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FLUORIDE REMOVAL FROM MOLTEN SALT SOLUTIONS BY $SiCl_4$ SPARGING

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ABSTRACT

Molten salts containing fluoride ion react destructively with Zeolite 4A through a mechanism that is typical of fluoride reactions with oxygen-bearing ceramics such as silica. The resulting product is one that no longer contains the molecular sieve framework and is therefore useless as an ion-exchange medium. Variations in either the temperature between 500 and 740°C or in the fluoride/chloride concentration ratio from 0.05 to 1.0 produced little improvement in the stability of the zeolite framework with respect to fluoride ion attack. Other ion-exchange media such as mica have been considered, but they should be equally affected by the fluoride ion. It was therefore determined that the fluoride ion must first be removed from molten salt mixtures if aluminosilicate zeolites are to be used as an ion-exchange media in contact with them.

Gaseous $SiCl_4$ has been found to remove fluoride ion in molten salts to at least 0.1 mol % by the reaction:

$$2CaF_2 + SiCl_4 = 2CaCl_2 + SiF_4 \uparrow.$$

The efficiency of the process is largely determined by the effectiveness of the gas\melt contact. Attractive features of this reaction include ease of separation of unreacted $SiCl_4$ from SiF_4 for eventual recycle of both.

INTRODUCTION

The Light Water Reactor (LWR) Actinide Recycle Program in a Department of Energy (DOE)-funded developmental project for the recovery and recycle of plutonium and transuranium elements (TRU) from the spent LWR fuel. The objectives are to recover plutonium and transuranium elements for conversion to fuel for an integral fast reactor (IFR) and to reduce the quantity and long-term toxicity of the high-level waste (HLW) streams reporting to HLW repositories.

As a major activity of the LWR Actinide Recycle Program, Argonne National Laboratory (ANL) is developing a pyrochemical process for converting the spent LWR oxide fuels into a feed for the IFR (1). The high-temperature processes (500 to 800°C) treat the spent fuel in two-phase molten salt/metal systems. Two salts have been under consideration as the solvent and main processing medium in the actinide recycle process: a $CaCl_2$-CaF_2 molten salt mixture with an operating temperature of about 800°C and a LiCl-KCl eutectic composition with an operating temperature of about 500°C.

In the reprocessing operation, the fuel is dissolved in the molten salt and the uranium and the transuranic elements are selectively removed, followed by some of the metallic fission products. However, Ba, Sr, Cs, I, Te, and Se fission products accumulate in the salt phase and need to be removed if the salt is to be recycled, or to be immobilized along with the salt for ultimate disposal as a solidified waste form that is suitable for a safe, long-term disposal.

A novel waste form concept using the high-temperature stability and ion-exchange properties of zeolites has been proposed and demonstrated by the ANL (2,3). The synthetic zeolite, molecular sieve, Linde 4A ($Na_{12}Al_{12}Si_{12}O_{48} \cdot 27H_2O$) has been shown to selectively remove Cs, Sr, and Ba (present as respective chlorides) from a simulated LiCl-KCl melt to form a sodalite-type product, ($M_{12}Al_{12}Si_{12}O_{48} \cdot 11$ MCl, where M = Na, K, Sr, Cs, Ba, and Li). The resulting fission-product-loaded zeolite was shown to have Cs and Sr leach rates below those for Cs and Sr in borosilicate glass at the same test conditions, and therefore had great promise as a waste form for the ultimate disposition of these fission products. As an extension of this novel zeolite application to molten salt cleanup, the then-proposed (1) LWR actinide recycle molten salt medium, $CaCl_2$-CaF_2 (82-18 mol%) was tested in contact with the fission product absorber.

In support of the ANL developmental program, a research effort at the Oak Ridge National Laboratory (ORNL) was initiated to investigate other aspects of concern in the further utilization of the zeolite waste form. The particular mission initially selected for ORNL was the determination of the zeolite stability in contact with the higher-melting $CaCl_2$-CaF_2 solvent, since both high temperature and fluoride ion were suspected of having deleterious effects on the zeolite cage structure.

