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Title page

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Chlorination of Uranium Metal in Molten NaCl-$CaCl_2$ via Bubbling HCl

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Abstract

Molten chloride salt fast reactors (MCFRs) will require UCl_3 dissolved in molten salt mixtures as fuel for nuclear fission. For infusing the salt with UCl_3, bubbling HCl into NaCl-$CaCl_2$ in contact with U metal was investigated. The reaction was run up to 9 hr and yielded U concentration up to 0.652 wt%. Open circuit potential between a W electrode and Ag/AgCl reference electrode yielded a potential consistent with uranium existing as U(III) in the salt. This demonstrates that HCl can be a very effective chlorinating agent to infuse MCFR fuel with UCl_3 starting from U metal.

Keywords

Molten salt reactors, Uranium(III) chloride, NaCl-$CaCl_2$ eutectic salt, HCl gas

Introduction

The molten chloride fast reactor (MCFR) is a molten salt reactor concept that is currently being developed by several nuclear reactor companies (TerraPower/Southern Company, Moltex, and

Elysium Industries) for commercialization. MCFRs are designed to use molten chloride salt containing UCl_3 as a liquid nuclear fuel which circulates in a loop that includes a reactor core and one or more heat exchangers [1]. Because such nuclear reactors would be a low-carbon energy source and safer than conventional light water reactors, a great deal of investment has been made in MCFR technology by both governments and the private sector [2]. Historically, there has never existed nuclear reactors designed to use uranium in chloride form, however. Thus, there is no industrial source of uranium chloride or process for its production at scale. Idaho National Laboratory (INL) currently operates two engineering-scale electrorefiners for treatment of Experimental Breeder Reactor-II (EBR-II), but INL either produces its own UCl_3 via reaction of $CdCl_2$ with U metal or obtains it from Argonne National Laboratory. The cadmium chloride-based reaction is shown below (Equation 1).

$$1.5\ CdCl_{2(molten\ salt)} + U_{(solid)} = UCl_{3(molten\ salt)} + 1.5\ Cd_{(liquid\ metal)} \quad (1)$$

The problem with forming UCl_3 from reaction with $CdCl_2$ is that it results in accumulation of a liquid cadmium pool below the electrorefiner salt pool. Cadmium is both toxic and volatile at the electrorefining temperature (500°C). In a remote operating environment such as a nuclear material processing hot cell, separation of molten metal below a pool of molten salt is extremely difficult to accomplish. A similar reaction to make UCl_3 has been reported using $ZnCl_2$ as the chlorinating agent [3]. Zinc is non-hazardous, but it also forms a liquid metal pool. A more convenient approach is needed for remote processing. At the time of the writing of this paper, there is no known industrial source of UCl_3 that could be utilized to chlorinate U from the metal state that would be compatible with using spent fuel as the starting material.

It has long been known that the following reaction will form UCl_3 starting with U metal or after converting the U metal to uranium hydride as shown in Equation 2 [4].

$$3HCl_{(g)} + UH_{3(s)} = UCl_{3(liq)} + 3H_{2(g)} \quad (2)$$

Recently, this reaction was tested from 250 to 400°C by our research group, and it was reported that it can be difficult to achieve high selectivity for UCl_3 rather than UCl_4 or UO_2 [5]. Meanwhile, we also reported the successful synthesis of UCl_3 with high selectivity for U(III) in NaCl-$CaCl_2$ via U metal oxidation with $FeCl_2$ or $FeCl_3$ [6]. The presumed reactions are given below.

$$FeCl_{2(liq)} + U_{(s)} = UCl_{3(liq)} + Fe \quad (3)$$

$$FeCl_{3(liq)} + U_{(s)} = UCl_{3(liq)} + Fe \quad (4)$$

The downside of using $FeCl_2$ or $FeCl_3$ is that, similar to reactions with $CdCl_2$ and $ZnCl_2$, it forms Fe metal solid particles that must be separated from the salt. Magnetic separation may be effective but has not been proven effective. It seems like a natural logical progression to pose the question of whether reaction (2) (involving U metal instead of UH_3) can be performed directly in the molten salt. The advantages of such an approach include eliminating remote handling of solids and favoring UCl_3 over UCl_4 via use of U metal as a redox buffer (see Equation 5).

