

**FY23 Milestone M3RD-23OR0603031  
Measuring the Dissolution of Cr and Fe at  
550°C-750°C in FLiNaK and FLiBe**



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Milestone M3RD-23OR0603031

Measuring the Dissolution of Cr and Fe at 550°-750°C in FLiNaK and FLiBe  
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## Introduction

Assessing the compatibility of 316H stainless steel with molten fluoride salts has been identified as a key research topic for molten salt reactor development.[1] Current developers are interested in 316H stainless steel due to its ready availability and ASME code qualification. Previous studies of 316H stainless steel compatibility in molten fluoride salts have shown general agreement that Cr is selectively removed from the alloy during the exposures in molten salts [2-5]. However, the extent of Cr dissolution depends on the initial purity of the salt and Fe also readily dissolves in the salt. In order to model dissolution [6], it is necessary to understand how time and temperature affect the dissolution rates of the alloying elements which may lead to saturation of these elements in the salt.

To study the dissolution of 316H, Cr and Fe specimens were exposed in FLiNaK and LiF-BeF<sub>2</sub> (FLiBe) salt at three different temperatures (550°-750°C) and three different durations (100-2000 h) in isothermal capsule experiments.

## Procedure

Isothermal capsule experiments were conducted in 4340 steel, or low carbon arc cast Mo capsules (25 mm outer diameter x 100 mm tall x 1.2mm wall) [2-5]. For these dissolution experiments, larger coupons (~10 x 20 x 1.5 mm) of unalloyed Fe and Cr (nominally 99.99% purity) were used and had a 600 grit polished finish. The purified, commercially produced FLiNaK salt (Comm1) contained impurities shown in Figure 1 determined by inductively coupled plasma, optical emission spectroscopy (ICP-OES) and combustion analyses [7]. It contained Zr as a redox agent [8] and had a lower O content than a second salt supplied by a different vendor (Comm2). For contrast, an imperfect laboratory-purified salt batch is shown where the higher Ni impurity resulted in greater dissolution attack [7]. Typical procedures used to purify salt using H<sub>2</sub>-HF have been presented elsewhere [9]. The characterization of the commercial batch of FLiBe being used in these experiments is currently in progress. Initially, Mo capsules were loaded with ~30 g of Comm1 FLiNaK in an Ar-filled glove box with impurity levels ≤1 ppm O<sub>2</sub> and H<sub>2</sub>O. The specimens were attached to one end using Mo wire and the capsules were sealed using gas tungsten arc (GTA) welding in the glove box. The capsule was then GTA welded in the glovebox into a larger type 304 SS capsule to provide secondary containment and prevent the primary capsule from oxidizing. The capsules were exposed in a box furnace in laboratory air. The test matrix is shown in Table 1. After the 100-2000 h isothermal exposure, the capsules were inverted to allow the salt to drain away from the specimen. After cooling, the capsules were opened in the same glove box. As shown below, Mo-Fe interaction was observed with FLiNaK, especially at 750°C. Therefore, those tests were repeated with a 4340 steel capsule and no Fe specimen using the same procedure described above. For the FLiBe experiments, an Fe specimen in a 4340 capsule was used with a Ni-200 wire attachment.

