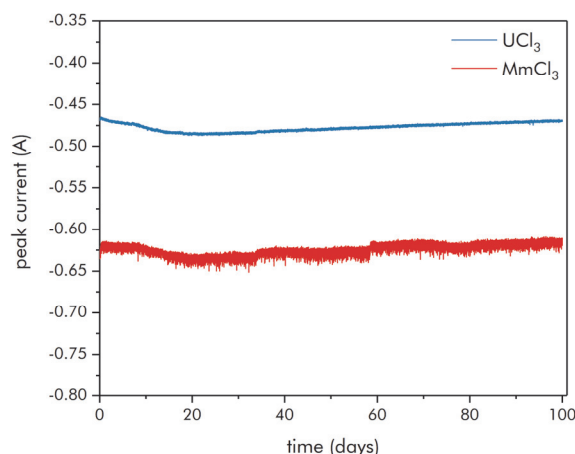


Fig. 2 Peak currents for uranium and mischmetal species during a 100 day measurement sequence

KEYWORDS

Electroanalytical Chemistry, Molten Salts, Safeguards, Process Monitoring

A Triple Bubbler Sensor for Determining Density and Depth in Molten Salts

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ABSTRACT

In the electrorefining process, uranium (U) in used nuclear fuel is transported through a molten salt electrolyte and deposited on a cathode for reuse. As part of this process, actinides accumulate in the salt over time. Periodically, a liquid cadmium cathode (LCC) is used to co-extract U and plutonium (Pu). As a result of these accumulation and extraction processes, the total mass of Pu and other actinides in the electrorefiner (ER) is constantly fluctuating. The actinide concentration in the salt can be determined by physically sampling the salt and analyzing it using an analytical technique such as inductively coupled plasma mass spectroscopy (ICP-MS). However, this analysis only provides the actinide concentration and does not provide any information on the total mass of the salt constituents of interest. In aqueous reprocessing, a single tube bubbler approach has been used to measure solution density and depth which allows for the calculation of solution volume and mass in the tank/vessel. At Idaho National Laboratory (INL), a triple bubbler sensor has been developed to accurately measure the salt density, surface tension, and depth in a molten salt vessel. The goal of this sensor is to provide real time and in situ determinations of the salt density and depth to within 1% of the actual/accepted values that can be used for material accountancy and process monitoring in the ER. Laboratory testing of the sensor has been completed in LiCl-KCl and CsCl-LiCl salts at 450 °C, 475 °C, 500 °C, and 525 °C using both a transparent furnace (for visualization) and a large two-zone furnace. In these pure salt systems, the density and surface tension are known. In addition, independent depth measurements in the salt were made using a digital height gauge equipped with a contact sensor (contact with the salt completes a circuit and illuminates an LED light). The independent depth measurements and known physical properties from one of the experiments (LiCl-KCl salt in the two-zone furnace) were used to develop fundamental equations to model and calibrate the triple bubbler sensor. Data from the other three experiments were analyzed using the developed governing equations and compared to the known properties and independent depths. For density, the percent differences between the known/measured values and the bubbler were between -0.2% and 0.2%. For surface tension the percent differences were between -1.6% and 5.9%. Finally, for depth, the percent differences were between -0.3% and 0.2%. The above comparisons served to validate the developed model and triple bubbler sensor design. In addition, the density and level determinations using the triple bubbler were well below the desired 1% for material accountancy purposes.

KEYWORDS

Pyroprocessing, Molten Salt, Safeguards, Material Accountancy, Process Monitoring

Title: “Determining Molten Salt Mass with a Radioactive Tracer Method”

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Abstract: It has been extremely challenging to determine the mass of molten salt in a container of an irregular shape. The proposed method, termed radioactive tracer dilution (RTD), starts with dissolving a radioactive source with known activity into the salt, a small amount of the salt will then be sampled and measured in terms of its mass and radioactivity. Simply by finding the ratio of the mass to radioactivity, the large unknown mass in the original container could be precisely determined. Samples of chloride salts with ^{22}Na activity were prepared, adding a common fission product, ^{154}Eu , due to its interfering gamma ray with ^{22}Na . The abundant fission product ^{137}Cs was also added to the mixture to emulate the Compton plateaus and deadtime effects, the study has found that the obfuscation of ^{154}Eu with ^{22}Na can be accounted for, and ^{22}Na can still be used to determine molten salt mass. It was also proved that the tracer was homogeneously mixed with the salt, and the accuracy of the method is preserved even with the addition of ^{154}Eu and a large amount of ^{137}Cs activities. The self-attenuation from the volumetric salt sample and the dead time are recognized but are considered trivial issues since not only the real-world application of the method will only sample at subgram level of salt, they can also be corrected with proper algorithms. This paper describes the methodology of the sample preparation, the results of the spectroscopy measurements, and the outlook of the RTD applications.

Study of Li₂O Entrainment for Reduced Uranium Product from Direct Electrolytic Reduction

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ABSTRACT

Carryover of Li₂O from direct electrolytic reduction (DER) to electrorefining needs to be minimized to avoid its reaction with UCl₃ in the electrorefiner electrolyte (LiCl-KCl-UCl₃). The effects of various DER process parameters on Li₂O entrainment in an oxide reduction process have been studied and will be presented. The parameters studied included particle size, current profile, and cathode basket rotation. A lab-scale electrolytic reduction cell was operated in an argon atmosphere glove box using samples of UO₂ powder as the starting material. Experimental techniques were developed to analyze the reduced product for both intraparticle hold-up of Li₂O (entrainment) and extent of reduction from UO₂ to U metal. Li₂O holdup was determined by immersing the cathode basket in an HCl solution held at a constant pH. A titrator kept the pH constant while recording the volume of 0.1 M HCl solution added to maintain a constant pH. The time dependence of volume versus time showed a fast titration followed by a slow titration. The fast titration was deduced to be due to residual salt coating the particles and inside of the basket. The slow titration was thus attributed to release of Li₂O that had been entrained inside of the reduced uranium particles. A post processing centrifugal salt removal technique was developed to remove excess salt and eliminate the fast stage of the titration of the cathode baskets. This involved rotating the cathode basket at 2000 rpm, in a 650°C furnace. Thermogravimetric analysis of the reduction product in air was used to quantify extent of reduction. After passing approximately 190 and 150% theoretical charge, for multiple tests at each, averages of 98 and 83% reduction were measured. This corresponds to an average of 53% current efficiency. The TGA technique was validated using pure U, and a measurement error of 2.6% (reduction extent) was calculated. Particle size was found to have little effect on Li₂O entrainment. The average entrainment was 256 μmole Li₂O per g UO₂ for the particle sizes ranging from 106 to 1000 μm. Li₂O results will also be presented for tests using interrupted current (3-12 minutes on, 0.5 – 8 minutes off) and cathode basket rotation rates ranging from 0-400 rpm.

KEYWORDS

Oxide Reduction, Pyroprocessing, Entrainment, Holdup, Lithium Oxide

Preparation of γ -Uranium-molybdenum alloys by electrochemical reduction of Solid Oxides in LiCl molten salt

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ABSTRACT

Uranium-molybdenum (U-Mo) alloys especially the γ -U-Mo alloys, with excellent irradiation performance in high temperature, has been extensively studied as low-enriched-uranium candidate fuels for strengthening nuclear security and nonproliferation worldwide. However, methods such as mechanical crushing, grinding and centrifugal atomization are of either low efficiency or high production cost. Herein, we provided a facile method to successfully prepare the monolithic γ -U-Mo alloys by direct electrochemical reduction of mixed powders of uranium oxide (UO_2) and molybdenum oxide (MoO_3) using constant voltage (3.2 V) electrolysis in LiCl molten salt at 988 K. The reduction mechanism was studied by cyclic voltammetry using the metallic cavity electrode (MCE). The electrolysis products were carefully characterized by XRD, SEM and EDS. It was found that the reduction process included 3 steps. MoO_3 was firstly reduced to MoO_2 , and then MoO_2 was converted into Mo. Finally, the intermetallic compound U_7Mo_2 was formed due to the underpotential deposition of U (resulting from UO_2 decomposition) on the pre-formed Mo. Interestingly, we found that the pure cubic γ phase was quite stable under our experiment conditions, since the main potentiostatic electrolysis product was $\gamma\text{-U}_7\text{Mo}_2$ invariably although the Mo atomic ratio of the mixed precursor varies from 50% to 24%.

