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Nuclear Energy and Fuel Cycle Division

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ABBREVIATIONS

FTIR	Fourier-transform infrared
SNF	spent nuclear fuel

EXECUTIVE SUMMARY

Chlorination of Zr alloy cladding with sulfur-chloride reagents is being considered as a means of separating the main metal from alloying elements, imbedded U, actinides, and fission and activation products to purify the Zr. This would allow the Zr to be disposed of as low-level nuclear waste or possibly be recycled. A multistage process was developed that involves several steps and waste streams. Recycling of sulfur-chloride reagents S_2Cl_2 and $SOCl_2$ is planned to minimize the waste stream. The generation of off-gas and entrainment of volatiles is anticipated to be minimized. However, given the complex nature of spent nuclear fuel (SNF), some volatile components will be generated, including the solvents themselves; Cl_2 used for the regeneration of S_2Cl_2; volatile fission product chlorides, such as Sb and ^3H; and chlorinated alloying components, such as Sn, Nb, Fe, and Mo.

This report discusses the chemical phenomena that might give rise to volatile species and their planned capture. The volatility of the transition metals will depend on their oxidation state and the compounds that are formed, such as Zr tritide. Loading radionuclides in the process off-gas will depend on the inputs to the process. For instance, processing separated Zr to reduce waste will have a much lower loading of radionuclides than if alternative chlorination were used for decladding SNF. Much of the volatile process streams will be part of the solvent recycling, which may involve online scrubbing. Generally, a caustic scrubber should be included in the off-gas to remove acidic vapors (e.g., Cl_2, $SOCl_2$).

The decontamination procedures for removing these species could involve pretreatment (i.e., heating) options or reduction by contact with H_2. This report discusses these options along with a framework for testing these alternatives in future experiments. Technologies for off-gas capture will leverage those developed in the Materials Recovery and Waste Forms program.

1. INTRODUCTION

Advanced chlorination using S_2Cl_2 and $SOCl_2$ has been proposed as a way to purify Zr from spent nuclear fuel (SNF) cladding, thus reducing the volume of high-level waste directed to a geological repository. Although the chemistry of chlorination has been studied (Vestal et al. 2022), the process involves several steps, including the recycling of the sulfur-chlorine solvents and reagents. Various off-gas waste streams will evolve during the process steps, and this report discusses how these might be handled. The extension of advanced chlorination to remove Zircaloy cladding from SNF components could increase the loading of volatile fission products in the off-gas, but this is less likely if the fuel matrix remains intact during the process.

2. ALTERNATIVE CHLORINATION

An alternative chlorination process is being considered to recycle Zr from spent fuel cladding. One advantage of this process is its ability to reduce the volume of waste going to a high-level repository by up to 50% (Bruffey et al. 2021). In a different scenario, advanced chlorination could replace gaseous chlorination agents HCl(g) or Cl_2(g) in the Zircex processing of SNF. The background and rationale of solvent-based chlorination was outlined in Bruffey et al. (2021).

Chlorinated S-based solvents were investigated for the alternative process, allowing the operation at relatively lower temperatures of <150°C. Both S_2Cl_2 and $SOCl_2$ were considered. Details on the chemistry of the chlorination of the metals, alloying components, and selected impurities were discussed in a separate manuscript submitted for publication (Vestal et al. 2022). A flowchart for using these reagents in Zr recovery is provided in Figure 1. Process expansion as a front-end for Zircex is shown in Figure 2.

