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To the Graduate Council:

I am submitting herewith a thesis written by Jennifer L. Ladd-Lively entitled "Separation of Fluoride Residue Arising from Fluoride Volatility Recovery of Uranium from Spent Nuclear Fuel." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

Robert M. Counce, Major Professor

We have read this thesis and recommend its acceptance:

Barry B. Spencer, Paul Bienkowski, Fred Weber

Accepted for the Council:

Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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Fred Weber

Acceptance for the Council:

Anne Mayhew

Vice Chancellor and

Dean of Graduate Studies

(Original signatures are on file with official student records.)

**SEPARATION OF FLUORIDE RESIDUE
ARISING FROM FLUORIDE VOLATILITY RECOVERY
OF URANIUM FROM SPENT NUCLEAR FUEL**

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Jennifer L. Ladd-Lively
May 2004

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Dedication

This thesis is dedicated to
my parents and my husband.

Acknowledgements

I wish to thank those people who helped to make this thesis research and graduate program possible. First, I would like to thank the United States Department of Energy (DOE) Nuclear Energy, Science and Technology Program who sponsors the Advanced Fuel Cycle Initiative University Fellowship Program, of which I am so fortunate to have been a part. I would like to thank Dr. Barry Spencer for his patience and his effort to help me more fully understand the nuclear fuel cycle. I would like to thank Dr. Robert Counce for his guidance and his insistence to write this thesis as I was doing the research. I would also like to thank Dr. Fred Weber and Dr. Paul Beinkowski for serving on my committee. I would like to thank Oak Ridge National Laboratory (ORNL) and the Nuclear Science and Technology Division (NSTD) for allowing me the opportunity to do my research there.

Abstract

The overall objective of this study was to support an alternative hybrid process to meet Advanced Fuel Cycle Initiative (AFCI) goals, using fluorination and aqueous processing techniques, for treatment of spent nuclear fuel (SNF). The specific goal was to develop a simple aqueous dissolution process to separate two high-heat fission products, cesium and strontium, from SNF fluoride residues. This separation study was based on solubility differences examined by modeling using the HSC Chemistry 5.0 and OLI Stream Analyzer 1.2 programs. HSC automatically utilizes an extensive thermochemical database, which contains enthalpy (H), entropy (S), and heat capacity (Cp) data for more than 17,000 chemical compounds. The OLI Stream Analyzer 1.2 program is the result of over 30 years of effort and represents the state-of-the-art technology in aqueous solution simulation. The work focused on the fluoride residues from the voloxidation and fluorination steps of the fluoride volatility process and was limited to SNF from commercial light-water reactors. Material balances were used to estimate the quantity of residue. A representative SNF was considered to be one with a burnup of 33,000 megawatt days per metric tonne initial heavy metal (MWd/MTIHM) after a 10-year cooling period, from a pressurized-water reactor (PWR). The dry fluorination method was used for uranium removal. The work described in this paper was based solely on computer modeling, which may serve as the basis for any necessary follow-on laboratory validation experiments. Observations from this study showed that the separation of fluoride residues by a simplified, alternative aqueous process is practical. The simulated process could be carried out at 1 atm and 30-50°C. The OLI model showed separation of cesium and strontium was possible with only one dissolution with water, whereas the HSC model indicated two dissolutions would be required. Plutonium and Np were removed together, which would maintain proliferation resistance. Because this research was based on computer modeling, follow-on laboratory experiments are necessary to validate the results and to improve the process flow diagram. Further development of the process flow diagram, with equipment design and cost estimation, is also recommended.

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1. Introduction and Background

Over the last fifty years, the principle reason for reprocessing has been to recover unused uranium and plutonium from spent nuclear fuel (SNF) elements. A secondary reason for reprocessing has been to reduce the amount of material to be disposed of as high-level waste and to create a more stable form of the material. For environmental and economic reasons, it is desirable to reduce the number and volume of waste streams from nuclear fuel processing operations (Arm et al., 1998). The development of advanced reprocessing technology should be planned to achieve economy, nonproliferation, and reduction of radioactive wastes at the same time (Hoshikawa et al., 1998). Currently in the United States, the motivation for reprocessing of civilian SNF is to extend the lifetime of the repository as a measure to reduce the life-cycle costs of nuclear electricity production.