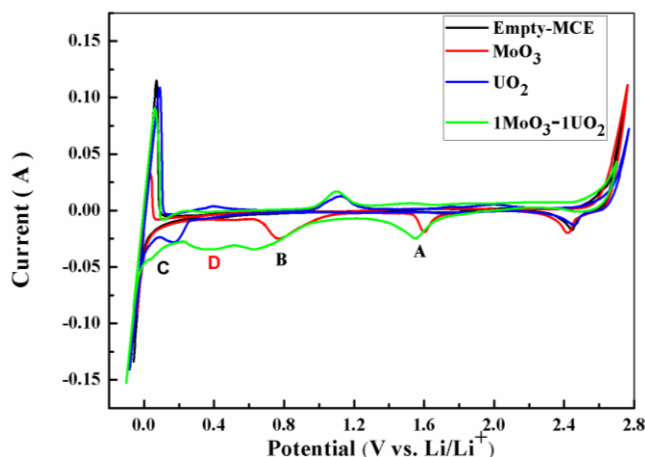


Figure.1. CV curves of a two-hole MCE without (black), with MoO_3 (red), with UO_2 (blue), and with mixed MoO_3 and UO_2 powders (Mo:U= 1:1) (green) in molten LiCl at 988 K. Scan rate: 100 mV/s.

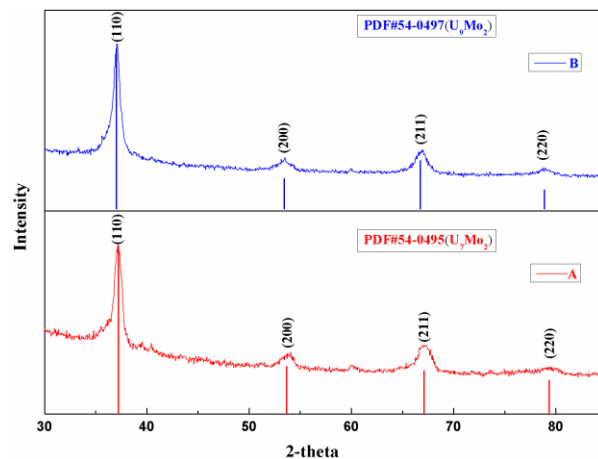


Figure.2. The XRD spectra of the potentiostatic electrolysis products of 0.8g sintered pellet of mixed UO_2 and MoO_3 powders (A) (Mo:U=24:76) and (B) (Mo:U= 21:79).

KEYWORDS

Nuclear fuel, Electrochemical reduction, Molten salt, $\gamma\text{-U}_7\text{Mo}_2$

ACKNOWLEDGEMENT

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Mechanism of UN + CdCl₂ interaction in LiCl-KCl molten eutectic

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ABSTRACT

The nitride spent nuclear fuel (SNF) dissolution in the molten LiCl-KCl eutectic is the first stage of the nitride SNF pyrochemical processing.

The aim of this work is to determine the mechanism of UN interaction with the CdCl₂-containing LiCl-KCl melt.

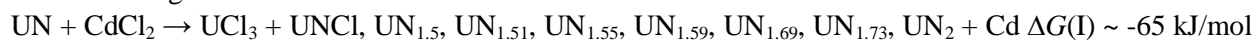
It was assumed that UN interacts with the LiCl-KCl + CdCl₂ melt according to reaction (1).



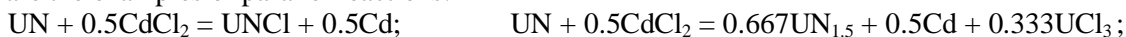
However, our experiments showed that only ~ 30% of UN dissolves with the UCl₃ formation. The rest of uranium forms a black precipitate at the bottom of the crucible, which consists of a mixture of UNCl, U₂N₃, U₄N₇, UN₂ phases, according to the X-ray phase analysis.

Using thermodynamic simulation, we showed that at 773 K reaction (1) proceeds in two stages, and each stage consists of several parallel reactions.

The first stage is as follows:

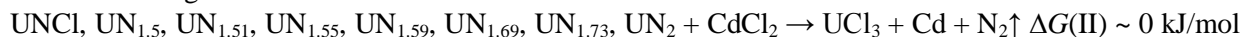


These are the examples of parallel reactions:



During the course of these reactions, nitrogen is not released, which agrees with the data of [1].

The second stage is as follows:



These are the examples of parallel reactions:



Thus, at 773 K reaction (1) proceeds only through the first stage. As a result, we get a certain amount of UCl₃ (for example, ~ 30% of the theoretically possible amount) and a sum of various nitrides. When the temperature is raised to 1023 K, the Gibbs energy of the first-stage reactions becomes $\Delta G(\text{I}) \approx -55.8$ kJ/mol, and for the second stage it is $\Delta G(\text{II}) \approx -34.3$ kJ/mol. As a result, the second stage proceeds completely and a 100% UN → UCl₃ conversion is achieved.

Conclusion

The mechanism of the UN + CdCl₂ interaction in the molten LiCl-KCl eutectic is ascertained.

Conditions, under which a 100% conversion of UN → UCl₃ is obtained, are found.

[1] Hayashi H., Kobayashi F., Ogawa T., Minato K. Dissolution of uranium nitrides in LiCl-KCl eutectic melt. J. Nucl. Science and Technology, Suppl.3. (2002) **39** pp.624-627.

KEYWORDS

Pyroprocessing, Uranium, UN, UNCl, "Soft chlorination", Thermodynamic simulation

Gas-Solid Chlorination of Metals with Impurities for Pyrochemical Pretreatment

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ABSTRACT

Many pyrochemical processes use molten chloride salts at high temperatures to achieve desired metal separation. It may be advantageous in some systems to directly chlorinate actinide and/or rare earth metals. Spent nuclear fuel from sodium fast reactors could in theory be recycled by direct chlorination followed by electroreduction of actinides from a molten chloride salt. The process being developed at University of Utah involves two gas-solid reactions—hydriding of metal followed by chlorination. The hydriding step uses H₂ and serves to reduce the particle size for chlorination. The chlorination step uses Cl₂ or HCl and converts the particles into porous chloride salts. The effects of varying process parameters, such as reaction time, temperature, chlorine concentration, particle size, and flow rate, on the extent of chlorination were tested on cerium metal with impurities of aluminum, iron, gallium, tantalum, and uranium. It was found that using concentrated chlorine gas at a furnace temperature of 250 °C for 60 minutes gave the maximum conversion of hydrides to chlorides at 92%. SEM images verified that small and highly porous particles were often formed, but in some cases the particles appeared to melt and eliminate pores. This is believed to be due to a spike in temperature in the particles due to exothermic chlorination, effectively inhibiting complete conversion to chlorides. Several methods for mitigating these limiting factors were integrated into the process and tested. Use of a peristaltic pump was tested to recirculate the reactant gas and slow down the reaction. Another method investigated was using HCl for the initial chlorination followed by reaction with Cl₂. Formation of intermetallic compounds appears to inhibit chlorination of all of the impurity metals. Uranium chloride, for example, readily forms from reaction of Cl₂ with pure U metal but not with U metal alloyed with Ce metal.

KEYWORDS

Pretreatment, chlorination, rare-earths, actinides

Application of Kinetic Model to Evaluate Behavior of Zeolite Column Systems for Spent Salt Treatment

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ABSTRACT

In the pyroprocess, spent salt containing most of the fission products (FPs) such as alkali, alkali-earth, and rare-earth elements must be treated to stabilize these FPs as a stable waste form. For this purpose, zeolite-A is considered as a candidate material to be used as a FP absorbent because it works to capture these FPs by ion-exchange and salt occlusion mechanisms. The resultant zeolite-A containing the FPs will be converted to a stable waste form, *i.e.*, glass-bonded sodalite.

As an actual process to be used for treating the spent salt, a zeolite column system is considered. In this system, the FPs in the salt are absorbed in the zeolite while the spent salt flows in the columns, and purified salt is collected at the exit. This column system has a potential to obtain a high decontamination factor of FPs with high throughput while utilizing the whole absorption capacity of the zeolite. Meanwhile, it is necessary to estimate the FP absorption rate because both FP absorption into zeolite granules and molten salt flow in the columns must be considered simultaneously for evaluating the column system's performance.

In the present study, a kinetic model, which was originally developed for estimating a performance of a contaminated water treatment facility at Fukushima-Daiichi nuclear power plant, was applied to the molten salt system. Schematic of this model is shown in Fig. 1. In this model, migration of an FP element to be absorbed in a zeolite granule is divided into five elementary steps, *i.e.*, Dispersion and Convection in inter-particle fluid, Transfer from inter-particle fluid to intra-particle fluid, Diffusion in intra-particle fluid, and Absorption in zeolite.

