

Thermal Reaction of Zeolite and Cs removal in Molten Salt

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1. Introduction

In radioactive waste treatment, it is important to simplify its process since each step on the separation, concentration or solidification of radionuclides could indispensably generate secondary radioactive wastes. Especially, in case of mixed wastes containing high content of non-radioactive elements, it should be carefully considered if the applied separation technology is capable of lowering the final volume of waste or not. Molten salt waste generated from electro-metallurgical process in nuclear facility exists as mainly metal chloride. The existence of volatile CsCl and the high content of alkali elements make conventional methods for the solidification such as vitrification not directly applicable to this waste. For this reason, it is necessary to separate radionuclides by appropriate separation technologies or control the volatility for guaranteeing no generation of secondary radioactive waste which increases the final waste volume. Using lithium phosphate or sodium phosphate, Volkovich et al. showed a selective reaction of radionuclide in molten salt phase [1]. However, CsCl in this research was not completely converted into Cs₃PO₄. Argonne National Laboratory has developed the method using zeolites which can selectively remove radionuclides in molten salt phase (LiCl-KCl) [2-5].

LiCl salt waste generated from electro-reduction process contains below 1wt% CsCl/SrCl₂ to be separated for the recycle of salt. Different from LiCl-KCl phase, the LiCl salt has higher melting temperature and this would make the difference on the removal of radionuclide by using zeolite since the chemical state of radionuclides in molten phase and property of salt might affect the interaction between zeolite and Cs.

For this reason, this study investigated the change of zeolite in molten LiCl salt and its effect on the removal of radionuclide, Cs.

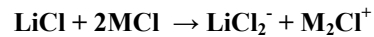
2. Experimental

Zeolite 4A (LTA) used in this study was sufficiently dehydrated before experimental. In order to investigate the stability of LTA structure in molten salt, zeolite 4A was added to molten LiCl and LiCl-KCl at 620~680 °C and then, sampled after 5, 10, 20, 30 and 60min. The samples were analyzed by XRD measurement.

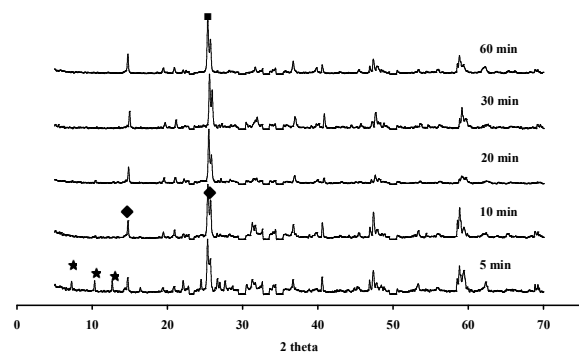
Ion-exchanging experimental in batch system was carried out with 5~20g of zeolite 4A in 200g of molten salt containing a series of concentration of Cs at 620~680 °C.

3. Result

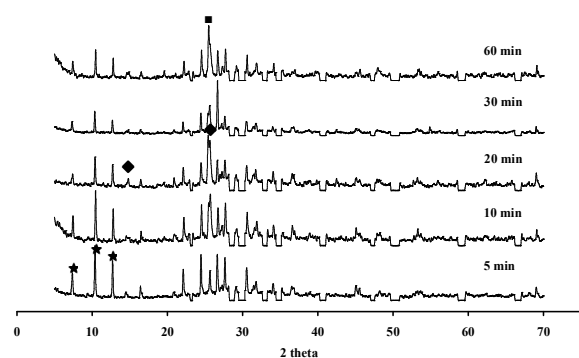
As a good separating material for Cs removal, zeolite 4A is reported to selectively remove Cs from LiCl-KCl at 450 °C or LiCl at 625 °C [6]. However, the mechanism on the Cs removal in molten phase has not been sufficiently explained. Chemical state of radionuclides in molten phase would be different from those in aqueous solution. Pascal Hebant and his co-worker suggested a structure of alkali chlorides at molten state as follows



According to their model, a fraction of complex anion or cation is dependent of the mole fraction of MCl in LiCl. Figure 1 shows the change of zeolite with time in LiCl or LiCl-KCl at 620 °C.



(a) zeolite 4A in LiCl



(b) Zeolite 4A in LiCl-KCl

Figure 1. XRD patterns of zeolite 4A with time in different salt (◆: LTA, ■: LiAlSiO₄(Eucryptite) *LiCl or KCl peaks removed

As shown in XRD analysis, LTA structure in LiCl salt was decomposed to LiAlSiO₄ in 10min while it remained even at 60min in LiCl-KCl. Figure 2 shows the removal of Cs with time by using different zeolites. Cs/Li molar ratio increase at about 20~30min and this trend similar to the change of LTA structure in figure 1.

This means that the selectivity of zeolite for Cs would disappear at 20~30min, namely, LiAlSiO_4 shows no selectivity on Cs.

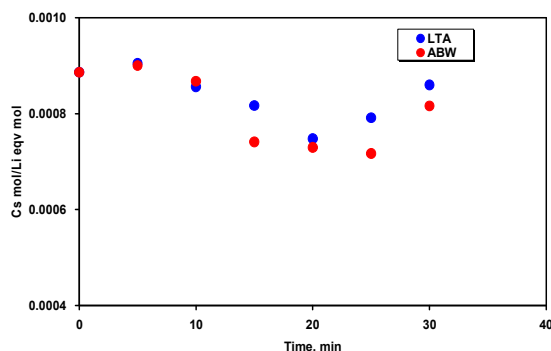


Figure 2. Removal of Cs with time in batch system
(200g salt/5g zeolite, 650°C, Na-4A(LTA), Li-A(ABW))

From these results, when using zeolite 4A for Cs removal from molten salt, the separation process should be finished in 20~30min.

4. Conclusion

This study investigated the thermal reaction of zeolite in molten salt and its effect on the Cs removal. Zeolite 4A in molten LiCl changed into eucryptite (LiAlSiO_4) with time, where selectivity on Cs disappeared in 20~30min. However, zeolite 4A in LiCl-KCl has a fraction of LTA structure even after 60min. These phenomena would be attributed by the difference on the kind of complex ions interacting with zeolite 4A. More researches on the Cs removal mechanism are going on.

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