$$3UCl_{4(liq)} + U_{(s)} = 4UCl_{3(liq)} \quad (5)$$

A scalable process is needed to generate UCl_3 in situ either from virgin materials or from waste salt produced by an MCFR. Consider how such waste salt could be recycled. In the first stage of a hypothetical process, UCl_3 from waste salt can be recovered as U metal on a cathode after electrowinning or galvanic reduction [7]. Next, the uranium-free salt could be dechlorinated via ion exchanged with H-Y zeolite [8]. This reaction (Equation 6) off-gases HCl while immobilizing the cations from the salt waste into a zeolite matrix that can then be sintered into a ceramic waste form [9].

$$MCl_{x(salt)} + H\text{-}Y_{(zeolite)} = HCl_{(g)} + M\text{-}Y_{(zeolite)} \quad (6)$$

The final step of this hypothetical process for recycling U from MCFR step would be to rechlorinate the recovered U metal and allow it to partition back into the salt. This would accomplish the goal of keeping U (and TRU) in the salt and out of the waste stream from the MCFR. Thus, the feasibility of Equation 2 being performed directly in the molten salt is potentially of great importance. This paper reports feasibility study of this reaction.

Experimental

Materials and Equipment

NaCl (99%, Sigma Aldrich, anhydrous), $CaCl_2$ (99.5% Alfa Aesar, hydrated), HCl gas (5.038 ± 2%, AirGas), and a uranium rod (760 mm length x 21 mm diameter, depleted uranium) were all used as received. 60 g of equimolar NaCl-$CaCl_2$ was purified by removal of water and hydroxide contaminants using thermal dehydration and hydrochlorination. $CaCl_2 \bullet 2H_2O$ and NaCl salt were transferred to an alumina crucible and put under vacuum in a gas-tight quartz reactor as it heated up. The effluent gas flowed through a dry ice trap to protect the vacuum from water. The salt was heated to 200^{o}C at a rate of 300^{o}C/hr under vacuum, held at this temperature for an hour, and then heated to 600^{o}C at the same rate with ultra-high purity Ar (UHP, AirGas) flowing into the reactor through an N_2 factory-calibrated thermal mass flow controller (MKS, GM50A013502SMM020) at 100 cc/min at ambient pressure and temperature. The mass flow controller automatically corrects for the use of Ar instead of N_2 by applying a gas correction value of 1.36. At this temperature, the eutectic NaCl-$CaCl_2$ is molten, and 160 cc/min of 5 vol% HCl balanced with Ar was bubbled into the salt until the reaction stopped as determined by the titration of the effluent gas using a Titroline 7000 auto-titrator in pH-stat mode with a pH=10.0 starting solution.

Methods and Analysis

The experimental setup for U chlorination is essentially the same as the salt purification (Fig. 1), so U chlorination was started immediately after the conclusion of the salt purification while the salt was maintained at temperature in the molten state. The U rod was wrapped tight enough to prevent slippage in stainless steel wire (0.041 gauge, Malin Co.), and the opposite end of the wire was threaded through a rubber stopper so that it would be suspended from the lid in the crucible of salt. Once the stopper was secured, 160 cc/min of 5 vol% HCl gas was bubbled into the salt adjacent to the rod. Each experiment was run for 6-9 hours with salt samples taken intermittently using a threaded rod as a dipstick and a continuous titration of the effluent gas using an autotitrator.