Among these steps, kinetic constants of Transfer and Diffusion were unknown. Therefore, parameter fittings were conducted using literature results of zeolite immersion tests in LiCl-KCl-CsCl and LiCl-KCl-SrCl₂ melts to find the best values to reproduce the test results for cesium and strontium at first. Then, validity of the model and the optimized parameters were verified by comparing with the results of zeolite column tests conducted using simulating spent salt containing cesium or strontium.

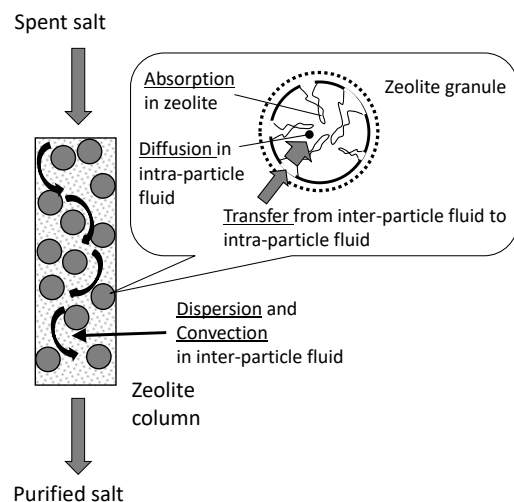


Fig. 1 FP migration model in zeolite column

KEYWORDS

Spent salt treatment, Zeolite column, Fission product absorption, Kinetics

Development of Fuel Debris Treatment Technology by the Fluorination Method

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ABSTRACT

In the past severe accidents of nuclear power plants, fuel debris was generated. These accidents occurred in different reactor types, TMI-2 (PWR), Chernobyl (RBMK), Fukushima Daiichi (BWR), which means we should consider the countermeasures for next generation reactors as well as current ones. Fuel debris contains fuel, cladding tube, control rod, structural material, concrete, and its chemical composition and characteristic are significantly different from each reactor type and accident situation. As accurate nuclear material (U+Pu) accountancy is quite important for Japan, we need to consider treatment method transforming fuel debris into manageable form. However, considering that the fuel debris generated in TMI-2 was difficult to be dissolved in nitric acid [1], it is assumed that fuel debris treatment is difficult. Therefore we propose its innovative treatment technology by the fluorination method.

The technology fluorinates almost all elements by fluorine gas, separates volatile U+Pu fluorides from other non-volatile impurities, and converts them to oxide forms (Fig.1). As the separated oxide fuel is stable and easy to be dissolved by nitric acid, this technology can flexibly respond to various options of accountancy, long-term storage, recycle (reprocessing) and disposal.

The experiments were carried out with simulated debris derived from FBR/LWR to evaluate basically the fluorination behavior of U and other impurities. In these experiments, U was volatilized as UF_6 (>99%) and recovered >90% at cold trap (CT), major impurities (Fe, Zr) were mostly remained in fluorination reactor as solid (FeF_3 , ZrF_4) for various debris types (powder or lump, simple mixture or compound or solid solution of the components, oxidation states, etc.). Fluorination behaviors of other impurities were also confirmed. As a result, it is clarified that fluorination reaction can separate U from most impurities.

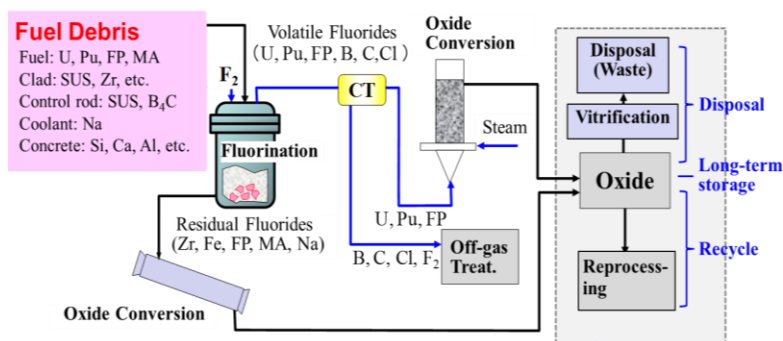


Fig.1 Fluorination treatment for fuel debris

This study is the result of “R&D of Fuel Debris Stabilization Treatment Technology by the Fluorination Method” entrusted to Hitachi-GE Nuclear Energy, Ltd. by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT).

[1] D. W. Akers, *American Chemical Society*, 293, pp.146-167 (1986)

KEYWORDS : *Severe accident, Fuel debris treatment, Fluorination, U(Pu) separation*

Casting Process Improvement for Reducing the Loss in the Metallic Fuel Fabrication Using the Pyroprocessed Materials

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ABSTRACT

Metallic fuel has been considered to provide the feasible way to transmute transuranic (TRU) materials separated from spent nuclear fuels by pyroprocessing. One of the key issues with the metallic fuel is to control the loss in the fuel slug fabrication process at a low level, the ultimate target of which is less than 0.1% to make the TRU recycling feasible. The casting methods such as an injection casting and a gravity casting have been employed to fabricate fuel slugs. The two main routes of loss during the casting process are the evaporation of volatile element such as Am and the reaction between the crucible/mold and the melt. The Am evaporation is expected to be suppressed effectively by applying high pressure of cover gas during the melting. However, the reaction between the crucible/mold and the melt poses challenge to the loss control especially when the pyroprocessed materials contain more than a certain amount of rare earth (RE) elements.

In this study, research efforts have been made to prevent the reaction between the crucible/mold and the melt during the fuel slug fabrication. Y_2O_3 layer was coated on the inside of graphite crucible by the plasma spray method. The effect of coating condition on Y_2O_3 layer properties was investigated to optimize the capability for preventing the reaction between the crucible and the melt. The characteristics of the plasma-sprayed nitride coatings were also investigated to see if the loss by reaction can be reduced further for the development of reusable crucible. The effect of the inner surface roughness of quartz mold on the adhesion of Y_2O_3 coating was examined to find an effective way to reduce the loss by the reaction between the fuel slug and molds.

The fuel fabrication leaves the scrap such as a melt residue and pieces of fuel slugs, which should be recycled in the casting process because the scrap contains TRU materials. The recycling process in the fuel fabrication was developed to control the loss on the basis of the chemical and mechanical treatments. In the chemical treatment, the scrap was cut into pieces, cleaned in nitric acid to remove the surface contamination, and then used as feedstock materials for the casting. The microstructure and chemical composition of the fabricated fuel slugs were not significantly different depending on the amount of the recycled scrap. The mechanical cleaning method, which is anticipated to be more favorable for the process operated in a hot cell, showed the similar results with the chemical treatment. The feasibility to apply the laser ablation cleaning was also assessed with a target to develop the innovative recycling process in the fuel fabrication.

KEYWORDS

Metallic fuel, Fabrication loss, Casting, Crucible, Coating, Scrap recycling

Study on Fluoride Volatility and Low Pressure Distillation Technology at TMSR

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ABSTRACT: Shanghai Institute of Applied Physics, which is in charge of developing Thorium Molten Salt Reactor System (TMSR), would use the ${}^7\text{LiF-BeF}_2$ as carrier salt and coolant in the new reactor system. The objective of the project is for thorium utilization and self sustainable Th/U fuel cycle. Fluoride volatility method, which is regarded as a promising pyroprocessing technology, can be used to achieve the separation of uranium from fuel salt in TMSR. Meanwhile, the low pressure distillation, based on the differences in the vapor pressure between carrier salt and fission products, is suitable to purify carrier salt ${}^7\text{LiF-BeF}_2$. The recycle of uranium and ${}^7\text{LiF-BeF}_2$ can reduce the inventory of fuel and carrier salt effectively.

In order to demonstrate the feasibility of the fluoride volatility method in fluoride salts, the study scale of the fluorination process was amplified step-by-step and was from small to large (from 10 g to kilograms) in the FLiBe molten salt system. After the fluorination, the concentration of U in fluoride salt decreases from 2-6 wt% to 20ppm, and the UF_6 total recovery was above 95% in the Kg-scale experiments. The DF for fission product Nb was more than 10^3 , the DF for Cs was 10^4 , and the DFs for Sr, Ce, Nd, and Sm were more than 10^7 . The Fourier transform infrared spectroscopy (FTIR) was used to monitor the uranium fluorination process in this study with high precision and fast response.

