DEVELOPMENT OF PYROCHEMICAL TREATMENT PROCESS FOR USED MOLTEN SALT FAST REACTOR FUELS: NOVEL PROCESS FOR REMOVAL AND VITRIFICATION OF FISSION PRODUCTS IN MOLTEN SALT

T. MURAKAMI
Central Research Institute of Electric Power Industry (CRIEPI)
Tokyo, Japan
Email: m-tsuyo@criepi.denken.or.jp

T. KOYAMA
Central Research Institute of Electric Power Industry (CRIEPI)
Tokyo, Japan

M. YAMAWAKI
Beyond Energy Research and Development Association (BERD)
Tokyo, Japan

Abstract

1. INTRODUCTION

Chloride is one of the promising chemical forms for nuclear fuel salt of molten salt fast reactor (MSFR) [1-3]. To utilize efficiently nuclear fuel resources and to transmute long half-life nuclides effectively with MSFR aiming to reduce environmental burden of the radioactive wastes, it is required to reprocess the used chloride fuel salt. The authors have proposed new pyrochemical process for the reprocessing of MSFR fuels [1-3]. The pyrochemical process is composed of compact batch steps where chemical and electrochemical reactions in the molten salt and liquid metal system are used for the actinides recycle and fission products removal from the used salt, and for the stabilization of the removed fission products in waste forms. The proposed flowsheet of the pyrochemical process is shown in Fig. 1 [2, 3]. Actinides (An) in the used salt are reductively extracted in liquid metal, for example liquid Bi (step [1-1]).

$$An^{3+}{}_{\text{in used salt}} + 3Na_{\text{in liq. Bi}} \rightarrow An_{\text{in liq. Bi}} + 3Na^{+}{}_{\text{in used salt}} \quad (1)$$

The actinides in liquid Bi are then chlorinated by the reaction with $BiCl_3$ to supply the recycled fuel salt (step [1-2]).

$$An_{\text{in liq. Bi}} + BiCl_3 \rightarrow AnCl_3 + Bi \quad (2)$$

Rare earth fission products (RE) remain in the used salt after step [1-1]. They are removed from the used salt by reductive extraction (step [2-1]).

$$RE^{n+}{}_{\text{in used salt}} + nNa_{\text{in liq. Bi}} \rightarrow RE_{\text{in liq. Bi}} + nNa^{+}{}_{\text{in used salt}} \quad (n = 2 \text{ or } 3) \qquad (3)$$

The obtained RE-Bi alloy is melted in air with a glass, for example borosilicate glass, where the selectively oxidized RE are stabilized in the glass leaving liquid Bi as metallic state (step [2-2]).

$$REBi_x + y/2O_2 \rightarrow REO_{y\ \text{in glass}} + xBi \qquad (4)$$

The reductant used at steps [1-1] and [2-1] is electrochemically recovered: Na^+ cation left in the melt after reactions (1) and (3) is reduced to be collected on the cathode (step [3]). Then, the alkali and alkaline earth fission products in the used salt can be converted from chloride form to stable phosphates (step [4]) [4].

The advantageous characteristics of the pyrochemical process are summarized as follows. Each pyrochemical step can be constructed based on the well-developed technologies for reprocessing the used metallic fuel [5], which indicates the technical basis of the pyrochemical process has already been established. Fuel salt with various compositions can be flexibly treated with the pyrochemical process. The volume of the waste released from the pyrochemical process would be expected to be smaller than that of hydro metallurgical process. The waste forms assumed here do not contain chlorine since ^{37}Cl-

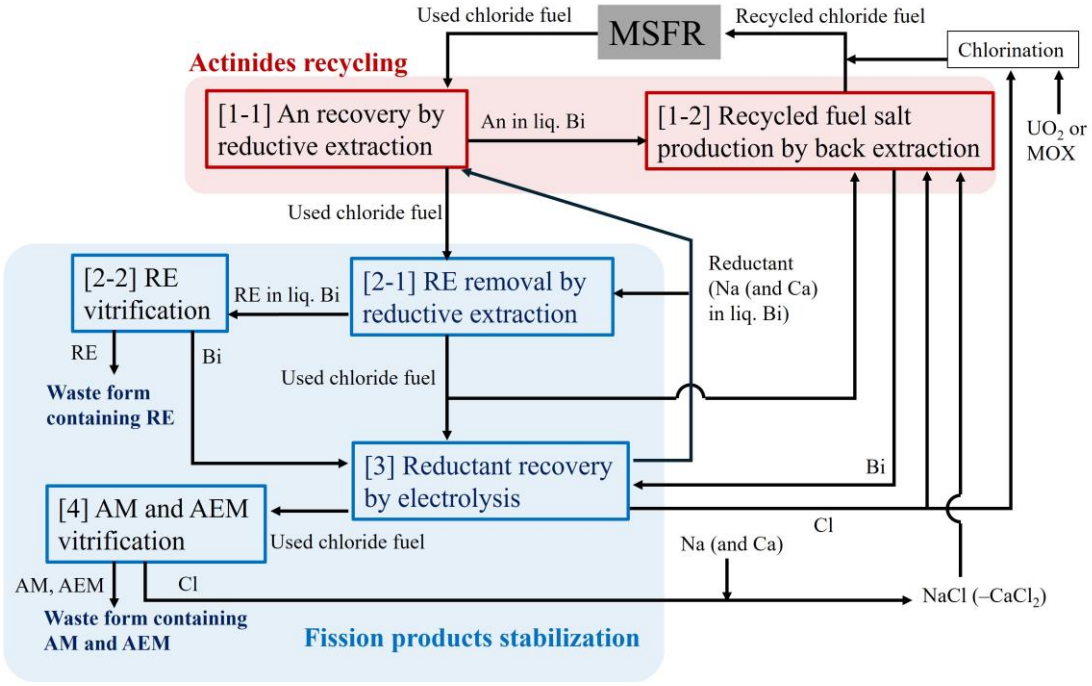

FIG. 1 The flow sheet of the pyrochemical process for reprocessing the used chloride fuel salt. MSFR: molten salt fast reactor, An: actinide, RE: rare earth, AM: alkali metal, AEM: alkaline earth metal.