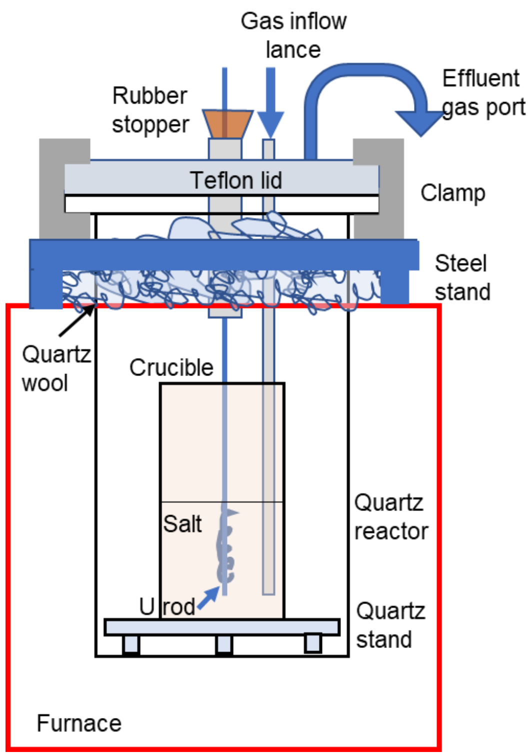

Fig. 1 Experimental set up for the U chlorination

In one of the experiments, the effluent gas was also routed through a quadrupole mass spectrometer (Pfeiffer Vacuum QMS, QME 220) to analyze the concentration of H_2 gas. After the desired amount of time, the input gas lance was raised out of the salt while 25 cc/min of UHP Ar flowed into the reactor to prevent atmospheric water from contaminating the salt, the rod was removed, and the furnace was set to cool down at 30^{o}C/hr. Once at room temperature, the crucible was transferred into a glove box where it was reheated to 600^{o}C, and the open circuit potential (OCP) was measured using an Ag/AgCl reference electrode (RE) and a tungsten working electrode (WE) submerged in the salt and connected to a potentiostat (Autolab PGSTAT302N) to measure the equilibrium potential of the salt.

Each of the dipstick salt samples was dissolved using 2% nitric acid (HNO_3, 68.5%, Fisher Chemical) for inductively coupled plasma mass spectrometry (ICP-MS) ^{238}U concentration measurements (Agilent 7900 ICP-MS).

Results and Discussion

Test #1: 3-hour chlorination

Two separate experiments were run with metallic U immersed in molten NaCl-$CaCl_2$ in which HCl gas was bubbled. The objective was to measure U concentration in the salt as a function of time in addition to determining the selectivity for UCl_3 rather than UCl_4 considering the following two reactions (Equations 7 and 8) as possible.

$$U_{(solid)} + 3HCl_{(gas)} \rightarrow UCl_{3(salt)} + 1.5H_{2(gas)} \quad (7)$$

$$U_{(solid)} + 4HCl_{(gas)} \rightarrow UCl_{4(salt)} + 2H_{2(gas)} \quad (8)$$

Total reaction time was the only variable that changed between the two experiments. Masses, concentrations, and flowrates were held constant. Experiment #1 involved reaction for 3 hours. The first indication of successfully synthesizing UCl_3 is the color change in the salt samples from bright white to lavender to wine red as shown in Fig. 2.

Fig. 2 The salt samples taken during Test #1 displayed chronologically according to chlorination time from left to right

Each salt sample taken during experiment #1 was analyzed using ICP-MS and the results are plotted against time in Figure 3. The trendline has a slope that corresponds to 1.51 x 10^{-4} mol U/hr). HCl flowed into the reactor at a rate of 0.03 mol/hr which would theoretically generate 0.01 mol U/hr according to Eq. (1). Thus, the HCl flow is not the limiting factor in UCl_3 production. The final average ^{238}U concentration for experiment #1 as measured by ICP-MS was 0.184 wt.% U after 3 hours of chlorination.