The low pressure distillation behavior of fluoride salts has been investigated at 1000°C and at pressures from 0.05 to 1.0 mm Hg using our vacuum thermogravimetric furnace. The experimental results show the decontamination factors of most rare earth fluorides in recovered salt are more than 10^2 , and this process was feasible to recycle the carrier salt. In the kilogram-scale demonstration experiments, distillation rate of carrier salt can reach 6kg/h, and the amount of recovered salt was achieved more than 98wt%. We also find that the variation of temperature of condenser can timely revealed the distillation process.

KEYWORDS: *Fluoride volatility, Low pressure distillation, Molten salt reactor, carrier salt, uranium.*

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Study on Vaporization Phenomena of Cesium and Iodine Dissolved in Molten LiF-NaF-KF Salt

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ABSTRACT

From the view point of the severe accident analysis of molten salt reactors, the vaporization phenomena of Cs and I dissolved in molten LiF-NaF-KF eutectic salt (46.5-11.5-42.0 mol%, FLiNaK) at 873-1073K were investigated by a ThermoGravimetry-Differential Thermal Analysis combined with Mass Spectrometry (TG-DTA-MS) and Molecular Dynamics (MD) simulations. The molar concentration of Cs and I in the specimens were respectively controlled under 5mol% by mixing CsI, CsF and/or KI with FLiNaK. The vapor pressure was derived from the weight loss of TG and the flow rate of the atmospheric He gas. From the result of MS, no mass peaks of the compound of alkali halides but those of ions were observed, and the vapor pressures were also derived from the ion currents of detected ions. The MD simulations were carried out on the similar composition system as the experiments in order to examine the local structure of Cs and I in the molten FLiNaK.

The dependence of the vapor pressure of Cs estimated by the MS on the concentration of I by are shown in Fig.1. The vapor pressure of Cs was remarkably low without iodide solute ("1-0" in Fig.1.), and the pressure when I was 5mol% ("1-5" in Fig.1.) was relatively higher than those when I was 1-2mol%. Therefore, the vapor pressure of Cs increased as the concentration of I in the salt increased although the concentration of Cs in the salt was kept constant. From the local structure analysis by the MD simulations, Cs and I in the molten FLiNaK had the tendency to locate close together. This tendency was consistent with the experimental result which Cs tend to evaporate with I. Accordingly, it was concluded that Cs tend to evaporate with I from the result of the vapor pressure measurements by MS and the MD simulations, and it increased Cs evaporation from the salt.

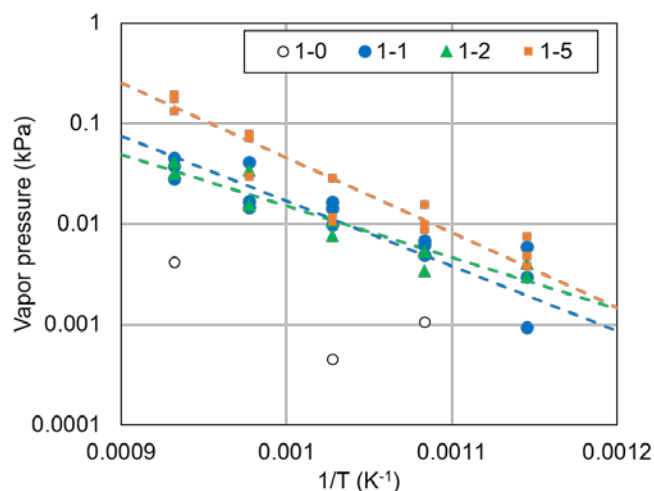


Fig. 1 Vapor pressure of Cs by MS from FLiNaK-1mol%Cs-(0-5)mol%I
(The legend represent mol% of [Cs]-[I] in specimen salt)

KEYWORDS

Molten fluoride, Vaporization, TG-DTA-MS, Molecular dynamics

Proof-of-concept for in-pile electrochemical corrosion studies of molten fluoride fuel salt

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ABSTRACT

In order to mitigate the effects of human-made climate change, new technologies are required which allow for the large-scale production of electricity without the emission of CO₂. While all nuclear power plants operate without emitting CO₂, constant safety concerns regarding for example the proliferation of weapons-grade material, the potential for a core-melt accident and the production of long-lived radioactive waste render current-gen nuclear power plants extremely expensive and politically challenging. These concerns have created the desire for a new generation of power plants (Gen IV) which address these issues. The Molten Salt Reactor (MSR) concept was identified by the Generation IV International Forum (GIF) as one of six possible candidates for a new generation of safe and reliable nuclear power plants.

In an MSR, the nuclear fuel is dissolved in a molten salt which acts as both the fuel matrix and the coolant. This design has several potential advantages over current-gen reactors such as inherent safety mechanisms and a much easier to realize closed fuel cycle. However, the realization of an MSR poses several technological challenges. Among those challenges are the high operating temperature and the corrosive nature of the molten salt which require the development of new alloys for structural materials as well as methods to monitor and control corrosion processes during operation. In order to enable the investigation of in-pile corrosion of different alloys by molten fluoride salts, we are currently working on a proof-of-concept experiment to measure the changing redox properties of a molten fluoride fuel salt during irradiation by using electrochemical techniques. In this contribution we present the status of the design of the irradiation rig and review the proposed setup for the proof-of-concept measurements.

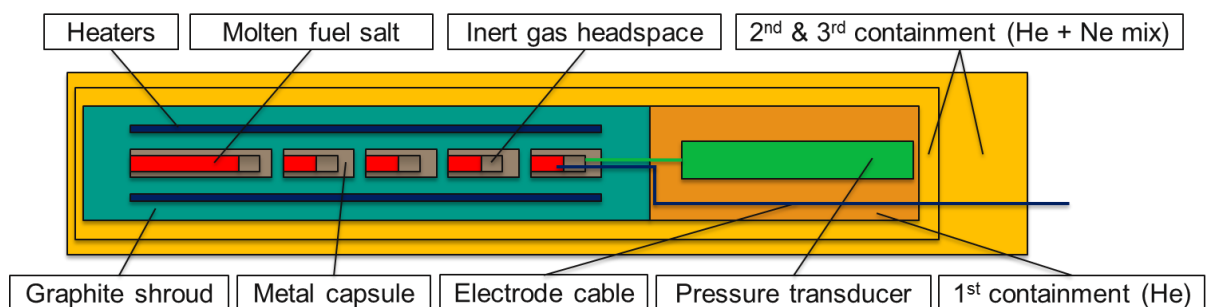


Fig. 1: Schematic view of the SALIENT-03 experiment.

KEYWORDS

Molten Salt Reactor, Electrochemistry, Corrosion, Molten Fluorides

Safety of the chemical plant of the Molten Salt Fast Reactor concept in the frame of the SAMOFAR H2020 project

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ABSTRACT

The Molten Salt Fast Reactor (MSFR) is a new molten salt reactor concept being developed since more than 15 years by the National Centre for Scientific Research (CNRS, France). The reactor has been designed to use a liquid fuel based on LiF-ThF₄-UF₄ molten salt at temperatures ranging between 650 and 750°C and it can be operated in the same time as a burner and a breeder. A corresponding reprocessing scheme in an associated chemical plant has been proposed during the previous projects in order to clean-up the fuel salt from the fission products and to recycle the actinides to the reactor core.

Since August 2015, the safety aspects of the overall MSFR concept are studied within the project SAMOFAR (Safety Assessment of the Molten Salt Fast Reactor). SAMOFAR is one of the research and innovation projects in the Horizon 2020 EC/Euratom research programme and its grand objectives are to prove the innovative safety of the MSFR concept by advanced experimental and numerical techniques, to deliver a breakthrough in nuclear safety and optimal waste management, and to create a consortium of stakeholders to demonstrate the MSFR beyond the project. It is consisting of 6 technical work packages (WP), which are addressing different safety aspects of the MSFR concept. This work is describing the goals and achievements of the WP5 dedicated to "Safety evaluation of the chemical plant".

The proposed chemical plant consists of several separation and/or storage stages, indicating the distribution of the processed fuel salt. The inventory of the radionuclides in each stage of the plant is studied in the frame of WP5 of the SAMOFAR project. The main goal is to establish a database of activity coefficients and transfer coefficients of actinides and fission products in the molten salt of interest, which could be used for MSFR and for other MSR concepts. The results are compiled from thermochemical calculations, bibliographic studies and experimental data in collaboration between IPNO Orsay and JRC Karlsruhe. The experimental work is focused on synthesis of pure actinide fluorides needed for the electrochemical studies and on measurement of activity coefficients by electrochemical methods.