EXPERIMENTAL

Reagents

All salts were Fischer reagent grade materials except for $CaCl_2$ and CaF_2, which were Johnson Matthey ultradry and 99.95 and 99.99% pure. The chlorine 99.5% and HF 99.9% gases were from Matheson. The zeolite was Union Carbide Linde 4A molecular sieve powder. The helium carrier gas used in molten salt sparging operations was 99.996% pure, and further purified by passing through Ti sponge at 600°C to remove oxygen-containing gases. $SiCl_4$ was Fischer Scientific technical grade.

Salt Handling

Minimal exposure of salt components to atmospheric impurities is necessary for reliable control of the molten salt chemistry at high temperatures. Therefore, the chloride salt mixtures were purified of the residual oxide and moisture content by Cl_2 gas sparging of the molten salt mixture in a graphite crucible enclosed in a nickel reactor tube and excluded from the air. The reactor was placed in a temperature-controlled furnace and connected to a gas-handling manifold, which provided the necessary inert gas atmosphere (helium), vacuum, and a mixture of the Cl_2 gas with helium, as required. The temperature of the melt depended on the melting point of the salt mixture (500-800°C).

The purified salts were cooled to ambient temperature and handled in an inert atmosphere glove box of ≤ 1 ppm moisture and oxygen content. The solidified salt was first crushed into ~2-mm chunks, or smaller and combined with the zeolite in a 6:1 weight ratio, placed back into the graphite-crucible-lined reactor tube, and connected back to the manifold avoiding the air exposure.

The molten salt/zeolite contact treatment was performed in a purified helium atmosphere. After melting a sparge tube was inserted into the melt to increase the zeolite-salt contact by bubbling dry helium through the mixture. After several hours contact time at 740°C, the sparge tube was removed from the melt, the system was cooled, and it was then transferred to the glove box. In order to characterize the zeolite after interaction with the salt the excess salt was washed away with distilled water, and the insoluble portion was characterized by X-ray powder diffraction.

$SiCl_4$ Sparging

The experimental setup for the fluoride removal by $SiCl_4$ sparging is shown in Figure 1. The liquid $SiCl_4$ was pipetted in a glass trap without exposure to air and held at 40-50°C to control the vapor pressure at ≈½ atm. The $CaCl_2$-CaF_2 molten salt was placed in a graphite-crucible-lined nickel pot. A thermocouple well extended into the molten salt from the flange-cover for direct temperature readings. The flange cover was also provided with a ½-in. ball valve, through which a nickel sampling tube could be passed into the molten salt without exposing the hot salt to the air. After a known amount of $SiCl_4$ had passed through the salt, a 1- to 2-g salt sample was removed, and its fluoride content was determined using a fluoride ion-selective electrode. This procedure is described elsewhere (4).

The presence of SiF_4 in the exit gases was confirmed by IR spectroscopy on a portion of the gas stream that had been trapped at the liquid nitrogen temperature and subsequently expanded into an evacuated IR gas cell.

Instrumentation

For characterization of the solid products, a SCINTAG X-ray powder diffraction instrument with a germanium detector and Cu Kα radiation was used. The X-ray spectra were compared with the Powder Diffraction File compiled by the International Center for Diffraction Data.

RESULTS AND DISCUSSION

The diffraction pattern of the Zeolite 4A contacted with fluoride-containing molten salt ($CaCl_2$-CaF_2) indicated that the zeolite cage framework was no longer present. Peaks due to the insoluble CaF_2 were identified, but the rest of the X-ray