A great deal of reprocessing has occurred since the 1940s, mainly for military purposes, to recover plutonium for weapons. The reprocessing of irradiated nuclear fuel to recover uranium and plutonium is a well-established and successful technology, with a number of large plants operating throughout the world. Light Water Reactor (LWR) SNF is currently reprocessed in France, the United Kingdom, Russia, and Japan. All commercial reprocessing plants currently use the well-proven Plutonium-Uranium Extraction (PUREX) process (Tomiyasu and Asano, 1995). Reprocessing to recover uranium and plutonium avoids the waste of a valuable resource because most of the spent fuel can be recovered and recycled. Removal of plutonium from SNF decreases the long-term proliferation risk. However, there are important pressures on the operators of reprocessing plants, which lead to a continuing need for technological development both for the improvement of the performance of existing plants and for advanced concepts for the next generation of plants (Arm et al., 1998). The first of these pressures is economic and the second arises from environmental considerations. The current method of reprocessing reduces the volume of high-level waste for disposal, but it creates significant volumes of low and intermediate level waste.

Recently, interest has grown in separating individual radionuclides from SNF reprocessing waste to (1) reduce long-term radiotoxicity in residual wastes, (2) support transmutation of long-lived radionuclides into shorter-lived or stable isotopes, and (3) improve repository heat management. The management of vitrified high-activity waste arising from the reprocessing of SNF is often made questionable by the existence of long-lived radionuclides: especially the minor actinides and certain fission products (Madic et al., 2002). The elimination of these radionuclides from commercial SNF intended for disposal in a mined repository has a significant positive effect on the overall performance of the repository (Laidler, 2000; Laidler et al., 2001). The main radionuclides targeted for separation are the actinides: Np, Am, and Cm (along with U and Pu) and the fission products: I, Tc, Cs, and Sr. Removal of the later two significantly reduces the heat load of the residual conditioned wastes. Strontium⁹⁰ and ¹³⁷Cs, both short-half-life fission products (<300 years), almost completely determine the total toxicity and heat generation of the fission product nuclides (Sagara et al., 2002). High-activity wastes, which contains minor actinides (Np, Am, Cm, and higher actinides) and fission products arising from the reprocessing of spent fuels, are currently being immobilized in a glass matrix for subsequent disposal in a deep underground repository (Madic et al., 2002).

Better decontamination from fission products, new methods for uranium-plutonium partitioning, and removal of actinides from high activity waste are challenging areas in process chemistry (Sood and Patil, 1996). Spent fuel-reprocessing helps in the isolation of plutonium and unused uranium from highly radioactive fission products. SNF reprocessing also helps in recycle of Pu and U for nuclear power production. Recycle of neptunium with plutonium is thought to be beneficial because this leads to a build-up of ²³⁸Pu, which increases the proliferation resistance. Fuel reprocessing also enables proper management of radioactive waste.

Currently, there is interest in treatment of SNF to extend the life of the geological repository and reduce the need for a second repository. In addition, it is desired that the cost of processing SNF be reduced. In 2001, the total costs for a geological repository at Yucca Mountain for the disposal of SNF and high-level radioactive waste was estimated to be between \$42.8 billion and \$57.1 billion (DOE, 2002). Such a costly endeavor

provides incentive to more seriously consider techniques that would extend the life of the repository, if not completely avoid the need for additional repositories in the future. At current production rates and without reprocessing of SNF, the SNF inventory will reach the statutory capacity of the Yucca Mountain Repository before the year 2010 (DOE, 1996). Separation of SNF into various components offers a way to extend the life of the repository. For example, uranium could be removed to reduce the mass of SNF, and cesium and strontium could be removed to reduce the short-term heat load on the repository. Additional products could also be recovered for use as fuels (U, Pu, and Np) or for transmutation (Am, Cm, I, and Tc).

The goals of the Advanced Fuel Cycle Initiative (AFCI) are outlined in the Report to Congress (DOE, 2003). The first goal of the AFCI is to process SNF in order to reduce the volume of waste requiring repository disposal. This is accomplished by separation of the SNF into its main components. Spent fuel from commercial light-water reactors (LWRs) is approximately 96% uranium, 1% plutonium, and 3% fission products. Separation permits the removal of uranium, which would greatly reduce the mass of SNF. Separation of cesium and strontium reduces the short-term heat load on the repository. Plutonium, Am, and Cm are long-term heat generators, which provides an incentive for separation and burning or transmutation. The second goal of the AFCI is to separate long-lived, highly toxic elements such as plutonium for mixed oxide (MOX) fuels and americium and curium for transmutation. A third goal is to reclaim the valuable energy reserves of SNF. This might be accomplished by re-enriching the recovered, depleted uranium and by using the recovered plutonium and neptunium in MOX fuels. Finally, the AFCI strives to accomplish the goals discussed above in a proliferation-resistant manner. This may be accomplished by co-processing plutonium and neptunium, therefore, avoiding separation of purified plutonium.

Traditional reprocessing methods require high temperatures, acidic conditions, and organic solvents, which increase the volume and variety of wastes that must be disposed of as low-level or intermediate wastes. The wastes contain phosphates from the solvents, which potentially limit the amount of radionuclides that can be vitrified. A simplified and less costly reprocessing technique is desired.