The evaluation of the chemical plant inventory requires the knowledge of the initial radionuclide inventory in the reactor core, which is calculated by CNRS, LPSC Grenoble, using the LET (Lightweight Evolution Tool) code. The evolution of radioactivity and residual heat, as well as evaluation of criticality and the required shielding at each stage is calculated by CEA using a dedicated code.

The last part of the WP5 is focused on the compatibility of the construction materials with the molten salt, both in the reactor core and in the chemical plant. Special samples of Hastelloy N alloys covered with yttrium stabilized zirconia layers are being prepared by CINVESTAV in order to increase their resistance in contact with the molten salt. Corrosion tests are carried out both in active and inactive salts.

KEYWORDS

Molten Salt Fast Reactor, SAMOFAR, Horizon 2020 EC/Euratom research programme, safety evaluation of the chemical plant, Molten Salt Reactor fuel salt clean-up

UCl₃ production using electrochemical and chemical reactions with Zinc chlorides

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ABSTRACT

In the electrorefining step of pyroprocessing, uranium (U) is recovered in a metallic form and transuranic (TRU) elements are transported as chloride forms into the salt phase for subsequent recovery using liquid cadmium cathodes (LCC). For a high through-put U recovery with a minimum contaminants incorporation, a high initial UCl₃ concentration over ~ 6 wt.% is required to be added in LiCl-KCl molten salts. In order to produce UCl₃, CdCl₂ is used to chlorinate metallic U by way of the following reaction: $\text{U} + 1.5\text{CdCl}_2 \rightarrow \text{UCl}_3 + 1.5\text{Cd}$ ($\Delta G = -287.8$ kJ at 500 °C). However, Cd is difficult to use because of its toxicity and high vapor pressure. In addition, should Cd be deposited on the U surface, it would interrupt the continuous chemical reaction with CdCl₂.

This work demonstrates the production of UCl₃ using chemical and electrochemical reactions of ZnCl₂ with depleted U (DU), of which Zn has lower vapor pressure than Cd. We performed electrochemical measurements in 500 °C LiCl-KCl molten salts by immersing a tungsten (W) wire as a working electrode, 12.98 g of DU metal as a counter electrode, and 1 mol% Ag/Ag⁺ as a reference electrode. Figures 1(a)–1(c) show the current transients for three runs at -0.9 V continuously applied for 3 h, 2.7 h, and 3 h, respectively. As shown in Fig. 1(d), we confirmed that the redox peaks for U(III)/U(0) at ~ -1.4 V were gradually increased in accordance with a decrease in the redox peaks for Zn(II)/Zn(0) at around -0.7 V.

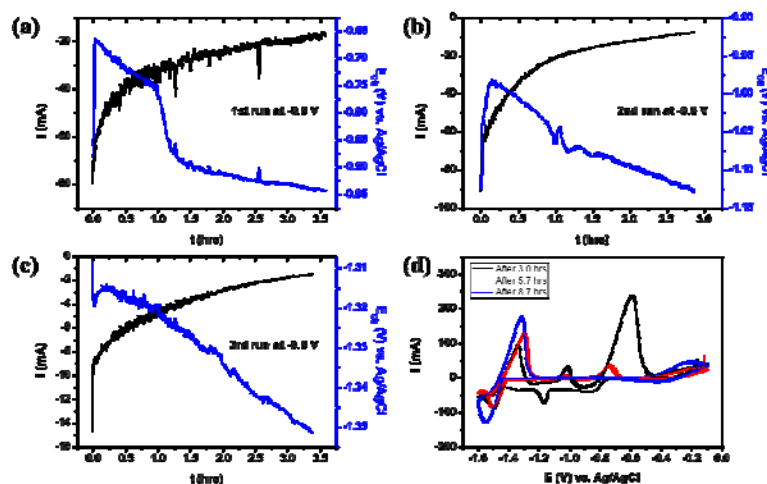


Fig. 1 Chronoamperometries at -0.9 V for (a) 1st run, (b) 2nd run, and (c) 3rd run, and (d) cyclic voltammograms at the end of each run.

KEYWORDS

Pyroprocessing, Uranium Trichloride, Electrorefining, Zinc

Effect of tungsten electrode on U recovery in LiCl-KCl molten salts

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ABSTRACT

Electrorefining is a process whereby metallic uranium (U) is recovered from a reduced oxide fuel in the electroreduction step of the pyroprocess. Korea Atomic Energy Research Institute (KAERI) found a self-scraping characteristic of graphite cathodes for U recovery and applied them to an engineering-scale electrorefiner. However, such cathodes have an intrinsic weakness compared to their metallic counterparts; that is, their physical strength and durability in the case of a long-term operation. Therefore, we investigated alternative metallic electrodes for U recovery: stainless steel, molybdenum (Mo), and tungsten (W).

Regarding experiments, we used the above metals as working electrodes and approximately 100 g of depleted U (DU) as an anode material with a Ag/AgCl reference electrode in 500 °C LiCl-KCl-3 wt.% UCl₃ molten salts. We performed cyclic voltammetries to compare the electrochemical behavior of U on various electrodes. The U was recovered on each cathode with an initial area of 8 cm² at a constant current of -400 mA.

Figure 1(a) shows the chronopotentiometric response and the corresponding anodic potential on the W electrode shown in the first column of Fig. 1(b) at -400 mA. After the U electrorefining for 3 h, U dendrites were detached from the cathode by gently scraping them in a vapor space above the salt in the reactor, as shown in the second and third columns of Fig. 1(b).

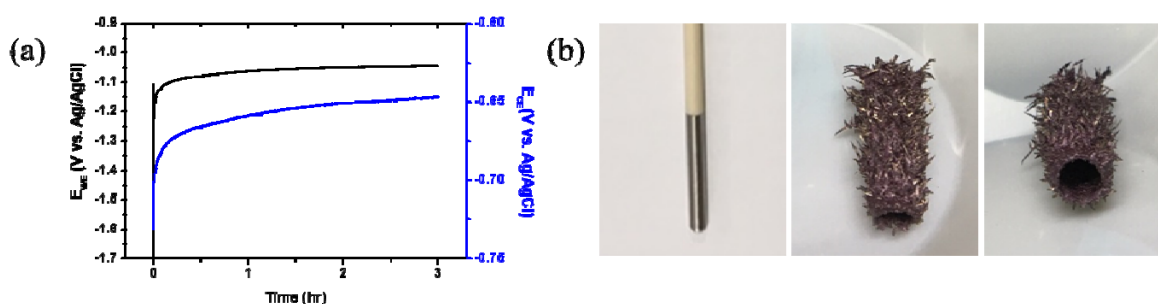


Fig. 1 (a) Potential responses corresponding to a constant current of -400 mA in 500 °C LiCl-KCl-3 wt.% UCl₃ salts and (b) tungsten electrode (*left*) and recovered U dendrites after electrorefining (*center* and *right*).

The U dendrites retained their shape (that is, the shape of the W electrode) after scraping, thus demonstrating a self-scraping property comparable to that of graphite cathodes. We intend to examine surface characterizations regarding the W electrode through SEM-EDX observations.

KEYWORDS

Pyroprocessing, Uranium, Electrorefining, Recovery, Tungsten

Investigation of current-potential relation of anode-liquid cathode module for LCC(liquid cadmium cathode) electrorefining

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ABSTRACT

An anode-liquid cathode module designed for LCC (liquid cadmium cathode) electrorefining process was characterized by chrono-potentiometric measurement. Two-types of structures in the module were used to investigate its effect on the cathode potential. One is symmetric structure (A-C-A) and the other is non-symmetric structure (A-C) (A: anode, C: cathode). No significant effect of mass transfer on the cathode potential in both of the A-C-A and A-C structures was found in the range of slat stirring (50 – 150 rpm). As shown in Fig. 1, the log scale value of current density linearly increased with the cathode potential in case of A-C-A structure, indicating the potential – current density relation follows the Butler-Volmer model. Although a linear curve was found in A-C-A, there was two parts in A-C structure. The difference current – potential behaviors of A-C-A and A-C structures may be induced by the effect of electric field depending on the symmetric and no-symmetric position of anode. This work was supported by a National Research Foundation of Korea grant funded by the Korean Ministry of Science, ICT and Future Planning [grant number 2017M2A8A5015079].