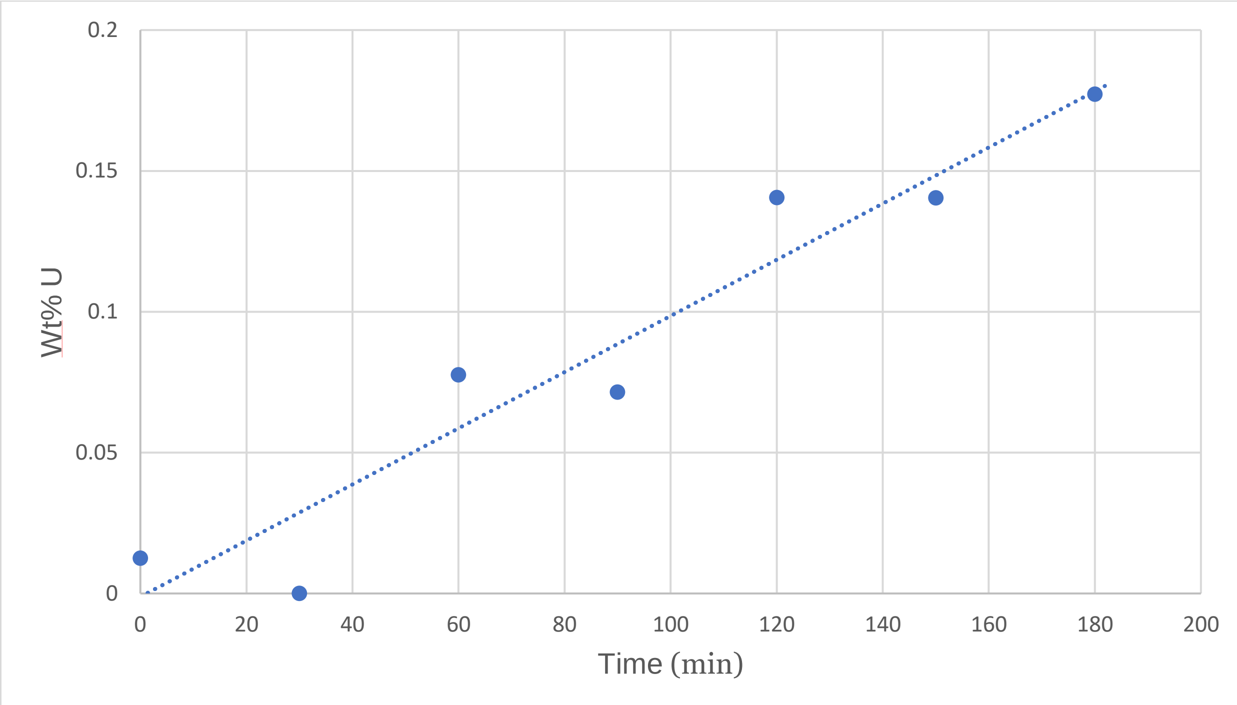

Fig. 3 U concentration in molten NaCl-$CaCl_2$ as a function of time of reaction with HCl for Test #1 measured via ICP-MS.

The HCl flow out of the reactor was directed into the autotitrator cell, where it was reacted continuously with NaOH solution to keep the pH at 10.0. Fig. 4 shows the cumulative volume of NaOH titrant added over time for the duration of the experiment, including the salt purification stage. Region 1 (0-110 minutes) is the calibration stage where 160 cc/min of 5% HCl flows directly into the autotitrator through the bypass. After the rod is inserted, the slope decreases slightly as some of the HCl is consumed by the reaction in Region 2 (110-290 minutes). The ΔV of the titrant relates to how much of the HCl was consumed by the reaction. From the difference in the extrapolated volume of titrant and actual volume of titrant shown in Figure 4, it was calculated that 1.83 ml of titrant was added solely for the purpose of chlorinating U metal. This corresponds to 0.24 wt% U in in the salt, roughly consistent to what was measured via ICP-MS. A third approach to measuring the amount of U chlorinated involved measuring the change in mass of the U wire from Experiment #1. Based on that measurement, it was calculated that the salt contained 0.25 wt% U after Experiment #1. Thus, the ICP-MS, titrator, and mass changes all were consistent in confirming partitioning of U into the salt and the concentrations were within a tight range (0.18 to 0.25 wt%). These results are summarized in Table 1.

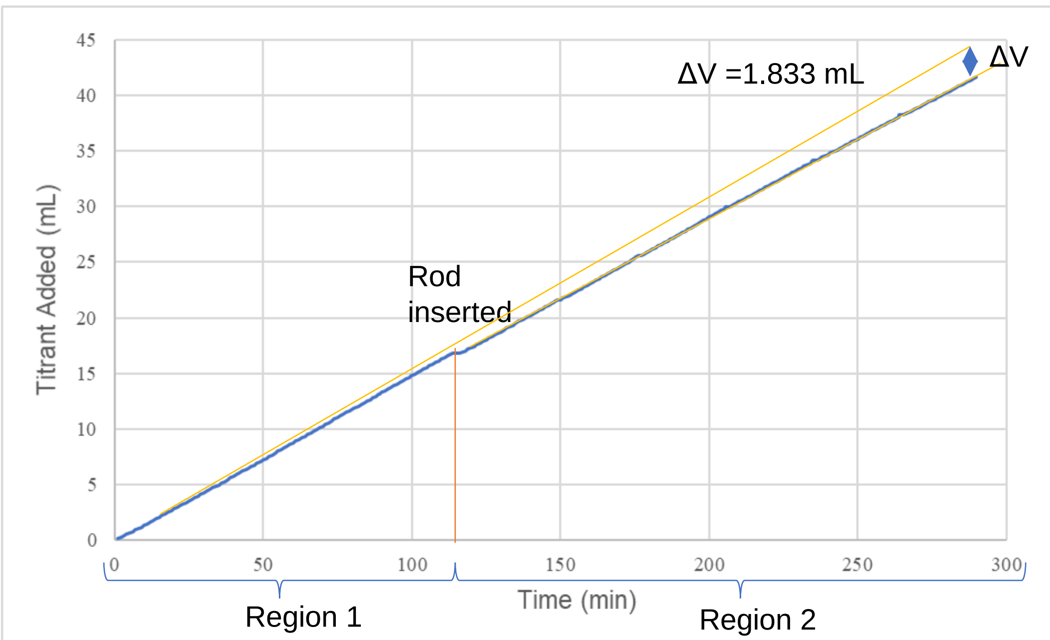

Fig. 4 Titration data for the 3-hour U chlorination trial (Test #1)