1.1 Objectives

The overall objective of this work was to support an alternative hybrid process to meet the AFCI goals using fluorination and aqueous processing techniques for treatment of SNF. The specific goal was to develop a simple aqueous process for partitioning the residue from the fluorination stage of the fluoride volatility process. The work was designed to examine the separation of high-heat fission products from fluoride residues using simple dissolution methods. This separation study was based on estimates of solubility differences predicted by computer simulations. The remainder of the residue was considered either a waste or potential intermediate for further processing to recover Pu/Np and/or Am/Cm.

The volume of SNF may be reduced by the removal of uranium via fluorination. Plutonium, neptunium, americium, and curium may be separated from the fluoride residues. Uranium might be re-enriched and recycled as fuel, and Pu/Np might be used as MOX fuel, both of which would recover the economic value of the fuel. Finally, all of this may be accomplished in a proliferation resistant manner by keeping Pu/Np together as a combined stream.

Conceptual process flow diagrams for the processing of SNF and the separation of fluoride residues is shown in Figures 1.1 and 1.2. Figure 1.1 shows the treatment of SNF from disassembly through fluorination. The fuel rods are disassembled and decladded. The hardware goes to additional processing or disposal, while the SNF enters a voloxidizer. In the voloxidation process, air and/or oxygen are used to convert the components of the SNF to oxides. Volatile oxides are treated as needed and non-volatile oxides are sent to fluorination where fluorine gas is used to convert the oxides to fluorides. Volatile fluorides, comprised mainly of UF_6 , are sent to uranium clean-up and recovery. The non-volatile fluoride residues are treated using aqueous separations. Figure 1.2 shows a conceptual process for the aqueous separation of fluoride residues. The dashed line encompasses the steps upon which this study focused. First, the residues

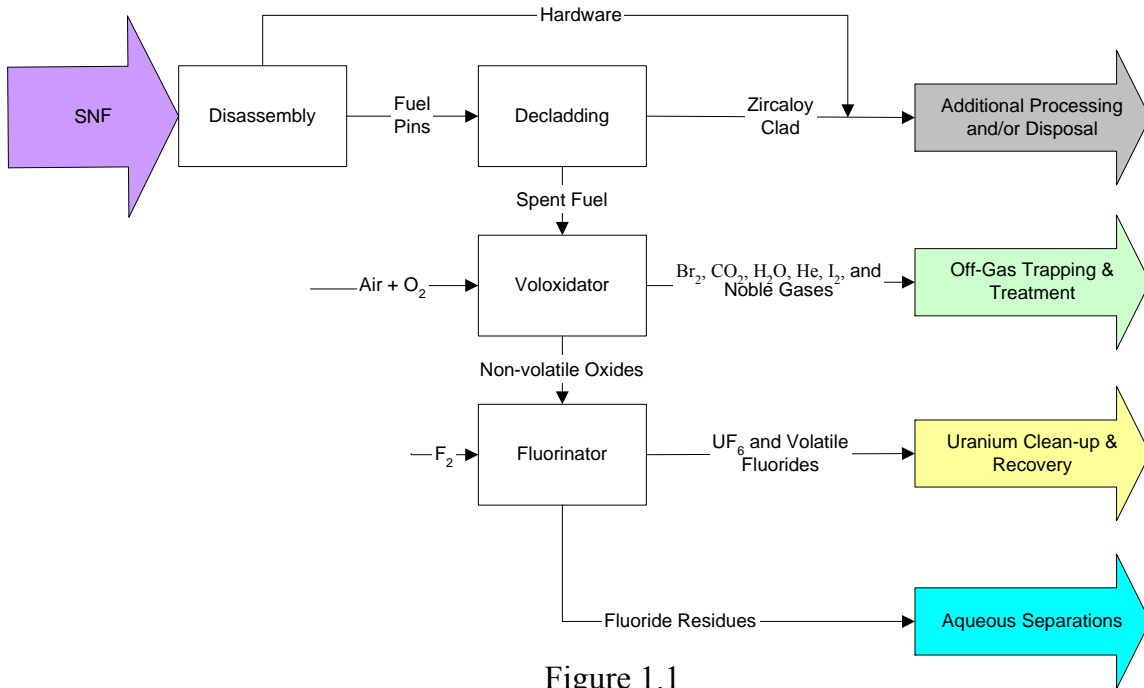


Figure 1.1
 Flow Diagram for Processing
 of SNF, Leading to Aqueous
 Separation of Fluoride Residues