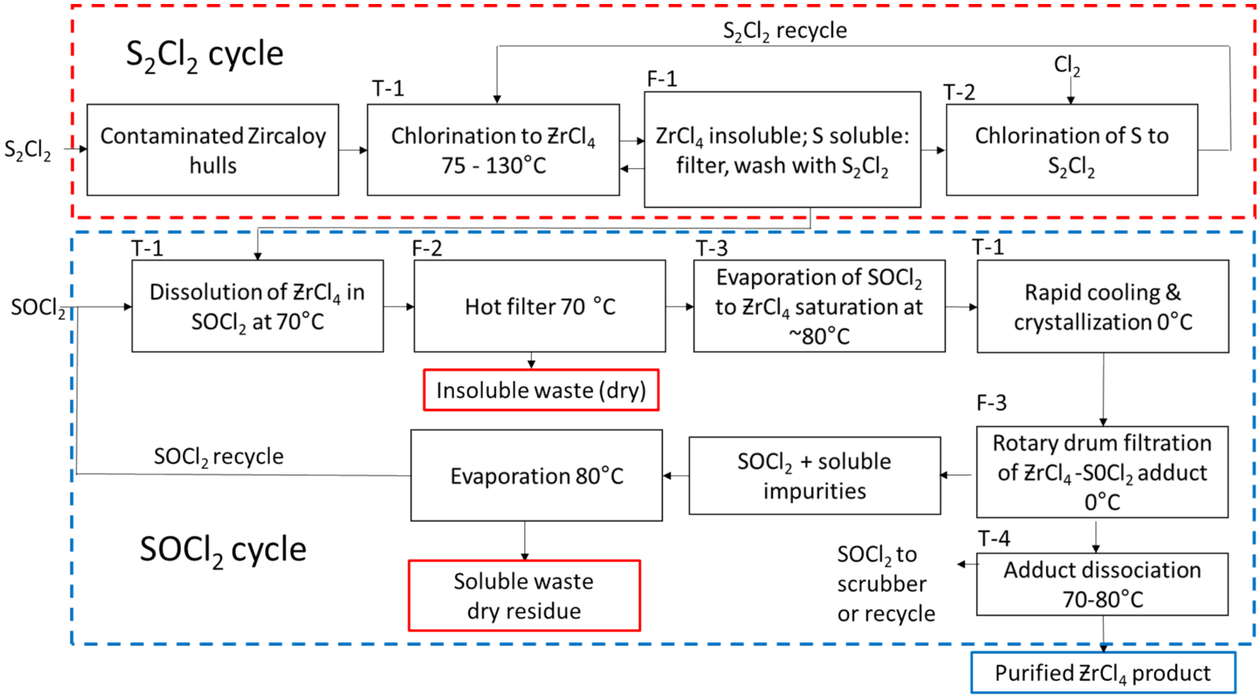

Figure 1. Flow sheet for Zr purification using the advanced chlorination process.
From McFarlane et al. (2022).

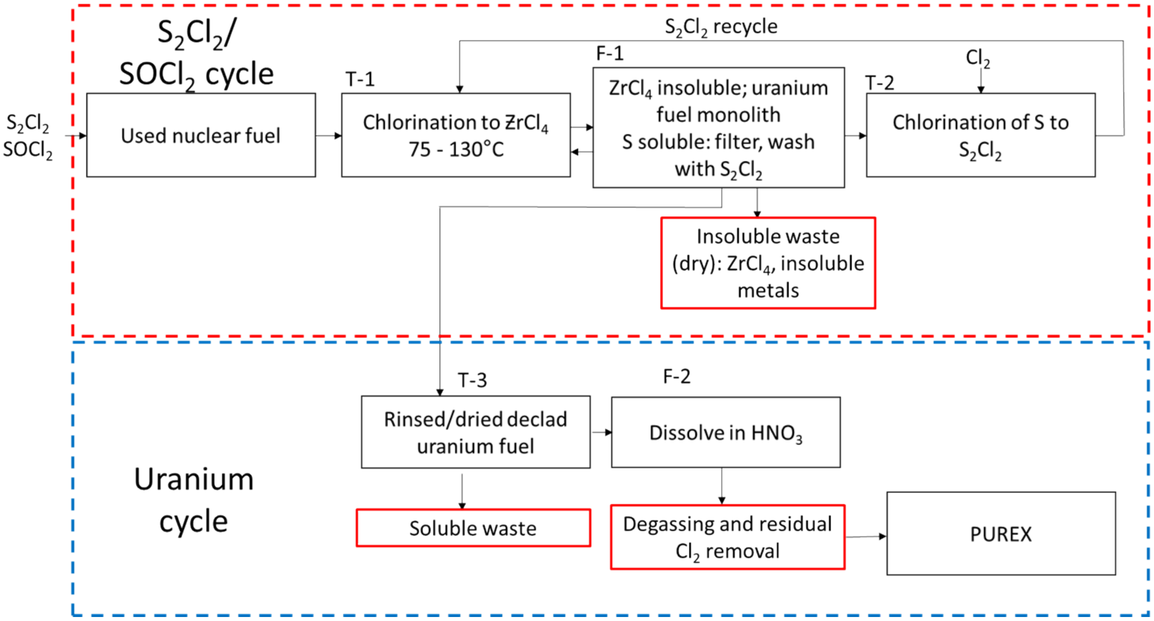

Figure 2. Advanced chlorination for decladding of used nuclear fuel. If Zr recovery is desired, then the $SOCl_2$ process from Figure 1 must be added. From McFarlane et al. (2022).