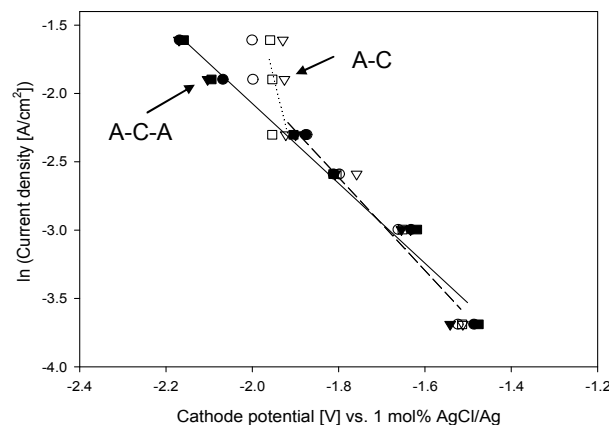


Fig. 1 The log scale of current – potential curve of A-C-A and A-C structures for 4 wt% UCl_3 in LiCl-KCl at 773 K under various stirring conditions (\bullet \circ 50rpm, \blacktriangledown \triangledown 100rpm, \blacksquare \square 150 rpm) at d_{A-C} of 10 mm)

KEYWORDS

Liquid cadmium cathode, Electrorefining, Uranium

The Development and Testing of an Oxide Reduction Voltammetry Sensor at Idaho National Laboratory

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ABSTRACT

In electrochemical reprocessing (i.e. pyroprocessing) of used nuclear fuel, an oxide fuel must first undergo an oxide reduction (OR) step to convert the fuel to a metal form suitable for electrefining. In normal operation of the OR, soluble rare earth and actinide salts are not expected to form. To safeguard the OR process, means to monitor the OR salt to detect abnormal operation or misuse of the system in a timely manner are necessary. Idaho National Laboratory (INL) has developed a voltammetry sensor to monitor the salt and OR process in situ. During the development of the sensor, tungsten (W) tantalum (Ta), platinum (Pt), stainless steel (SS), and iridium (Ir) were tested as working electrodes in lithium chloride-lithium oxide ($\text{LiCl-Li}_2\text{O}$) salt. Criteria for the material selection was good sensitivity to Li_2O (between 0 and 1 wt%), a broad potential window, and corrosion resistance. Iridium and W had the best performance between the studied materials. Iridium could be operated from the Li reduction potential through oxygen (O_2) oxidation, had good Li_2O sensitivity, and had no observed corrosion/degradation. Tungsten could also be operated through the full potential window, had good Li_2O sensitivity, but did show some corrosion/degradation over time when operated in the positive potentials. Following the initial testing, a prototype sensor was built consisting of a SS counter electrode, W and Ir working electrodes, and two independent nickel/nickel oxide (Ni/NiO) reference electrodes. The working and reference electrodes were housed in a magnesium oxide (MgO) tube that is supported by the SS counter electrode. The developed sensor was tested in $\text{LiCl-x wt\% Li}_2\text{O}$ ($x = 0, 0.25, 0.5, 0.75$, and 1.0) salt to validate the sensor geometry and design. Furthermore, the sensor was tested in a more complex salt containing rare earth chlorides and oxides. The sensor was successful in monitoring the Li_2O concentrations in the complex salt and a full scale voltammetry sensor has been fabricated as shown in Fig. 1. Additional testing is to be performed using the full scale sensor.



Fig. 1. Photo of the full scale OR voltammetry sensor.

KEYWORDS

Pyroprocessing, Molten Salt, Voltammetry, Safeguards, Process Monitoring

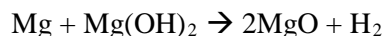
Electrochemical Studies of Molten MgCl_2 -KCl-NaCl salts to Measure Hydroxide Impurities and Study Effect of Mg Addition

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ABSTRACT

Molten chloride salts recently have attracted interest for thermal fluid applications because of their high thermal stability. Some concentrating solar power (CSP) plants currently use molten nitrate salts for heat transfer and thermal energy storage (TES), but those salts thermally decompose above about 500°C. The U.S. Department of Energy has recently funded several projects to study application of molten chloride salts such as MgCl_2 -KCl-NaCl to CSP systems with the goal of reaching temperatures of at least 700°C and driving down the cost of CSP-generated electricity. These salts may also be considered to be suitable for molten salt reactors or serve as a model for MSR salt in fundamental electrochemistry and corrosion studies. For either application, the salts need to be operated at temperatures of at least 700°C to provide the necessary efficiency of thermal to electrical energy conversion. This has raised concern over corrosion of structural metals that contact the salt. Interaction of water with molten chloride salts is known to result in formation of volatile HCl and soluble oxide/hydroxide. In order to perform reproducible corrosion experiments, it is necessary to measure and control the impurity content in the salt. In this work, we have used an electrochemical method based on cyclic voltammetry (CV) to measure the hydroxide impurity in MgCl_2 -KCl-NaCl salts at 500 °C. In addition, we added Mg metal in the MgCl_2 -KCl-NaCl salts with the objective of removing the hydroxide impurity. Before each CV experiment, we also measured open circuit potential (OCP) in order to characterize the salt's redox potential. Acid titrations of salt samples were also employed to calculate the moles of hydroxide in the salt. Prior to addition Mg metal, the CV of salt shows the hydroxide peak at -2.4 V (vs. $\text{Cl}^-|\text{Cl}_2$). However, the hydroxide peak disappears after addition of Mg metal. A large and broad oxidation peak is recorded for salt containing dissolved Mg. The results of titrations show that the moles of OH^- also were decreased by addition Mg metal. The results indicate that the addition of Mg metal forms MgO, which has low solubility in the melt. The hydroxide consumption reaction is believed to be as follows.



We measured H_2 gas by using the Quadrupole mass spectrometer (QMS) and observed the morphologies and element mapping of the film on the working electrodes by using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) to underpin above reaction.

KEYWORDS

Concentrated solar power (CSP), Corrosion, Cyclic voltammetry (CV), Magnesium, Hydroxide

Measurement of Gibbs Free Energy of Formation of GdCd₆

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ABSTRACT

Pyroprocessing of nitride fuel for minor actinide transmutation has been developed in JAEA. Molten salt electrolysis is the main process to separate and recover the transuranium elements (TRU) into liquid cadmium (Cd) cathode. The TRU-Cd alloys obtained by the electrolysis are converted to nitrides by nitridation-distillation combined process, in which distillation of Cd in vacuum is followed by heating the alloy in nitrogen gas atmosphere. Formation of TRU-Cd intermetallic compounds (i.e. PuCd₆ and Am₁₁Cd₄₅) as intermediate products has been reported in the process [1,2]. It is important to evaluate the thermodynamic stability of TRU-Cd intermetallic compounds to select the detailed conditions of the nitridation-distillation combined process. In this study, Gibbs free energy of formation of gadolinium (Gd)-Cd alloy which is used as a surrogate of the TRU-Cd alloy was measured.

Gd-Cd alloy was prepared by heating Gd metal with Cd metal (atomic ratio=1:10) in a tungsten crucible sealed in an evacuated quartz tube at 773K for 4 hours. The prepared alloy was identified as the mixture of GdCd₆ and Cd with X-ray diffraction measurement of the filed samples at room temperature. The potential of Gd-Cd alloy sample set in a tungsten crucible versus Ag/AgCl reference electrode ($X(\text{AgCl}) = 0.0039$) was measured in $(\text{LiCl-KCl})_{\text{eut.}}\text{-GdCl}_3$ ($X(\text{GdCl}_3) = 0.00211$) at 673-923 K. The alloy is considered as the mixture of solid GdCd₆ and liquid Cd phase in the measured temperature range according to the phase diagram [3]. The electromotive force (ΔE) of the cell ($\text{Gd} | (\text{LiCl-KCl})_{\text{eut.}}\text{-GdCl}_3 | \text{Gd-Cd}$ (two phase alloy)) was calculated from the difference of the measured potential of Gd-Cd alloy sample and that of Gd metal. The latter was deposited on a tungsten electrode by potentiostatic electrolysis in $(\text{LiCl-KCl})_{\text{eut.}}\text{-GdCl}_3$ ($X(\text{GdCl}_3) = 0.00211$). Gibbs free energies of formation (ΔG_f^0) of GdCd₆ calculated with the equation $\Delta G_f^0(\text{GdCd}_6) = -3F\Delta E$ agree well with our data obtained by the electrochemical technique using the sample formed by co-deposition of Gd and Cd in a molten salt [4] and the reported data obtained by Cd vapor pressure measurement [5] (Table 1). This result shows that method of this study is valid for the measurement of $\Delta G_f^0(\text{GdCd}_6)$. Similar measurements using other Gd-Cd intermetallic compounds are planned to evaluate thermodynamic stability of Gd-Cd alloy.