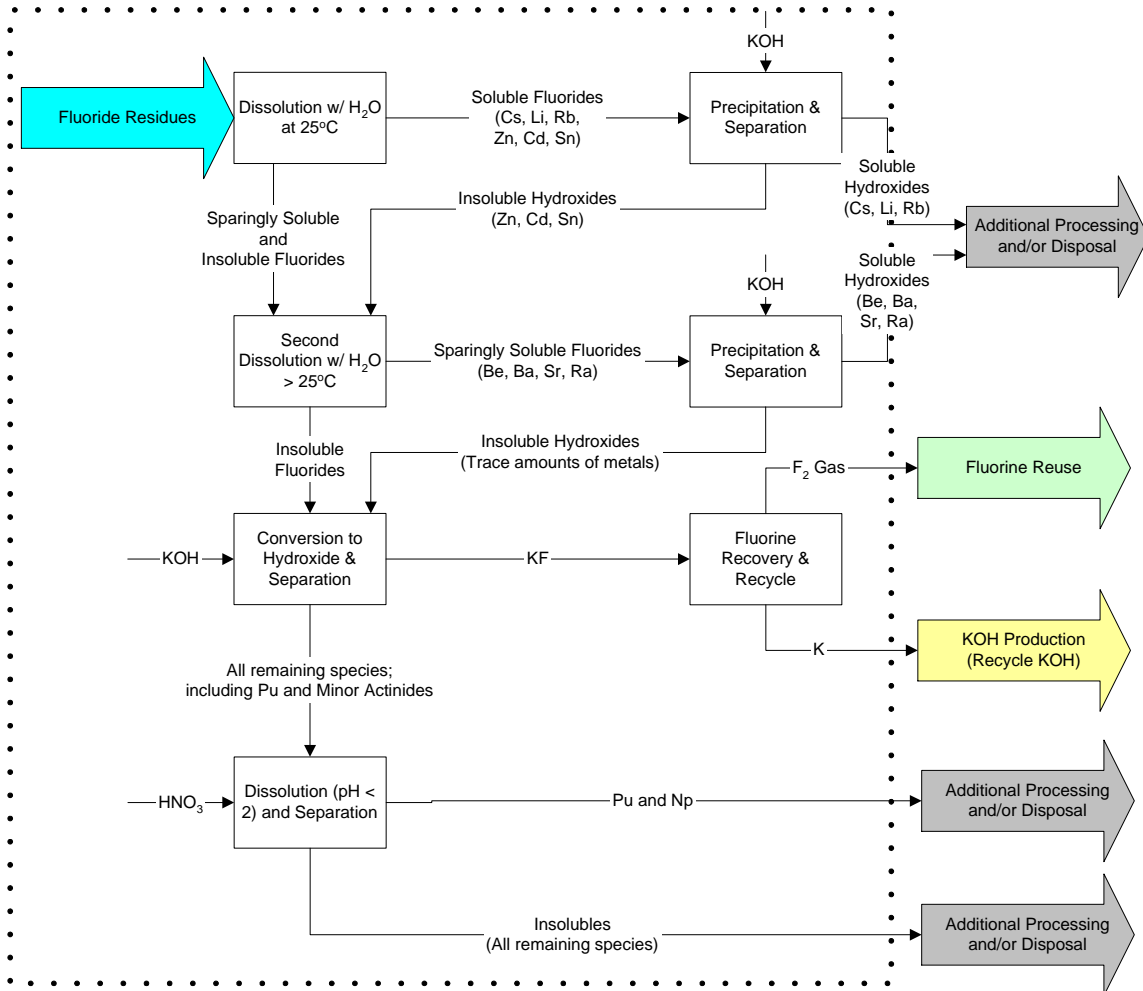


Figure 1.2
 Conceptual Flow Sheet of
 Aqueous Separation of Fluoride
 Residues

are treated with water to remove soluble fluorides. These soluble fluorides are treated with KOH to remove impurities, such as those portions of actinide fluorides that solublize. The soluble hydroxides are sent for additional processing as necessary. The insoluble fluorides are treated a second time with water, and the soluble fluorides from this treatment are also treated with KOH. The second water treatment is necessary due to the common ion effect of CsF and SrF₂ interactions. The highly soluble CsF causes SrF₂, a sparingly soluble species, to be less soluble. These soluble hydroxides are sent for additional processing as needed. Potassium hydroxide is added to the insoluble fluorides. Potassium fluoride is eventually sent to fluorine recovery and recycle. Fluorine and potassium are assumed to be recovered by known process techniques. The fluorine gas is reused in the fluorinator, while the potassium is used in KOH production. Any remaining insoluble species are acidified with HNO₃ and then sent for additional processing and disposal.