The ΔV between the calibration slope and chlorination slope was 1.833 mL of 1.0 M NaOH titrant. This translates into a predicted 0.00183 moles of HCl reacting with the U rod resulting in 0.652 wt.% U in the 60 g of base salt.

The stabilized OCP value was used to analyze the activity ratio of UCl_4 to UCl_3 according to the Nernst Equation.

$$E_{eq} = E^{o}_{UCl4} + \frac{RT}{F} ln\left(\frac{a_{UCl4}}{a_{UCl3}}\right) \quad (9)$$

where E_{eq} is the measured value, E^{o}_{UCl4} is the standard reduction potential of UCl_4 to UCl_3, R is the gas constant, T is the temperature in K, F is Faraday's constant, a_{UCl4} is the activity of UCl_4, and a_{UCl3} is the activity coefficient of UCl_3. E^{o}_{UCl4} was calculated using free energy data from HSC Chemistry in addition to reference correlations reported by Yang and Hudson [10] to be -0.332V vs. Ag/AgCl (100%) at 600°C. This is based on a free energy of reaction of -99.3 kJ/mole for the following reaction (10). Note the uranium chlorides are specified to be supercooled liquids, which seems reasonable given that they are dissolved in molten salt.

$$UCl_{3(l)} + 0.5Cl_{2(g)} = UCl_{4(l)} \quad (10)$$

The correction between a Cl^-/Cl_2 reference electrode and 100% AgCl/Ag was calculated to be +0.697 V. In other words, the potential versus AgCl/Ag is 0.697 V higher than the potential versus Cl2/Cl-, based on a correlation derived from the paper by Yang and Hudson [10].

The open circuit potential (OCP) of the salt produced from Test #1 was measured using a W working electrode (WE) and a pure Ag/AgCl/mullite reference electrode (RE). The stabilized OCP value was measured to be -1.064 V which translates to a ratio activity of UCl_4 to activity of UCl_3 of 5.9×10^{-5} using Eq. (9). Because the ratio is so small, there was essentially no UCl_4 synthesized. The lack of UCl_4 makes this process a viable industrial choice because of its selectivity.

Test #2: 9-hour trial

Like Test #1, the salt gradually darkened throughout the second test resulting in the dark wine-red sample shown in Fig. 5. Unlike the 3-hour trial, the uranium rod lost significant mass, especially at the surface of the salt as shown in Fig. 6. The rod became so thin that it broke into two parts when it was removed from the stainless-steel wrapping. Interestingly, the thinnest part of the rod was closest to the surface of the molten salt. The lance was lowered to the bottom of the crucible then raised slightly, but the U rod was lowered all the way to the bottom. This slight difference prevents the gas from interacting with the bottom of rod because gas rises and never interacts with the bottom portion of the rod.

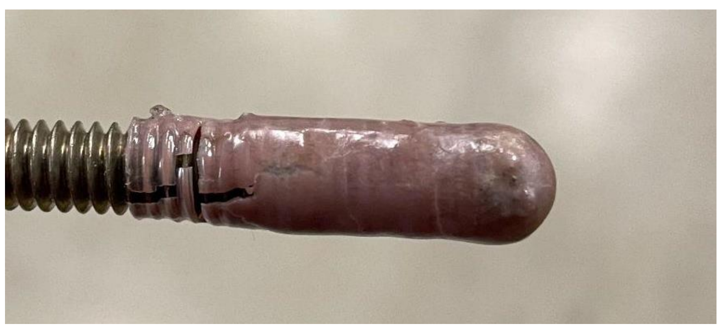

Fig. 5 Salt sample after 9 hours of U chlorination in Test #2.

Fig. 6 Uranium rod after 9 hours of chlorination in Test #2.