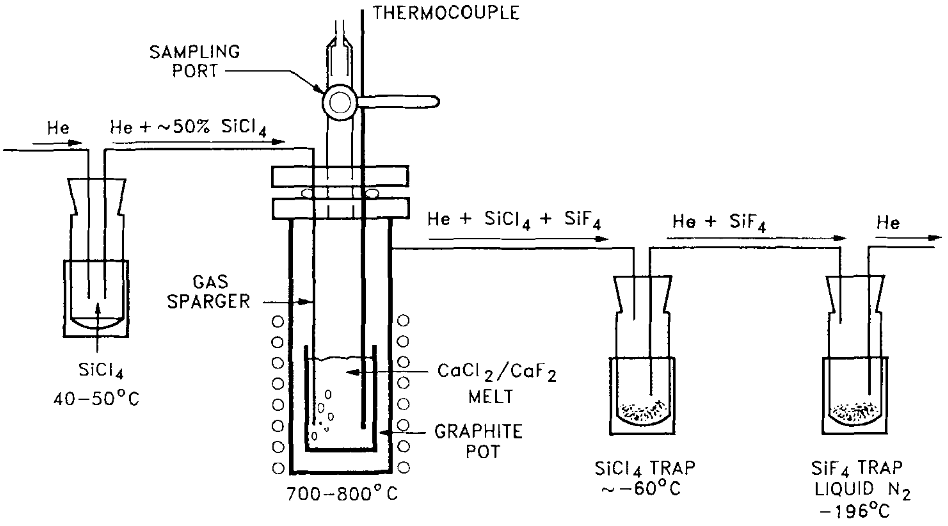

FIGURE 1. Apparatus for the fluoride removal from molten salts by $SiCl_4$ sparging.

diffraction patterns could not be matched with any silicate, aluminate, or aluminosilicate spectrum listed in the database.

In order to establish whether the fluoride ion, high temperature, and a combination of both contribute to the decomposition of the zeolite in the $CaCl_2$-CaF_2 molten salt, a series of experiments was performed, which consisted of testing the zeolite at (1) high temperature with no salt contact, (2) low temperature and high fluoride content, and (3) low temperature and low fluoride content salt contact. The prolonged heating of the Linde 4A molecular sieve with no salt contact destroyed the cage structure of the zeolite and formed the sodium aluminosilicate, nepheline. However, the X-ray diffraction pattern of the reaction product of zeolite with the $CaCl_2$-CaF_2 molten salt at comparable temperature was completely different from that of nepheline. Two low-temperature experiments were performed using lower-melting molten salts: the LiF-NaF-KF (46-10-44 mol %) eutectic ("FLINAK", mp 454°C) with the high fluoride content and the LiCl-NaCl-KCl(55-9-36 mol %) eutectic (mp 355°C) with low fluoride, 5 mol %, added in the form of FLINAK. The X-ray analyses showed that even at the low temperature (where the zeolite had been shown to be stable in contact with the all-chloride molten salt), both the high-fluoride and the low-fluoride-content salts cause the destruction of the zeolite framework. Fluoride contents below 5% of fluoride were not considered because this composition would be of no practical value in the LWR Actinide Recycle Program.

Table 1 summarizes results of the interaction of the zeolite with various molten salt compositions at different reaction temperatures. Experiments with molten fluorides (4) in contact with other silicate structures suggest that all aluminosilicate structures should be deleteriously affected by fluoride-containing molten salts. It was therefore evident that the presence of the fluoride ion in the molten salt is the mayor factor contributing to the destruction of the zeolite framework, and if zeolites are to be used for the selective sequestering of the Sr and Cs fission products, the fluoride component of the salt must be removed prior to its contact with the zeolite.

Displacement of the fluoride with another halogen using a gas sparge is an ideal way of reducing the fluoride concentration. Candidate chloride containing gases are listed in Table 2 with associated free energy changes for the displacement reaction: $CaF_2 + (2/x)\ MCl_x \rightleftarrows CaCl_2 + (2/x)\ MF_x$, (where M = Si, B, or C) at selected temperatures above the melting point of the salt. Based on the potential for easy recycle of the product gases and the stable by-products that would result, $SiCl_4$ was selected as the most ideal reagent for the fluoride removal process.

Samples of the melt were taken after a known amount of $SiCl_4$ has been sparged through the $CaCl_2$-CaF_2(82-18 mol %) melt and the fluoride content determined. The fluoride content in the molten salt mixture as a function of $SiCl_4$ sparged through the melt is shown in Table 3. In the initial experiment an open 5-mm-diameter graphite tube was used as the gas sparger, which produced large bubbles with a poor gas-to-molten salt contact, and consequently low reaction efficiency. The reaction efficiency was considerably improved by using a 1/8-in. nickel tube with a flattened gas exit end which supplied many small gas bubbles into the melt. By using the more efficient gas-to-molten salt contact the fluoride removal rate was increased by a factor of 3 for the same initial fluoride concentration, and the fluoride concentration was reduced from 18.3 to 0.1 mol % when the experiment was terminated. Further improvement in the efficiency of the gas-to-molten salt contact was not warranted at this stage of the work.