1.2 Scope

The present work was a study of the selective dissolution of fluorides remaining from the fluoride volatility process. The work focused on the fluoride residues from the preceding voloxidation and fluorination steps of the fluoride volatility process, as shown in Figure 1.2, and was limited to a representative SNF system from a pressurized-water reactor (PWR) with an average fuel burnup of 33,000 megawatt days per metric tonne initial heavy metal (MWd/MTIHM) and a 10-year cooling period. This particular fuel was a reasonable representative fuel based on current inventories of SNF. Most commercial reactors are PWR and the selected burnup is typical of these reactors. All spent fuel is cooled at least 5 years. The longer SNF is allowed to cool; the less radioactive material remains due to decay. Short-term heat producing radionuclides have decayed by at least one half-life in fuel that has been cooled for more than 30 years. The majority of SNF currently in inventory has been cooled for more than 10 years. Material balances were used to estimate the quantity of residue. The dry fluorination method was used for uranium removal. The work described in this paper was based solely on

computer modeling, which may serve as the basis for any necessary follow-on laboratory validation experiments.

1.3 Roadmap

In order to complete this work, much information and analysis were needed. First, the conceptual flow sheets were needed to determine where to begin and on which steps to focus the study. Next, the composition of SNF fed into the process, shown in Figure 1.1, had to be determined (refer to Section 3.2.1). The output of each stage of the process in Figure 1.1 had to be determined using material balances and the HSC Predominance Module. The volatile species from each step were determined based on the literature values for boiling point (refer to Table 3.1). After the material balances were completed, the composition of the fluoride residue solids fed into the process, shown in Figure 1.2, was known. Information about the solubility (refer to Section 2.3) and the stability of the fluorides in water (refer to Section 3.2.2) was needed. Finally, each stage of Figure 1.2 was studied and the flow sheet was updated to reflect the results. A final process flow sheet was developed (refer to Figure 4.7).

2. Literature Review and Analysis

2.1 Nuclear Fuel Cycle and Current Reprocessing Methods

Nuclear power is a significant component of the world's energy supply. About 17% of total world electricity production comes from nuclear power (Purushotham et al., 2000). The nuclear fuel cycle is the series of industrial processes, which involve the production of electricity from uranium in nuclear power plants. The activities associated with the nuclear fuel cycle include: uranium mining and milling, conversion of U_3O_8 to gaseous UF_6 , enrichment in the ^{235}U isotope, conversion of UF_6 to UO_2 , fuel fabrication, energy production, spent fuel storage, and finally direct disposal or reprocessing and recycling of the spent fuel. Each step is discussed below:

1. Mining and Milling - Uranium is usually mined by either surface (open cut) or underground mining techniques, depending on the depth at which the ore body is found. The mined uranium ore is sent to a mill which is usually located near the mine. At the mill, the ore is crushed and ground to a fine powder, which is leached in sulfuric acid and an oxidizing reagent to allow the separation of uranium from the waste rock. In the solvent extraction step, the uranium is purified and concentrated. The uranium product is precipitated with ammonia and transferred as a slurry. The slurry is thickened and centrifuged. The concentrate is calcined and pulverized. The final product is uranium oxide (U_3O_8) concentrate, known as "yellowcake".
2. Conversion - Uranium needs to be in the form of a gas before it can be enriched, therefore U_3O_8 is converted into gaseous uranium hexafluoride (UF_6) at a conversion plant. This conversion is accomplished by the dry hydrofluor method. The dry hydrofluor method processes the concentrates directly in a succession of fluidized-bed reactors followed by fractional distillation.
3. Enrichment - The vast majority of all nuclear power reactors in operation and under construction require enriched uranium fuel in which the content of the ^{235}U isotope has been raised from the natural level of 0.7% to approximately 3.5% or

higher. The enrichment process removes 85% of the ^{238}U by separating gaseous uranium hexafluoride into two streams. One stream is enriched to the required level and then passes to the next stage of the fuel cycle. The other stream is depleted in ^{235}U and is called “tails”. The first enrichment plants were built in the U.S. and used the gaseous diffusion process, but more modern plants mostly use the centrifugal process. Centrifugal processing has the advantage of using much less power per unit of enrichment and can be built in smaller, more economic units.

4. Fuel Fabrication - Enriched UF_6 is transported to a fuel fabrication plant where it is converted to uranium dioxide (UO_2) powder and pressed into small pellets. These pellets are inserted into thin tubes, usually of a zirconium alloy (Zircaloy), to form fuel rods. The rods are then sealed and assembled in clusters to form fuel elements or assemblies for use in the core of the nuclear reactor.
5. Energy Production - Several hundred fuel assemblies make up the core of a reactor. Roddy et al (1985) discusses in detail the mechanical design parameters of fuel assemblies. In the reactor core the ^{235}U isotope fissions, producing heat in a continuous process called a chain reaction. The process is moderated using water and is fully controlled. Some of the ^{238}U in the reactor core is transmuted to plutonium and about half the plutonium also fissions, providing about one third of the reactor's energy output. As in fossil-fuel burning power plants, the heat is used to produce steam to drive a turbine and an electric generator. To maintain efficient nuclear reactor performance, about one-third of the spent fuel is removed every year and replaced with fresh fuel.
6. Spent Fuel Storage - Fuel discharged from nuclear reactors contains appreciable quantities of unburned fissile uranium and plutonium fuel. Spent fuel assemblies are highly radioactive and give off thermal energy due mainly to decay of fission products. These assemblies are stored in cooling pools which are typically located at the reactor site, to allow both heat and radioactivity to decrease. The water in the pools serves the dual purpose of acting as a barrier against radiation and dispersing the heat from the spent fuel. Spent fuel can be stored safely in the