Fig. 7 shows the concentration of U in the salt for Test #2 that continued for 9 hrs. The U concentration data from Experiment #1 is overlaid on the plot, showing a consistent rate of increase for the two experiments. The linear fit equates to a rate of increase of 0.0688 wt.% U/hr. Note that in both experiments the U metal was also present in excess, and its surface area probably did not change appreciably. So, the consistent linear increase seems reasonable with a constant rate of reaction that could be limited by mass transfer of HCl to the surface of the U metal rod.

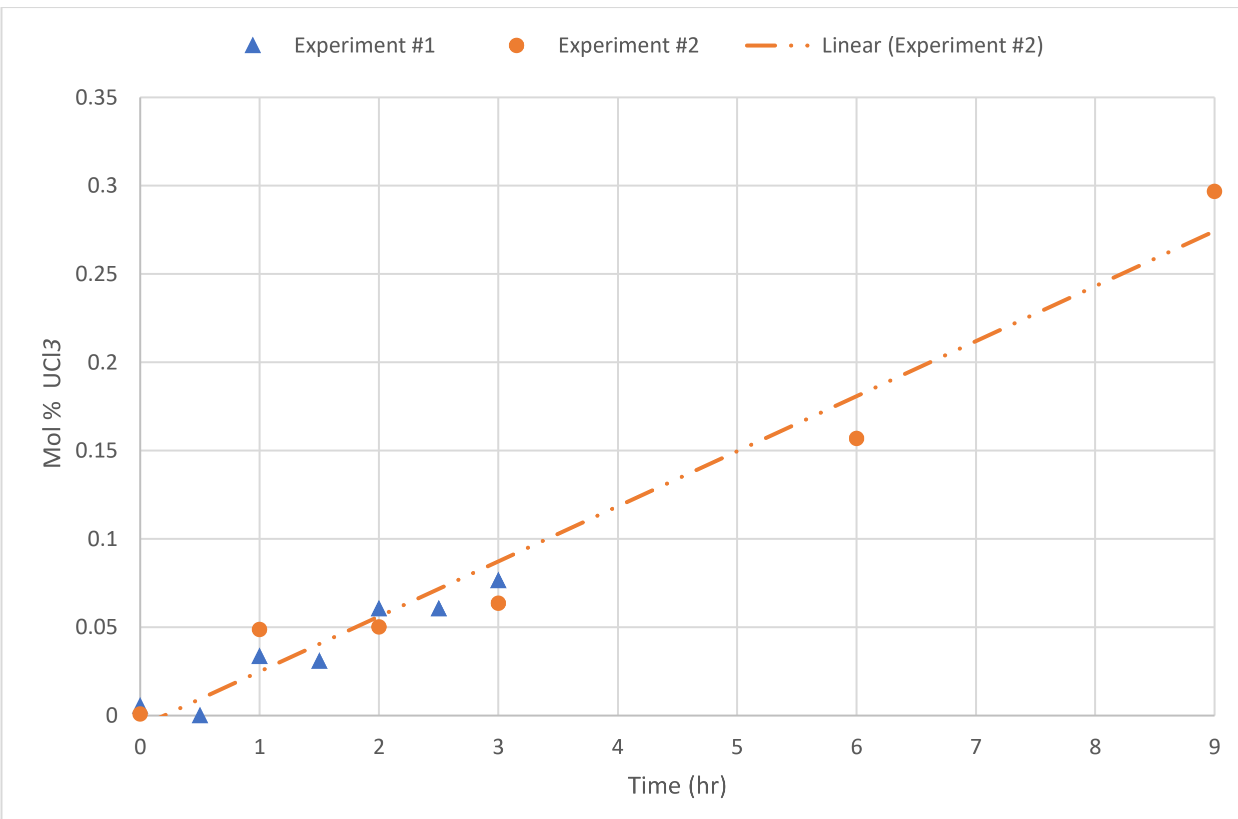

Fig. 7 U concentration in molten NaCl-$CaCl_2$ as a function of time of reaction with HCl for Tests 1 and 2 measured via ICP-MS.