Table 1: ΔG_f^0 of GdCd₆ at 773K

Method	$\Delta G_f^0(\text{GdCd}_6)$ kJ/mol
This Study	-122.8
Electrochemical co-deposition method [4]	-124.0 ± 0.4
Cd vapor pressure [5]	-112.7

[1] Y. Arai *et al.*, *Nucl. Tech.*, 162 (2008) 244-249. [2] H. Hayashi *et al.*, Proceedings of GLOBAL'99, August 29-September 3, (1999). [3] K. A. Gshneidner Jr., *et al.*, T. B. Massalski (Ed.), Binary Alloy Phase Diagrams (2nd ed.), (1988) 980-983. [4] S. Akashi *et al.*, 2018 Annual Meeting of AESJ, March 26-28, (2018). [5] T. L. Reichmann *et al.*, *J. Alloy Compd.*, 610 (2014) 676-683.

KEYWORDS

Cd Distillation, Gd-Cd Intermetallic Compound, Gibbs Free Energy of Formation

Material balance evaluation in pyro-reprocessing of ADS nitride fuel

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ABSTRACT

Japan Atomic Energy Agency has been pursuing research and development on partitioning and transmutation of minor actinides (MAs) by accelerator-driven system (ADS) using uranium-free nitride fuel. The target transmutation ratio of 99% MAs can be achieved if $\geq 99.9\%$ of MAs in the spent fuel are recovered in reprocessing [1]. From the point of view of neutronics design, the weight ratio of rare-earths (REs) against MAs in the refabricated fuel should be 5.0% or less [2]. In this study, we calculated the material balance in the pyro-reprocessing of nitride fuel to evaluate the processing conditions to meet the above-mentioned requirements.

Figure 1 illustrates the flowsheet of spent nitride fuel processing [3], which was proposed by reference to the metallic fuel reprocessing. The REs impurity concentration in the recovered actinides at the liquid Cd cathode should be maintained at the adequate level. Therefore, it is needed to remove REs accumulating in the salt bath. In the salt recycling process, actinides in the salt are extracted into liquid Cd by multistage countercurrent extraction, and then the fission products (FPs) such as REs remaining in the salt are removed by absorption into zeolite. The composition of spent fuel was given by the previous burnup calculations [2]. Assuming that ~ 7800 kg of spent fuel (~ 4200 kg of actinides) from a unit of ADS is reprocessed with an electrorefiner (1000 kg of molten salt and 200 kg of liquid Cd cathode) for 200 days, we calculated material balance using the previously reported data such as separation coefficients and absorption ratios [4].

We evaluated the processing conditions to meet the requirements with varying the stage number of countercurrent extraction in the molten salt recycling process (Table 1). The amounts of the salt transferred to recycling process and the reducing agent (Li) used in the multistage countercurrent extraction decrease with the stage number. At more than 3 stages, the increase in the stage number will be relatively ineffective in reducing the glass-bonded sodalite waste, since the change in the amounts of spent salt is small.

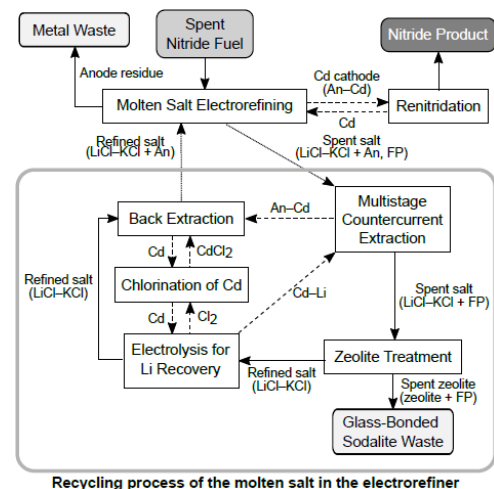


Fig. 1. Flowsheet of spent nitride fuel processing.

Table 1. Conditions in recycling process.

Stage number	Salt transferred to recycling process (kg/day)	Li (kg/day)
2	31	0.238
3	22	0.138
4	20	0.118
5	19	0.112

References. [1] H. Hayashi *et al.*, Proc. 13th OECD/NEA IEMPT, 370–377 (2015). [2] T. Sugawara *et al.*, Ann. Nucl. Energy, 111, 449–459 (2018). [3] T. Satoh *et al.*, Proc. 11th OECD/NEA IEMPT, Internet (2012). [4] M. Kurata *et al.*, J. Nucl. Mater., 227, 110–121 (1995); T. Tsukada & K. Takahashi, Nucl. Technol., 162, 229–243 (2008).

KEYWORDS

Nitride fuel, Pyro-reprocessing, Material balance, Electrowinning, Accelerator-driven system

Estimation of the composition of MA nitride fuel irradiated in ADS

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ABSTRACT

In Japan Atomic Energy Agency (JAEA), research and development for reduction of radioactive wastes with accelerator driven system (ADS) has been conducted. Minor actinides (MA) recovered from high level liquid waste of aqueous reprocessing such as PUREX, will be converted to MA nitride fuel, and burned in the ADS core. Irradiated MA fuels will be discharged and processed by pyro-method. Recovered MA will be converted again to nitride to be used as the fuel of the next burning cycle. Estimating the composition of the irradiated MA nitride fuel is necessary to evaluate MA recovery performance, process safety, and the amount of the secondary waste. In this study, burnup calculation of irradiated nitride fuel using a computer program ADS3D [1] (Three-dimensional Reactor Analysis Code System for Accelerator-Driven System) developed in JAEA was carried out.

According to a reference ADS design proposed by Sugawara et al. [2], the core consists of the inner and the outer region, thermal power is 800 MWt, irradiation period is 600 days. Table 1 shows the compositions of the MA nitride fuel of the 1st cycle after irradiation (cooling time = 4 years), compared with those before irradiation. Reduction rate of MA (Np, Am, Cm) was 29 %, and that of actinides (An ; MA, U, Pu) was 16 % at the central part of the inner region. Reduction rates were smaller at the bottom of the outer core (12 % for MA, 5 % for An). Compositions of fission products are shown in Table 2. Estimation of the chemical forms of FP elements based on the calculation of the spent fuel composition is in progress.

Table 1 Compositions of the ADS nitride fuel
(at.%, * Zr is excluded from “FP”).

	center of the inner core, %			bottom of the outer core, %		
	before	after	Δ	before	after	Δ
N	50	49		50	49	
Zr	30	30		25	24	
U	0.0	0.1		0.0	0.1	
Pu	5.4	6.2	+19%	6.9	7.5	+11%
MA	14.4	9.9	-29%	18.3	15.8	-12%
Np	7.1	4.6	-33%	9.0	7.6	-13%
Am	6.6	4.5	-31%	8.5	7.3	-11%
Cm	0.7	0.9	+34%	0.8	0.9	+5%
FP *	-	5.4		-	3.6	

Table 2 Compositions of FP
elements (at.%, Zr is excluded.)

	center of the inner core	bottom of the outer core
Mo	12	8
Ru	10	11
Rh	3.3	3.7
Pd	9.3	9.7
Xe	12	13
Cs	10	11
Ba	4.1	4.3
La	3.2	3.5
Ce	5.7	6.1
Nd	9.4	10
others	21.0	19.7

This study contains the results of “R&D on Nitride Fuel Cycle for MA Transmutation to Enhance Safety and Economy” entrusted to Japan Atomic Energy Agency by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT).

References. [1] T. Sugawara et al., J. Nucl. Sci. Technol., 53, 2018 - 2027 (2016). [2] T. Sugawara et al., Annals of Nuclear Energy, 111, 449 - 459 (2018).

KEYWORDS : Nitride, Pyro-processing, Accelerator-driven system, Actinide

Nitridation of dysprosium and gadolinium dissolved in liquid cadmium

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ABSTRACT

Transmutation of long-lived minor actinides (MA: Np, Am, Cm) has been studied in Japan Atomic Energy Agency (JAEA) under the double strata fuel cycle concept. It is composed of a commercial reactor fuel cycle and a fuel cycle dedicated to MA transmutation. The MA transmutation fuel cycle consists of the MA transmutation by a Pb–Bi cooled sub-critical ADS, MA fuel fabrication and pyrochemical reprocessing of spent MA fuel. ¹⁵N-enriched (MA, Pu, Zr)N mixed nitride fuel is a promising candidate for MA transmutation.