TABLE 1. INTERACTION OF MOLTEN CHLORIDE AND FLUORIDE SALTS WITH ZEOLITE

Experimental Conditions	[F]/[zeolite]	Temperature (°C)	Products Identified by X-ray Diffraction
Chloride salt, low temperature	0	500-600	Sodalite
$CaCl_2$-CaF_2 molten salt	48	740	CaF_2 + unidentified peaks
"FLINAK" molten salt	288	513	K_2NaAlF_6 + LiF + 2 small unidentified peaks
Li-Na-K chloride eut. plus 5% fluoride	15	508	LiF + unidentified peaks
No salt, high temperature	0	800	$NaAlSiO_4$

TABLE 2. DISPLACEMENT REACTION FOR FLUORIDE ION REMOVAL USING SOME VOLATILE CHLORIDE-CONTAINING GASES

Gas	ΔG_{rxn}(Kcal/mol) at 800°C	900°C	1000°C
$SiCl_4$	-30.3	-31.8	-33.4
BCl_3	-52.7	-55.0	-57.3
CCl_4	- 0.8	- 2.3	- 3.7

The rate of fluorine removal also strongly depends on the concentration of fluoride in the melt. As the fluoride content in the salt decreased, more of the $SiCl_4$ passed through the melt unreacted (Figure 2). However, due to the large difference in the $SiCl_4$ and the SiF_4 boiling points, they can be efficiently separated and the unreacted $SiCl_4$ recycled into the process, as required. Recycle of the SiF_4 through a hydrolysis process (6), though not developed here, would lead to a satisfactory leach resistant SiO_2 for waste disposal. The HF would be conveniently recycled to back into the process to re-establish the fluoride content of the melt.

TABLE 3. REMOVAL OF FLUORIDE FROM THE $CaCl_2$-CaF_2 MOLTEN SALT BY $SiCl_4$ SPARING

Experiment	Temperature (°C)	$SiCl_4$ used (mL)	Fluoride in molten salt (mol %)
1	770	0.0	18.7
	770	20.6	15.0
2	747	0.0	18.3
	759	7.0	10.4
	760	14.0	6.5
	771	24.8	2.4
	772	36.8	0.3
	791	48.8	0.1

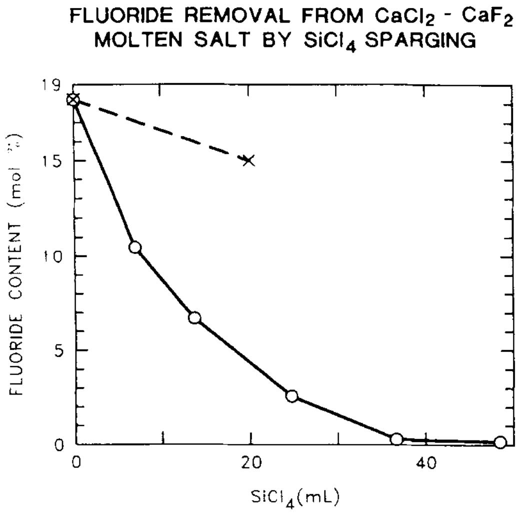

FIGURE 2. Fluoride removal from the $CaCl_2$-CaF_2 molten salt as the function of the $SiCl_4$ consumption: —○— efficient sparging, —×— inefficient sparging.

CONCLUSIONS

It was demonstrated that fluoride ion must be removed if zeolite materials are to be used in the molten salt high-level waste process. The fluoride content of a $CaCl_2$-CaF_2 (82-18%) molten salt mixture can be efficiently removed to a concentration below 1% by sparging the melt with a stream of a mixture of $SiCl_4$ and helium gasses at ~800°C. Due to the large difference in the boiling points of SiF_4 and $SiCl_4$, the unreacted $SiCl_4$ can be recycled and used efficiently.

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