cooling pools for long periods. However, storage is intended only as an interim step before the spent fuel is either reprocessed or sent to final disposal. The longer spent fuel is stored, the easier it is to handle, due to decay of short-lived radioisotopes. There are two disposition alternatives for spent fuel: reprocessing to recover the usable portion or long-term storage and final disposal without reprocessing.

7. **Reprocessing and Vitrification** - Spent fuel still contains approximately 96% of its original uranium, of which the fissionable ^{235}U content has been reduced to less than 1%. Approximately 3% of spent fuel comprises waste products and the remaining 1% is plutonium produced while the fuel was in the reactor. Reprocessing to separate uranium and plutonium from waste products (and from the fuel assembly cladding) begins by chopping up the fuel rods and dissolving them in acid to separate the various materials. Recovered uranium can be recycled for conversion to uranium hexafluoride and subsequent re-enrichment. The reactor-grade plutonium can be blended with enriched uranium to produce a MOX fuel; this usually is completed in a fuel fabrication plant. The remaining 3% of high-level radioactive wastes can be stored in liquid form and subsequently solidified. After reprocessing, the liquid high-level waste is usually calcined to produce a dry powder which is incorporated into borosilicate (Pyrex) glass to immobilize the waste. If spent fuel is not reprocessed, it will contain all the highly radioactive isotopes, and then the entire fuel assembly is treated as high-level waste (HWL).
8. **Final Disposal** - The waste forms envisioned for disposal are vitrified high-level wastes sealed into stainless steel canisters or spent fuel rods encapsulated in corrosion-resistant metals such as copper or stainless steel. The most widely accepted plans are for these wastes to be buried in stable rock structures deep underground. Many geological formations such as granite, volcanic tuff, salt or shale are suitable disposal environments.

The Nuclear Fuel Cycle is well known and discussed in detail by Benedict et al (1981), Cochran et al (1990), and Moghissi et al (1992).

The treatment of SNF from storage to disposal includes mechanical and chemical processes to prepare the SNF for final disposal. SNF discharged from commercial LWRs is a reasonably homogeneous collection of oxide fuel in zirconium alloy cladding (Laidler, 2000; Laidler et al., 2001). The fuel assemblies are first sent through a disassembly and shearing process, where the cladding may also be removed. The cladding could be sent to a metal decontamination process, and then it would be disposed of or recycled. The sheared fuel rods or declad pellets are burned in air and/or oxygen in a voloxidation step, which is not necessary if the material is to be disposed of without separation. Volatiles from voloxidation are sent to off-gas treatment. These volatiles include: H, He, C, Br, Kr, Xe, I, and possibly Se and Ru. Separation of the oxide powders and cladding are performed if the cladding had not been removed prior to voloxidation. The oxide powder is sent to an optional crushing and grinding step if necessary. At this point, the powder could be further prepared for disposal by vitrification, or it could be reprocessed to separate actinides, high-heat fission products (Sr and Cs) and low-heat fission products (all the remaining radionuclides) (Forsberg, 2000). Separation of actinides reduces the heat load on the repository. Once separated, high-heat fission products, cesium and strontium, could be allowed to cool outside in pools prior to being moved inside the repository. Low-heat fission products are ready for repository disposal upon separation and appropriate packaging.

Currently, all commercial reprocessing plants use the well-proven PUREX process (Tomiyasu and Asano, 1995). The PUREX process is a solvent extraction process using tri-n-butyl phosphate (TBP) as the organic extractant. It produces an excellent separation of plutonium and uranium, with decontamination factors as high as 10^7 and recovery efficiencies for uranium and plutonium on the order of 99.9% (Laidler, 2000; Laidler et al., 2001). However, fission products and the minor transuranic elements (Np, Am, and Cm) are not normally recovered. The main steps in reprocessing are the following: fuel elements are sheared to expose the fuel material for subsequent leaching in hot nitric acid. The hulls from the cladding that are not dissolved are