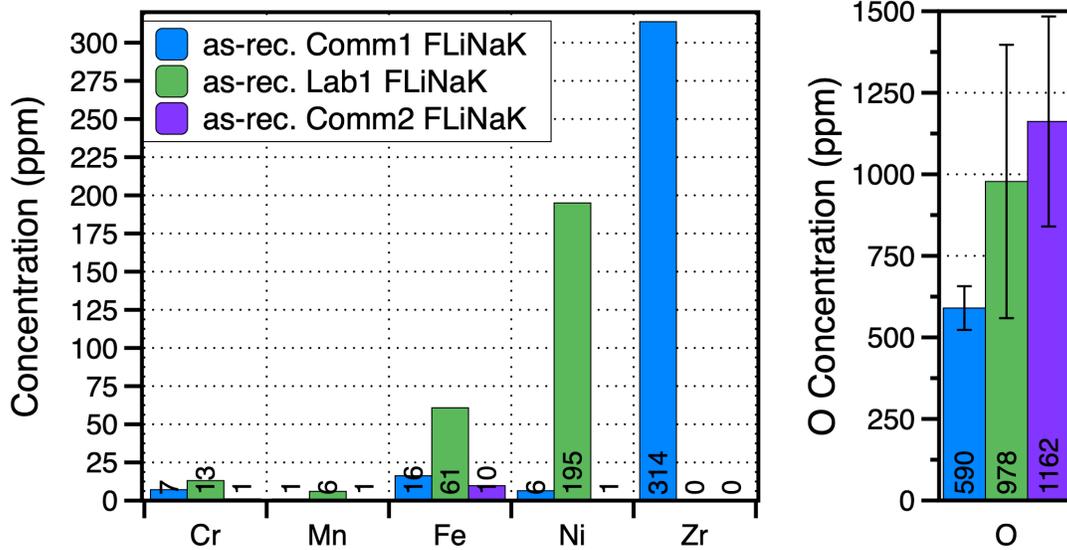


Figure 1. FLiNaK salt chemistry of three salt batches before testing determined by ICP and combustion analysis (O). Three O measurements were made and the average and standard deviation are shown.

Table 1. Capsule test matrix for FLiNaK and FLiBe (in progress) experiments with Cr and Fe specimens. Initial tests used 1000 h exposures but a 100 h exposure was used in later experiments.

Time/Temp.	100 h	500 h	1000 h	2000 h
550°C	FLiBe	FLiNaK/FLiBe	FLiNaK	FLiNaK/FLiBe
650°C	FLiBe	FLiNaK/FLiBe	FLiNaK	FLiNaK/FLiBe
750°C	FLiBe	FLiNaK/FLiBe	FLiNaK	FLiNaK/FLiBe

For all experiments, the specimens were cleaned prior to exposure using acetone and methanol and after exposure using deionized water sonication at 40°C for 1 h.

## Results

The mass change results for Cr specimens exposed to commercial FLiNaK salt (Comm1) in Mo capsules are shown in Figure 2. The relatively uniform specimen appearance after cleaning suggested uniform dissolution and no further characterization was performed. The initial 500-2000 h times were selected to show an effect of time but almost no effect was evident. For the second round of experiments, the times were adjusted to include 100 h, Table 1. Similar experiments were conducted with Fe specimens in Mo capsules but the very high mass losses at 750°C (14.3 mg/cm<sup>2</sup> after 2,000 h) raised the suspicion that there was an interaction between the dissolved Fe in the salt and the Mo capsule wall that might accelerate dissolution.

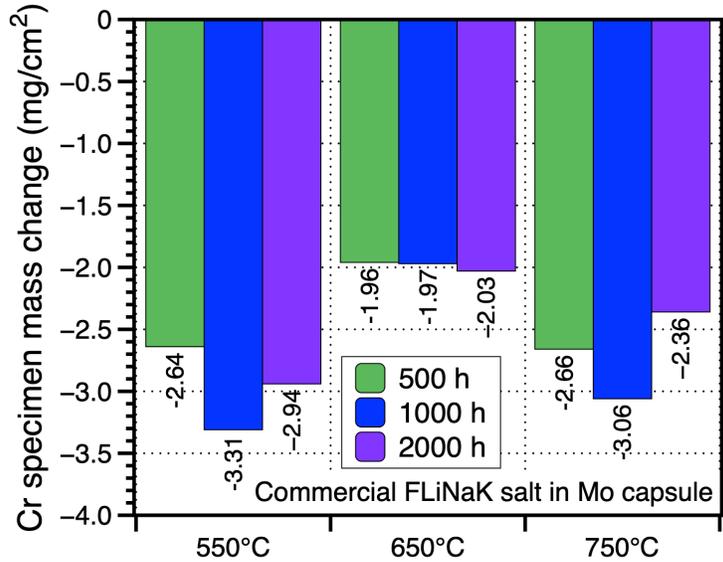


Figure 2. Specimen mass change of Cr specimens exposed at several times at each temperature to commercial FLiNaK salt (Comm1) in Mo capsules.

Rather than relying on mass change, the salt was characterized using ICP-OES after each experiment to measure the amount of Cr and Fe dissolved. Figure 3 shows there was a reasonable correlation between Cr mass loss and Cr concentration in the salt. However, large mass losses for Fe specimens at 750°C (three highest mass loss points) did not correspond to high Fe levels in the salt. Subsequent characterization using scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) of the Mo capsule wall after the 2000 h exposures showed Fe was deposited on the capsule wall, thereby accelerating the mass loss. No Cr was detected in Mo capsule walls with a Cr specimen.