The autotitrator did not save the data from this experiment, so the titration results cannot be compared with those from Test #1. However, the effluent gas from Test #2 was sampled and analyzed using a quadrupole mass spectrometer (QMS) to measure concentrations of hydrogen, argon, and HCl throughout Test #2. When the feed HCl gas mixture was bypassed around the chlorination reactor, the QMS read an HCl concentration of 5.20%. Figure 8 shows the HCl concentration in the gas as the flow was switched from bypass to go through the reactor at t = 0 hr. Right as the valves were switched there was a downward spike in HCl concentration. At this time, the U rod was inserted into the salt. At about the 7-hour mark shown in Figure 7, the QMS control valve was constricted in an effort to obtain a better reading. This caused the detector current to drop and concentration reading to spike. For the last two hours of the experiment, the HCl concentration trends appeared erratic. Assuming the concentration data measured prior to turning the QMS sampling valve is representative of the feed for the whole duration of the experiment, it can be seen that a relatively small percentage of the HCl reacted throughout the experiment. Prior to changing the sampling valve at the 7 hr mark, the HCl concentration was measured to be 4.4 vol%, which corresponds to a 16.5% conversion at that time. Changing the sampling valve caused disruption in the effluent HCl concentration measurement, so the concentration data line was extrapolated linearly from 7 to 9 hr as shown in Figure 8. The concentration curve was then integrated over the whole 9-hour experiment, and it was calculated that 5.73% of the total HCl that flowed into the system reacted. Thus, the unreacted HCl should be recycled in an industrial implementation of this process.

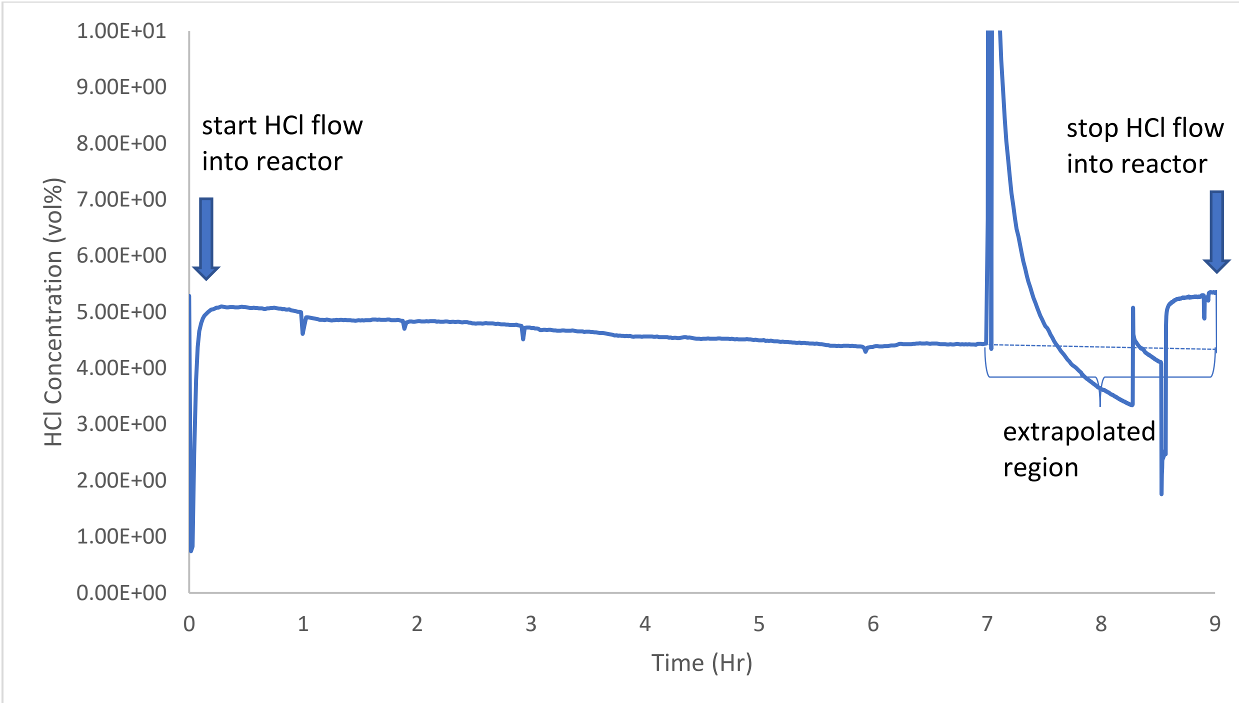

Fig. 8 Effluent HCl concentration (vol%) in Test #2 as measured by QMS.

The above HCl conversion calculation translates to 0.0115 moles of HCl consumed in the reaction assuming the 160 cc/min flow rate is 5.20% HCl (from the baseline reading). According to Eq. (1), UCl_3 is produced at a 1:3 stoichiometric ratio to HCl, so the predicted wt.% of U in 60 g of salt is 1.52 wt%. The actual measured value by ICP-MS was 0.65 wt%. The difference could be attributed to factors such as HCl leakage from the reactor and/or reaction/corrosion with other materials in the reactor.