removed. The result is an acid solution that contains a mixture of plutonium, uranium, transuranics, and fission products. The plutonium and the uranium are extracted together from that solution by using an organic solvent, nominally 30% TBP in n-dodecane. The result is an organic solution containing the majority of the plutonium and uranium. Fission products and other transuranics remain in the aqueous solution and are directed to high-level waste immobilization processes, such as vitrification. Usually plutonium and uranium are recovered separately from the organic stream using valence adjustment to achieve selective stripping. The plutonium in the form of plutonium nitrate is purified by extraction and liquid-liquid re-extraction, and is concentrated by evaporation. It is then precipitated from solution in the form of oxalate. The oxalate can be converted into metal or into plutonium oxide. For the metal, the plutonium oxalate is calcined, and fluorination is carried out by means of gaseous hydrofluoric acid (HF). Then, the fluoride is reduced using calcium (calciothermy). For the oxide, the oxalate is filtered, evaporated to dryness, and then calcined. Plutonium oxide (PuO_2), the preferred form, is recycled to fuel fabrication plants for MOX fuels. The uranium in the form of uranyl nitrate is purified by liquid-liquid extraction in several stages to eliminate the fission products, and the solution is concentrated after each stage. Uranium hexafluoride (UF_6) is produced from the uranyl nitrate solvent extraction product for recycle to fuel fabrication plants. Sood and Patil (1996), Benedict et al (1981), Cochran et al (1990), and Moghissi et al (1992) discuss the PUREX process in detail.

Conventional aqueous reprocessing of spent fuels has been carried out for several years in France and the United Kingdom, using updated versions of the PUREX process developed initially in the U.S. for production of defense materials (Laidler, 2000). Although the PUREX process has been developed and applied to commercial reprocessing plants for over 40 years, there remain some significant unsolved disadvantages such as generation of a great amount of waste and the utilization of large-scale extraction equipment (Wei et al., 2002). There are many problems associated with the PUREX process, including: dissolution of UO_2 fuel which occurs under severe conditions, such as dissolution in HNO_3 at nearly boiling temperatures; use of organic solvents which present a potential danger of explosion, and the degraded solvent must be

incinerated which produces contaminated phosphate waste; combining hazardous minor actinide elements (Np, Am, and Cm) and strongly radioactive elements (Sr and Cs) into high-level waste solutions; and production of a large quantity of wastes, particularly nitrate and phosphorus compounds (Tomiyasu and Asano, 1995). The nitrates could be destroyed but the phosphates would persist. Most importantly, PUREX cannot easily separate Am/Cm or Cs/Sr which are all high-heat producers, and will therefore limit the usefulness of the repository. These materials can be separated with other selective organic extractants designed for that purpose, but that requires several extraction cascades using different chemical systems.

2.2 Reprocessing via Dry Fluoride Volatility

A number of research projects worldwide, from the 1950s to the 1980s, showed the potential of the fluoride volatility process for the partitioning of spent fuel components and the difficulty of getting pure MOX after separation for conventional fuel fabrication facilities (Fukasawa et al., 2001; Amano et al., 2001). Several countries had stopped development of fluoride volatility reprocessing methods by the late 1970s due to the difficulty of isolating pure plutonium (Fukasawa et al., 2001); however the inability to isolate plutonium can be turned into an advantage.

The fluorination process consists of the following steps: (1) fuel element decladding, (2) transformation of the fuel to an oxide powder, (3) fluorination of the fuel, (4) separation of uranium and plutonium fluorides, and (5) purification of the products obtained (Uhlir, 1989). The fluorination process is discussed in detail by Benedict et al (1981), Steindler et al (1969), Jonke et al (1965), and Schmets et al (1970). In the fluoride volatility process, uranium is easily purified by a simple procedure because of the marked difference in chemical properties of the fluorides of uranium and the fission products (Kamoshida et al., 2000). Therefore, the fluoride volatility process could readily remove uranium from the spent fuel as UF_6 (Amano et al., 2001; Sood and Patil, 1996). In the past, recovery of plutonium was fraught with problems due to the instability of PuF_6 at process temperatures and radiation fields (Sood and Patil, 1996).

Kamoshida et al (2000) discusses a new reprocessing method using an improved fluoride volatility process, where uranium and plutonium are not separated together.

Compared to the PUREX process, the dry fluorination process presents certain advantages, such as a smaller volume of waste and the absence of liquid wastes. Fluorination eliminates the need to convert uranyl nitrate to UF_6 since that is done directly. The fluoride volatility process is based on the separation of uranium and plutonium in the form of volatile hexafluorides from fission products, the majority of which form non-volatile fluorides (Uhlir, 1989). A large decontamination factor ($\sim 10^8$) is achieved by passing the UF_6 through chemical traps of NaF to remove any partially volatile contaminants.