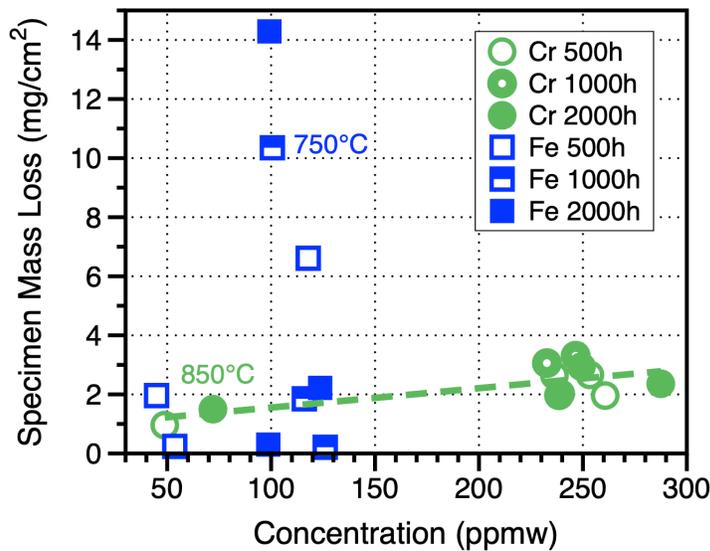


Figure 3. Specimen mass loss versus measured Cr and Fe concentration in Comm1 FLiNaK salt exposed in Mo capsules at 550°-850°C.

To address this Mo-Fe interaction issue, a new set of experiments were assembled using type 4340 steel capsules. For these first experiments, no specimen was included in the capsule and the shorter times at 550° and 650°C were not repeated.

All of the ICP-OES results are summarized in Figure 4, in this case plotted versus exposure time. The Fe results in Mo capsules are shown for reference. The Fe results in steel capsules were similar at 550° and 650°C after 2000 h. However, at 750°, the measured Fe levels were much lower in the steel capsule compared to the Mo capsule. In most cases, there was a minimal effect of time on the Cr or Fe concentration. The results for Cr all clustered around ~250 ppm. For the Fe results in Mo capsules, a similar clustering was observed near ~100 ppm. The same FLiNaK salt used in these capsule experiments also was used in the monometallic type 316H stainless steel thermal convection loop (TCL) that ran for 1,000 h with a peak temperature of 650°C [4]. Characterization of the salt after the 1,000 h exposure showed very similar Cr and Fe levels in the TCL as was observed in these experiments, Figure 4. In addition to Cr and Fe, 20 ppm Mn also was detected after operation as Mn was selected removed from 316H, which contained 1.9wt.% Mn [4]. Similar experiments with Mn could be conducted but there is concern about a Mo-Mn reaction and efforts to fabricate Mn capsules was not successful due to cracking during machining.

For the FLiBe salt experiments, Figure 5 shows the mass change results for Cr specimens exposed at 550°-750°C for 100-2000 h as shown in Table 1. The lowest mass loss was observed in specimens exposed at 550°C followed by specimens exposed at 650°C and 750°C. Based on these results, Cr specimen mass loss peaked at 500 h and did not increase after 2000 h.

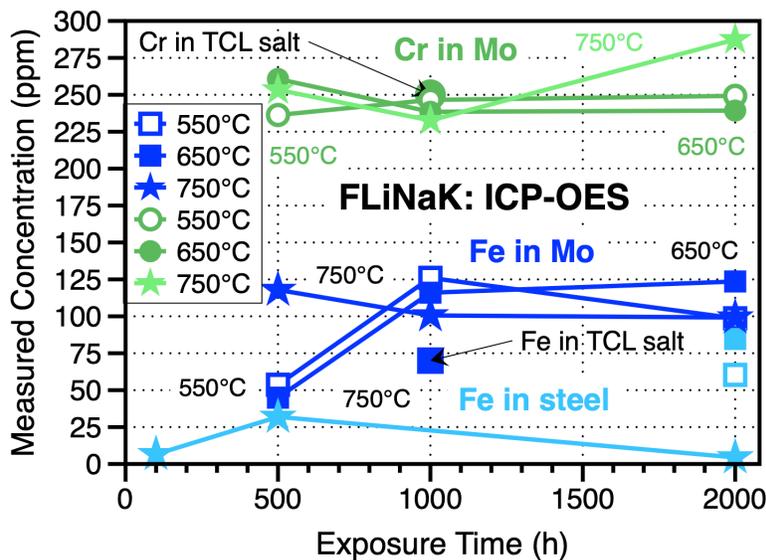


Figure 4. Measured Cr and Fe contents in commercial FLiNaK after exposures in Mo capsules. The results from the FLiNaK TCL after 1,000 h of operation also are shown.