These flow diagrams provide context for the discussion of the off-gas from the processing of spent cladding or spent fuel. The process investigated to date has focused on Zr chlorination in the presence of alloying metals. (Barnes et al. 2021) Chlorination using S_2Cl_2 and $SOCl_2$ were both tested, and the former showed preferable kinetics. Sulfur monochloride chlorinated Zircaloy at 135°C with no gas production. Earlier tests with $SOCl_2$ showed the evolution of SO_2 in the chlorination process, which was expected from the stoichiometry. The $SnCl_4$ from the Zircaloy will be trapped within the S_2Cl_2 that is removed from the crude $ZrCl_4$. In further tests, other fission products may be found; however, that has yet to be determined.

To purify the $ZrCl_4$, $SOCl_2$ is added to dissolve the crude $ZrCl_4$, and after adding $SOCl_2$, the solution is filtered to remove impurities. After crystallization with the $ZrCl_4$ from $SOCl_2$, the $SOCl_2$ is removed via roughing pump and heating. At this stage, no new components are likely to be volatilized and trapped with the $SOCl_2$ because this is only a purification step to remove solid impurities. Product purity was assessed by inductively coupled plasma mass spectrometry.

The project will continue with the investigation of Al chlorination. Preliminary experiments show that this process is highly exothermic, so it will be performed at lower temperatures than Zircaloy because the kinetics are highly favorable. To further slow the kinetics, a mixed S_2Cl_2-$SOCl_2$ solvent may be used for the first chlorination step.

2.1 NONVOLATILE ELEMENTS IN SOLID WASTE STREAMS

Many metals associated with SNF are expected to either not chlorinate in S_2Cl_2 or, if chlorinated, form an insoluble product. Cerium oxide, CeO_2, was tested in the process and did not react or solubilize in S_2Cl_2 or $SOCl_2$ (Vestal et al. 2022). Experiments with UO_2 showed the same unreactive behavior. (Barnes 2022) If chlorinated, some elements (e.g., Fe, Nb, Cs) will follow the $ZrCl_4$ into solution with $SOCl_2$. However, the $ZrCl_4$ can be purified by recrystallization to a very high purity. Most of the purified $ZrCl_4$(s) will be filtered from the other soluble chlorides remaining in the solvent $SOCl_2$. The $SOCl_2$-soluble impurities will be collected after solvent distillation in the $SOCl_2$ regeneration cycle.

3. OFF-GAS COMPOSITION AND CAPTURE TECHNOLOGIES

3.1 RESIDUAL SOLVENTS, CHLORINE, AND SO_2

The process plans to recycle both streams of solvents S_2Cl_2 and $SOCl_2$ from the process. During chlorination with S_2Cl_2, S is generated. The S can be recycled once the product solids are removed by bubbling Cl_2 through the reactor. Thus, the off-gas will include a mixture of Cl_2 and S_2Cl_2 and potentially volatile fission products or contaminants, such as $SnCl_4$. The amount of Cl_2 may be minimal if the reaction to reform S_2Cl_2 goes to completion in the reaction vessel with 100% yield, as was observed for bench-scale operation. Contaminants that were not chlorinated with S_2Cl_2 could be chlorinated during the addition of Cl_2. For instance, the chlorination of Fe to $FeCl_3$ and Nb to a volatile $NbOCl_3$ species will be investigated. The S_2Cl_2 will be removed from the precipitated $ZrCl_4$ for recycling. In the laboratory, this is performed with a roughing pump, heating the reactor as it is being evacuated through a cold trap.

Using $SOCl_2$ liberated S_2Cl_2 and SO_2 during the chlorination process. These gases were condensed and captured in a NaOH(aq) trap. Although $SOCl_2$ was abandoned as a reagent for Zr chlorination, it will be tested as a diluent for Al chlorination. The byproduct of using $SOCl_2$ during chlorination is SO_2. Desulfurization is a well-researched topic, and limestone-based wet scrubbing is the most prevalent method for flue gases (Srivastava et al. 2001). The output of the desulfurization can be waste or recycled SO_2, depending on the process. Selective and nonselective catalytic reduction are commonly used, forming a soluble SO_3^{2-} species. Novel reducing nanomaterials were also considered, but the benefits are better realized for SO_2/NO_2 mixtures (Ali et al. 2021).

After recrystallization, the $SOCl_2$ may be contaminated with residual chlorides and must be distilled before reuse. So, as shown in Figures 1 and 2, additional separation steps may be needed to control the transport of Cl_2 and removal of semivolatile fission products from the $ZrCl_4$.

If U or UO_2 is the desired product, a washing and drying step will ensure the removal of residual S and Cl. The headspaces from these processes will be connected to an off-gas to ensure that residual vapors are trapped before being released to the atmosphere.