Table 1 summarizes the wt.% U calculations for the three sources of data: change in rod mass, QMS results, and ICP-MS results after each of the two experiments reported here. Note that for each experiment, the different measurement methods yielded concentration within a factor of two or smaller. All measurements were consistent with the objective of partitioning U into the molten salt phase, and increased reaction time resulted in increased U concentration.

Table 1. Summary of wt.% U in salt as measured by various methods for Tests 1 and 2.

Data Source	Weight % U After Test # 1	Weight % U After Test #2
ICP-MS	0.18%	0.65%
ΔV Titrant	0.24%	nm
QMS	nm	1.52%
Change in rod mass	0.25%	0.89%

In agreement with Equation 2, the QMS did report ion current for H_2. But the QMS had not been calibrated for H_2, making it impossible to report concentration data for H_2. QMS ion current for H_2 is given in Figure 9.

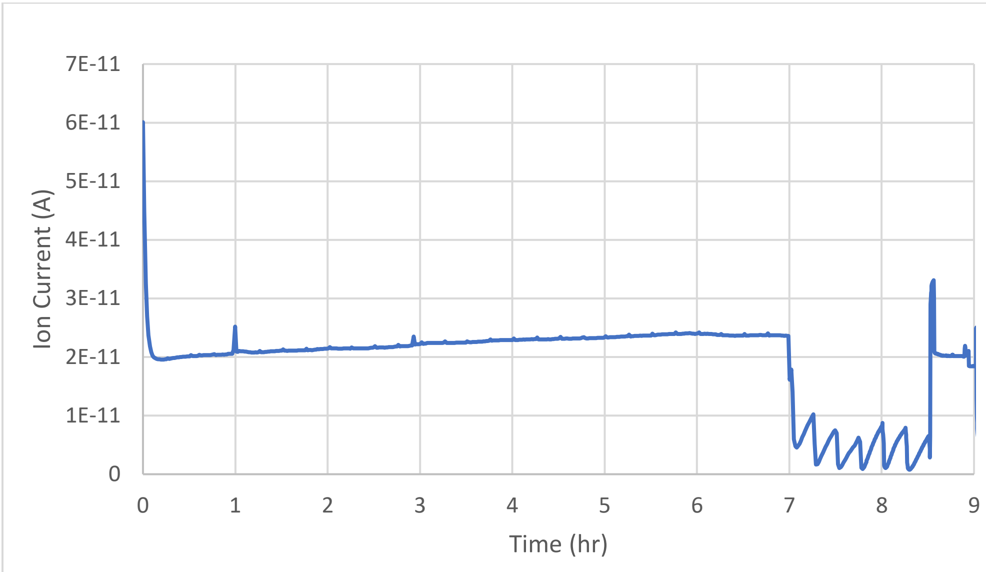

Fig. 9 QMS ion current of H_2 during Test #2.

The OCP of the salt after Test #2 stabilized at a value of -0.836 V versus Ag/AgCl which results in an activity ratio of UCl_4 to UCl_3 of $1.2x10^{-3}$ using Eq. (9). This indicates that again UCl_3 is the dominant uranium chloride formed in this reaction, though a relatively higher amount of UCl_4 is present after the longer duration run.

Conclusions

Uranium trichloride can be synthesized from uranium metal and hydrochloric gas while submerged in molten salt at 873 K. Starting with a depleted uranium rod submerged in equimolar NaCl-$CaCl_2$, 160 cc/min of 5% HCl gas was bubbled into the salt and reacted to produce 0.63 wt.% U in the form of UCl_3 dissolved in the base salt. The reaction produces H_2, supportive of a direct chlorination mechanism. With U metal remaining in contact with the salt, the UCl_3/UCl_4 ratio is extremely low ($1.2x10^{-3}$ to $5.9x10^{-5}$) as measured using an electrochemical open circuit potential measurement. The limiting step for this reaction may be diffusion in the salt phase or mass transfer to the U metal surface. Further study is needed to understand the kinetics of the reaction. But proven feasibility has been shown. This process has benefits over other synthesis methods for its simple hands-off set up and could be implemented into an actinide recycle scheme for a molten chloride fast reactor.

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