Pyrochemical process has several advantages over wet process in case of treating spent MA nitride fuels. Spent fuels with large decay heat and neutron emission can be treated, and recovery of ¹⁵N₂ gas is possible by pyrochemical process. In pyrochemical reprocessing of spent nitride fuels, actinides are recovered in a liquid cadmium (Cd) cathode by electrolysis and converted to nitride again by heating the MA-Pu-Cd alloys in N₂ gas stream [1]. Nitridation of actinides in Pu-Cd, U-Pu-Cd and Am-Cd alloys has been achieved on 1 to 10 g-Cd scale [2-4]. However, experimental data of a larger scale test is required to design industrial scale equipment. In the present study, nitride formation reactions of 2 wt% Dy-Cd and 2 wt% Gd-Cd alloys in N₂ gas stream have been studied in the temperature range of 973-1073 K using an apparatus developed for 100 g-Cd scale nitridation tests. Dy and Gd were used as surrogate materials of MAs and Pu. Most of Dy and Gd dissolved in Cd were converted to DyN and GdN at 1073 K, respectively.

This study contains the results of “R&D on Nitride Fuel Cycle for MA Transmutation to Enhance Safety and Economy” entrusted to Japan Atomic Energy Agency by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT).

References. [1] H. Hayashi et al., *Proc. 13th OECD/NEA IEMPT*, NEA/NSC/R(2015)2, 370–377 (2015). [2] Y. Arai et al., *Nucl. Technol.*, **162**, 244 (2008). [3] H. Hayashi et al., *Electrochemistry*, **77**(8), 673-676 (2009). [4] T. Satoh et al., *Proc. Global 2009*, 1278-1286 (2009).

KEYWORDS

Minor Actinides, Transmutation, Nitride fuel, pyrochemical reprocessing, nitridation of An-Cd alloys

LLFP recovery from simulated vitrified radioactive wastes by reductive decomposition of glass structure in molten salt

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ABSTRACT

For the reduction and resource recycling of high-level radioactive wastes through nuclear transmutation, it is necessary to recover Long Lived Fission Products (LLFPs) such as ^{107}Pd , ^{93}Zr , ^{79}Se and ^{135}Cs stabilized in vitrified radioactive wastes mainly composed of borosilicate glass. We have developed an LLFP recovery process consisting of a reductive decomposition method for breaking the glass structure in molten salt and pyrochemical methods, such as molten salt electrolysis or volatile separation (Fig. 1). The LLFPs are released from glass structure by reduction of SiO_2 frame of vitrified radioactive wastes and dissolve as ions or remain as metals or oxides, depending on their chemical characteristics. To investigate the feasibility of our process, we carried out Ca reduction tests in molten CaCl_2 at 850 °C on simulated vitrified radioactive wastes containing 34 elements. In particular, we investigated the chemical behaviour of Pd, Zr, Se and Cs during the reduction. More than 99 mass% of Se and Cs in the glass dissolved into the molten salt as Se^{2-} and Cs^+ after the reduction. By molten salt electrolysis on the residue containing Pd and Zr in LiCl-KCl at 450 °C, dissolution of Zr and non-dissolution of Pd were confirmed.

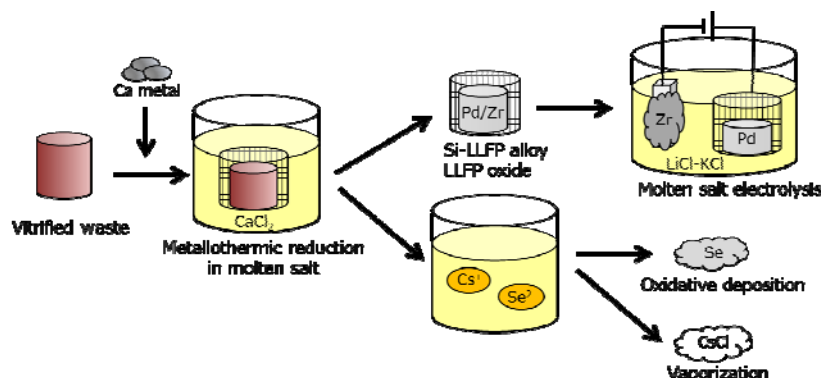


Fig. 1 LLFP recovery process from vitrified wastes with pyrochemical methods.

*Experimental conditions employed here are completely different from the practical ones subjected to the vitrified waste glasses.

This work was funded by the ImPACT Program of the Council for Science, Technology and Innovation (Cabinet Office, Government of Japan).

KEYWORDS

Vitrified waste, LLFP, Metallothermic reduction, Molten salt electrolysis

Redox Behaviors of Selenium and Tellurium in Molten Chlorides

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ABSTRACT

Chalcogen fission products such as Se and Te are expected to be dissolved in the form of Se^{2-} and Te^{2-} anions during electrolytic reduction of spent oxide fuels in molten chloride salt bath. In this study, the redox behaviors of Se and Te in LiCl-KCl eutectic and CaCl_2 melts were investigated. Moreover, the influence of O^{2-} ion on the extraction of Se and Te from the melts was examined.

The experiments in LiCl-KCl eutectic were conducted at ~ 723 K. Liquid Se metal was cathodically dissolved in the form of Se^{2-} ion. The cyclic voltammograms on glassy carbon electrode indicated that the deposition of Se proceeded in two steps at the anode: the oxidation $\text{Se}^{2-} \rightarrow \text{Se}_2^{2-}$ occurred followed by oxidation of Se_2^{2-} to Se metal, which was supported by the literature on the electrochemical behavior of sulfur [1]. The formation of Se_2^{2-} caused low current efficiency in the Se metal deposition on carbon anode. When active metals such as Cu and Ni were used as the anode, their selenides were deposited at the potentials more negative than the potential of Se_2^{2-} formation. It was demonstrated in a LiCl-KCl melt containing both Se^{2-} and O^{2-} ions that Se could be collected in the form of Cu_2Se by potentiostatic electrolysis using Cu anode. The deposition of Te proceeded in two steps at the anode similarly to Se. The redox potentials indicated that Te^{2-} was more easily oxidized than Se^{2-} and then Te could be deposited prior to Se. On the Cu electrode, various tellurides (Cu_7Te_4 , Cu_2Te and KCu_3Te_2) were formed.

The experiments in CaCl_2 were conducted at ~ 1093 K. It was indicated by cyclic voltammograms that dimeric ion of Se was less stable in melts at higher temperature. Ni was more suitable than Cu as an anode for Se deposition, because Cu was anodically dissolved with ease in CaCl_2 and the solubility of Cu_2O was much higher than that of NiO . Moreover, it was found that chemical reaction using NiO was quite useful for extracting Se and Te in this system.

[1] D. Warin, Z. Tomczuk and D.R. Vissers, "Electrochemical behavior of Li_2S in fused LiCl-KCl electrolytes", *J. Electrochem. Soc.*, **130** (1), 64-70 (1983).

This work was funded by the ImPACT Program of the Council for Science, Technology and Innovation (Cabinet Office, Government of Japan).

KEYWORDS

Selenium, Tellurium, Electrolytic reduction, Molten chlorides, LiCl-KCl, CaCl_2

Electrochemical properties of gadolinium on liquid gallium electrode in LiCl-KCl eutectic

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ABSTRACT

In this work, the electrochemical properties of gadolinium(Gd), a significant rare earth element in spent nuclear fuel (SNF), in the LiCl-KCl eutectic, are investigated. To explore the thermodynamic properties of Gd at the liquid gallium(Ga) electrode, experiments were performed both on the inert tungsten(W) and liquid gallium(Ga) electrode at different temperatures ranged from 723 to 823 K, which showed that the Gd metal could be oxidized to Gd(III) by exchanging of 3 electrons. Electrochemical techniques including cyclic voltammetry (CV), open circuit potential (OCP), potentiostatic electrolysis and galvanostatic electrolysis were utilized to detect the electrochemical behaviors and evaluate standard apparent potential of the Gd(III)/Gd couple. An empirical formula, $E_{Gd(III)/Gd}^* = -3.456 + 6.2 \times 10^{-4} T (\pm 0.046) (V \text{ vs } O_2/O^-)$, was obtained. In addition, the electromotive force and the coulometric titration were employed to calculate the activity and activity coefficient of Gd in metal Ga. The activity is 1.791×10^{-15} at 723 K and the activity coefficient as a function of temperature is $Lg\gamma = 3.485 - 10927/T (\pm 0.0875)$.

KEYWORDS

LiCl-KCl eutectic; Electrochemical properties; Liquid Gadolinium