3.2 RELEASE OF VOLATILE AND SEMIVOLATILE RADIONUCLIDES

Loading radionuclides in the off-gas system will depend greatly on the feed to the advanced chlorination process.

During the use of the advanced chlorination process to dissolve, recover, and purify the valuable nuclear-grade Zr, the feed will be the separated Zr alloy cladding, and the total impurities to be removed will be only 2–3% of the feed mass with most of the mass being the alloying agents—mainly Sn and/or Nb with minor amounts of Fe, Cr, and possibly Mo. The imbedded radioactive impurities are expected to be primarily U by mass with concentration of <100 ug/g Zr. However, the imbedded fission products—mainly ^{125}Sb, ^{137}Cs, and, to a lesser extent, lanthanide radionuclides—are the primary radioactive impurities. However, in claddings in which Nb is the main alloy, activation product ^{94}Nb is a major radioactive constituent. Up to 50% of the ^{3}H in the spent fuel may be contained in the cladding in the form of Zr tritide. (Rudisill 2009) The off-gas components that must be trapped before the gas is released to the environment will be small portions of the sulfur chloride solvent Cl_2 used to convert byproduct S to S_2Cl_2, all the ^{3}H perhaps as TCl, and small amounts of $SnCl_4$, $SbCl_3$, $FeCl_3$, and Nb as $NbCl_5$ and/or $NbClO_3$. Of these, fission product ^{125}Sb and activation product ^{94}Nb in the form of one of the volatile Nb forms can emit strong radiation in the off-gas stream. Design of the off-gas treatment system must consider these possibilities, at least until hot tests using actual SNF cladding can be performed.

In the rare case in which Zr cladding chlorination is performed from intact fuel rods or assemblies, radioactive components of the spent fuel must also be considered in the design of the off-gas treatment system. However, when the spent fuel is in an oxide form, tests have indicated the fuel is not chlorinated and does not release its radioactive components.(Bruffey et al. 2021) Thus, the off-gas treatment system may be as simple as the system used when the feed is separated cladding.

If the feed is the metal alloy matrix, Zircaloy hulls, or Al cladding, the fuel components may be more susceptible to chlorination and release of significant amounts of radioactive components. No metal-form spent fuel has yet been available for tests to determine the radionuclides released to the off-gas treatment system, so the extent of this problem cannot be determined. Tests are being planned to apply off-gas technologies developed for fission product capture during oxidation to advanced chlorination.

3.3 CHLORINATION CHEMISTRY FROM PYROCHEMICAL STUDIES

For many fission products, few data are related to the advanced chlorination process; however, lessons from pyroprocessing UO_2 and metal matrix fuel in chloride melts may provide guidance (Berger and Benedict 2017). In LiCl-KCl at 500°C, chlorides are formed from transuranic elements, active metal fission products (e.g., Cs, Ba, Rb, Sr), and rare earth fission products. In these systems, the cladding (i.e., stainless steel) and the noble metal fission products (i.e., Zr, Mo, Ru, Pd, Tc, Te, Rh, Cd, Sn, Ag, Se, Sb, In, Ge, As, Nb) remain undissolved and can be separated and solidified to metal ingots as waste. One important difference between the two processes is that Zr remains metallic in an electro-refiner yet is readily converted to a chloride in the advanced chlorination process. Even if chlorinated in the advanced chlorination process, the so-called active metals will form CsCl (melting point of 645°C), $BaCl_2$ (melting point of 963°C), RbCl (melting point of 715°C), and $SrCl_2$ (melting point of 874°C), none of which are volatile under the conditions of advanced chlorination.

In an electro-refiner, the volatile species include Kr, Xe, I, Br, and ^3H. However, for the halides, the release is not 100% for metal fuels. For instance, about 20% of the I is released, and the rest remains in the salt based on data collected at Idaho National Laboratory. (Berger and Benedict 2011)The other gases are assumed to be retained within pores in the metal fuel until the system reaches the highest processing temperature. Thus, the timing of the release and the extent to which they are released are likely significantly different for the advanced chlorination vs. pyroprocessing. The descriptions of the chemical processes are very different. Pyroprocessing can be described adequately by chemical thermodynamics because the temperatures are high. Advanced chlorination is driven by chemical kinetics because the temperatures are much lower and the rate is sensitive to the surface area of the target metal. The particulate U metal alloys embedded in the metal matrix will be associated with a large increase in surface area as the matrix is chlorinated, even if the U alloy is not directly chlorinated.