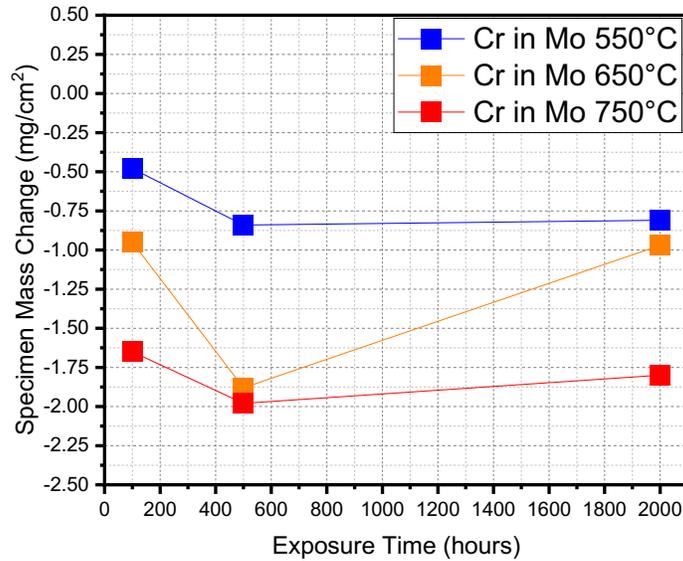


Figure 5. Cr specimen mass change after exposures at 550°C-750°C for 100-2000 hours in Mo capsules.

Figure 6 shows the mass change results of Fe specimens exposed in FLiBe using the matrix in Table 1. Compared to the Cr specimens, the Fe specimens displayed a notably lower mass loss. However, the 4340 steel capsule also was in contact with the salt which could have resulted in faster salt saturation with Fe.

The temperature effect in Fe specimens showed the opposite trend compared to that in Cr specimen exposures. Increasing the temperature from 550°C to 750°C resulted in lower Fe specimen mass loss. There was little effect of time on mass loss. However, the reduced

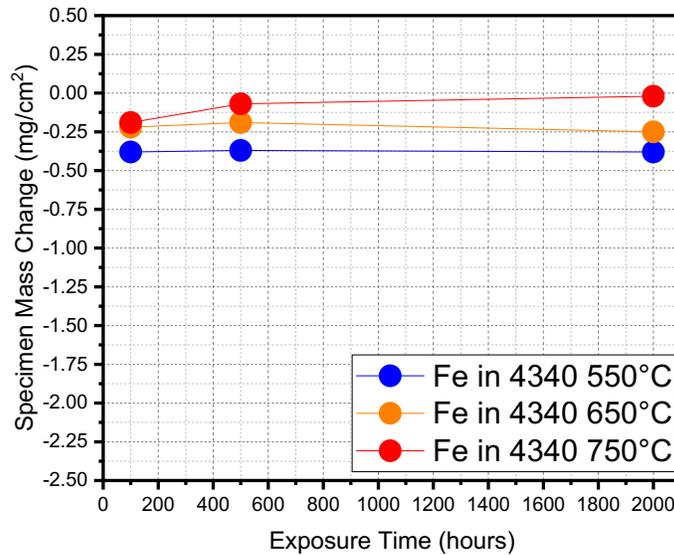


Figure 6. Fe specimen mass change after exposures at 550°C-750°C for 100-2000 hours in Fe4340 capsules.

mass loss with time at 750°C is unexpected and may indicate a surface deposition reaction on the Fe specimens. Thus, the specimen surfaces need to be characterized to see if anything (e.g. Mn from the 4340 steel) deposited during exposure.

Because the commercial FLiBe salt was received in the middle of the year, the specimen and FLiBe characterization could not be completed during FY23. Salt chemistry measurements are needed to compare the FLiNaK and FLiBe results and fully understand the effect of time and temperature on Cr and Fe dissolution in these two salts.

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