enriched chlorine in the fuel salt is recycled in the pyrochemical process, where ^{37}Cl-enriched chlorine is favorably used to limit the formation of the long half-life nuclide ^{36}Cl during MSFR operation.

2. FEASIBILITY OF THE PYROCHEMICAL PROCESS

To confirm the basic feasibility of the pyrochemical process, the mass distribution of actinides and fission products has been evaluated based on their distribution behavior between molten salt and liquid Bi at steps [1-1], [2-1] and [3], and migration behavior of rare earth from liquid Bi to a glass at step [2-2]. Small scale process tests were demonstrated to investigate behaviors of these steps. For example, reductive extraction tests of rare earths (La, Ce, Pr, Nd and Gd) were performed in NaCl-$CaCl_2$ | liquid Bi system at 823 K to obtain the separation factor of element M (SF_M) which was defined as the following equation [2].

$$SF_M = (X_{M\ in\ salt} / X_{M\ in\ Bi}) / (X_{Ce\ in\ salt} / X_{Ce\ in\ Bi}) \quad (5)$$

where $X_{M\ in\ salt}$ and $X_{M\ in\ Bi}$ denote concentration of M in molten salt and liquid Bi, respectively. Vitrification tests of Ce which had been reductively extracted in liquid Bi from NaCl-$CaCl_2$ melt at 823 K was carried out [6]. Ce in liquid Bi was selectively oxidized at 1373 K in air together with borosilicate glass, resulting in stabilization of more than 99 % of Ce in the glass leaving liquid Bi as metallic state (Fig. 2).

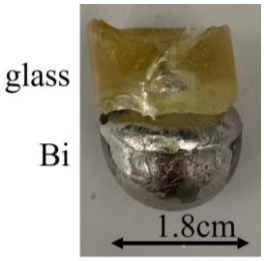

Fig. 2 Photo of the obtained borosilicate glass containing Ce and remaining Bi after demonstration test of step [2-2] [6].

The evaluated mass distribution ratio in the pyrochemical process for reprocessing the used chloride fuel salt discharged from a molten salt fast reactor with 700 MWth is summarized in Table 1 [2]. The supposed throughput of the pyrochemical process was 122 L in 30 days. It was shown that almost all of actinides were recycled as the new fuel salt with most of rare earth fission products stabilized in a glass waste form. In addition, the formation rate of the glass waste form for rare earth stabilization and that of phosphate glass waste form for alkali and alkaline earth stabilization were evaluated to be about 100 kg/month and 6.9 kg/month, respectively. Although the amount of Bi contaminated in the glass waste form was evaluated to be quite low (0.14 % of the total amount of Bi used at step [2-2]), further decrease of the Bi contamination would be expected by optimizing the oxidizing conditions, such as temperature and time, and by adding reducing agent, for example such as silicon or carbon, in the formed glass to induce the following reactions.

$$1.5Si + Bi_2O_{3\ in\ glass} = 2Bi + 1.5SiO_2\ (\Delta G^0 = -790\ kJ\ (at\ 1373\ K)) \quad (6)$$

$$1.5C + Bi_2O_{3\ in\ glass} = 2Bi + 1.5CO_2\ (\Delta G^0 = -385\ kJ\ (at\ 1373\ K)) \quad (7)$$

TABLE 1. MASS DISTRIBUTION RATIO OF ACTINIDES AND FISSION PRODUCTS IN THE PYROCHEMICAL PROCESS FOR REPROCESSING THE USED CHLORIDE FUEL SALT DISCHARGED FROM A MOLTEN SALT FAST REACTOR WITH 700 MWTH.

		Recycled as new fuel salt (%)	Stabilized in glass waste form (%)	Stabilized in phosphate glass waste form (%)
Actinide	U	99.9	0.1	-
	Np	99.9	0.1	-
	Pu	99.9	0.1	-
	Am	99.7	0.3	-
	Cm	95.7	4.3	-
Rare earth	La	3.6×10^{-1}	96.2	-
	Ce	1.3	98.2	-
	Pr	1.6	97.9	-
	Nd	1.7	97.9	-
	Gd	2.8×10^{-1}	93.0	-
Alkaline earth	Sr	6.0×10^{-2}	2.5×10^{-1}	1.5
Alkali	Cs	4.2×10^{-2}	8.7×10^{-2}	39

3. CONCLUSION

Pyrochemical process for reprocessing the used chloride fuel salt from molten salt fast reactor has been studied and new steps were proposed. Small scale tests were performed to confirm basic feasibility of the steps of pyrochemical process. It was evaluated that almost all of actinides were recycled as the new fuel salt, whilst most of rare earth fission products were stabilized in a stable waste form. In addition, the formation rates of the waste forms to be produced were estimated.

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