4. TESTING OFF-GAS CAPTURE TECHNOLOGIES

4.1 OFF-GAS CAPTURE TECHNOLOGIES

Earlier work has used a caustic scrubber to remove acidic gases and volatile chlorides.(Vestal et al. 2022) In the case of intact fuel assemblies, the off-gas treatment system from advanced chlorination will be expected to capture released volatile fission products, such as Xe and Kr isotopes, as well as ^3H and I. Residual volatiles from fuel cleavage are expected to be released during the initial chlorination event, although the temperatures are relatively low (<130°C). The release of these materials and semivolatile species (e.g., Te, Ru, and Re, which is a surrogate for Tc) will be studied in the off-gas systems for the initial condensed phase chlorination with $S_2Cl_2/SOCl_2$ and during S rechlorination. The fission products that are likely to chlorinate will be the same as those observed in the hydrochlorination process—that is, with HCl(g) (McFarlane and Walker 2021).

The capture of I species and ^3H was investigated at Oak Ridge National Laboratory in earlier studies. (Greaney et al. 2020, Jubin et al. 2019). Silver mordenite was identified as an optimal trap for I species. Tritium capture on solid media was not complete, but it is amenable to capture in a water trap, forming HTO by ion exchange. The noble gases can be trapped on chilled charcoal beds or an existing technology, or separated and retained in metal-organic frameworks (Riley et al. 2020). Because the SNF being considered for recycle will be several years old, ^{85}Kr ($t_{1/2}$ = 10.76 years) is the noble gas isotope of concern. This isotope is also of value and can be used for US Department of Defense technologies.

4.2 INSTRUMENTATION OF LABORATORY EXPERIMENTS

To determine the effectiveness of off-gas scrubbing, several methods can be used for inline analysis and offline characterization. Online measurements will include monitoring pressure drop across the filters and scrubbers, ensuring that flow conditions are maintained. In these processes, temperatures will be close to ambient, so temperature measurement will not be required on the off-gas system. The reactors themselves will be instrumented with thermocouples, as specified by process requirements (e.g., monitoring the chlorination process that is exothermic or the distillation and purification of $SOCl_2$ that requires a constant 80°C). In the current program with surrogate fuels, spectroscopic measurements can be used to monitor the evolution of gases, such as I_2 or ICl, SO_2, and Cl_2. Online Fourier-transform infrared (FTIR) and Raman spectrometers are available for off-gas analysis, both of which are useful for many of the species that will be generated. Because the selection rules are different depending on the symmetry of the molecules being monitored, the utility of each device will vary. Raman is useful for homonuclear diatomics and heavily water-saturated systems but is a less sensitive method than FTIR.

Offline elemental analysis will include characterizing the solids and solutions produced for elemental composition, as well as molecular speciation by optical spectroscopy. Elemental composition will be measured by inductively coupled plasma emission or mass spectrometry, depending on the element being targeted. Neutron activation analysis is also available and is particularly useful for low-concentration elements. Solids may be characterized via powder x-ray diffraction to determine changes to crystal structure during reactions. The chlorination processes appear to occur at surfaces, so changes in surface area are expected to correlate with overall changes in composition as the reaction progresses. The access of grain boundaries to the reagents during the chlorination process may greatly affect the rates of reaction for the metal alloys and the fuel matrix and entrained fission products.

5. FUTURE WORK AND CONCLUSIONS

Characterization and treatment of off-gas streams will be an important aspect of testing the feasibility of the S chlorination process. The following questions will be addressed during future study.

- What volatile reagents or products arise from alloy chlorination and the recovery of S as S_2Cl_2? Will $SOCl_2$ be used in the initial chlorination step of Al, and does that result in the liberation of SO_2?
- Are alloying elements such as Fe, Nb, and Sn chlorinated, and if so, do they produce volatile species during the initial chlorination step, the rechlorination of the sulfur, or the recovery of $SOCl_2$?
- What is the expected input to the S chlorination process, cladding hulls, metal matrix, or matrixed fuel assembly, and how does that affect fission product loading in the process? What is a representative surrogate for metal alloy SNF?
- How do volatile and semi-volatile fission products react and transport through the steps in the advanced chlorination process?

- What are the best ways to characterize the off-gas streams of the advanced chlorination process? Can data be gathered in real time? Can an accurate mass balance and an analysis of scrubber materials and solutions be obtained from feed characterization?

Ultimately, the goal will be to scale tests and work with actual cladding and matrix materials from SNF. These materials are available within the US Department of Energy complex. Understanding the disposition of radionuclides from advanced chlorination will be an important test of the feasibility of using advanced chlorination for recovery of nuclear-grade Zr or as a head-end process for recycling of metal-matrix SNF.

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