The fluorination process has also been modified to be more useful. One such example is FLUOREX. FLUOREX is a new reprocessing technology in which fluoride volatility and solvent extraction are applied (Fukasawa et al., 2001). The proposed system is a hybrid system that combines fluoride volatility and solvent extraction methods where the uranium, a major component in spent fuel, is separated efficiently by the fluoride volatility method and MOX is recovered by well-established conventional PUREX method (Amano et al., 2001). The system can recover pure U and MOX with a decontamination factor of over 10^7 and drastically reduces the cost and waste generation compared with conventional processes. The system also has high technical maturity, similar safety, and higher proliferation resistance compared with a conventional fuel cycle system (Amano et al., 2001 and Fukasawa et al., 2001). When the FLUOREX reprocessing system is adopted in the LWR fuel cycle, the conversion facility for re-enrichment can be deleted, which leads to a large reduction in fuel cycle cost (Amano et al., 2001). FLUOREX reprocessing can easily recover iodine in the decladding process, and recover Np and Tc in the uranium purification (adsorption) process (Amano et al., 2001). Americium and Cm can be recovered in the solvent extraction process. The FLUOREX process can effectively utilize and recycle fluorine (Amano et al., 2001). FLUOREX reprocessing consists of compact fluorination and uranium purification equipment, and less than 10% of materials in spent fuel (fluorination residues) are treated in the solvent extraction process. This leads to a large reduction in reprocessing plant

volume (Amano et al., 2001). Additionally, the total amount of the waste generated from FLUOREX reprocessing is about 1/10 that generated in conventional processes. High-level vitrified waste volume is reduced to 2/3 by removing Cs because the volume is controlled by dilution of this heat generator. Another feature is the flexibility in the choice of high-level waste geological disposal methods (Amano et al., 2001). Several key nuclides requiring geological disposal, such as Ru, Rh, Tc, I and Np, are easily removed in the uranium purification process, usually with chemical traps.

2.3 Solubility

2.3.1 Qualitative and Quantitative Solubility

Residues remaining from the voloxidation and fluorination processes are all fluorides and are of much less total mass than the original SNF. In order to reach the objective of this research, it was necessary to determine solubility of fission product and activation product fluorides. Single component solubility for most fluoride species is readily available in the literature. Table 2.1 lists the qualitative solubility of the fluoride and hydroxide residues from Lide (1997). Hydroxide solubility is listed as a reference for potential downstream processing of the residues. Table 2.2 lists the quantitative solubility of the fluorides and hydroxides from Weast (1989). Table 2.3 lists the Solubilities of Multi-Component Systems (Linke, 1958; Linke, 1965). The data in Table 2.3 was used to validate the model for multi-component systems.

2.3.2 Solubility Product Constant

The solubility product, K_{sp} , quantifies the equilibrium that exists between a slightly soluble salt and its ions in a saturated solution, as shown in Equations 2.1 and 2.2.



$$K_{sp} = [M^{+x}][F^-]^x \quad (2.2)$$

Unlike the solubility of a substance, the solubility product is independent of what else is

Table 2.1 - Qualitative Solubility of Fluoride and Hydroxide Residues in Water from Lide (1997)

	Elements	Oxidation State	F-	OH-
Alkali	Li	1	slightly soluble	soluble
	Rb	1	very soluble	very soluble
	Cs	1	very soluble	very soluble
Alkaline Earth	Be	2	very soluble	slightly soluble
	Sr	2	soluble	soluble
	Ba	2	slightly soluble	slightly soluble
	Ra	2		---
	La	3	insoluble	insoluble
Lanthanides	Ce	4	insoluble	---
	Pr	3		---
	Nd	3	insoluble	---
	Pm		---	---
	Sm	3	reactive	---
	Eu	3	insoluble	---
	Gd	3		---
	Tb	3	---	---
	Dy	3		---
	Ho	3	soluble	---
	Er	3	insoluble	---
	Tm	3	soluble	---
	Yb	3	insoluble	---
	Actinides	Ac	3	insoluble
Th		4		---
Pa		5	---	---
Np		6	---	---
Pu		4		---
Am		4		---
Cm			---	---
Cf			---	---
Transition Metals and Other	Zn	2	slightly soluble	slightly soluble
	Ga	3	insoluble	
	Y	3	insoluble	---
	Zr	4	slightly soluble	insoluble
	Ru	4	reactive	---
	Rh	4	---	---
	Pd	2	reactive	---
	Ag	2	reactive	---
	Cd	2	slightly soluble	insoluble
	In	3	slightly soluble	
	Sn	4	reactive	---
	Pb	4		---
	Bi	4	---	---

Table 2.2 - Quantitative Solubility of Fluoride and Hydroxide Residues in Water from Weast (1989)

Elements		Oxidation State	Solubility, in grams per 100cc water (^o C)	
			F-	OH-
Alkali	Li	1	0.27 (18)	12.8 (20), 17.5 (100)
	Rb	1	130.6 (18)	180 (15), very soluble (hot)
	Cs	1	367 (18)	395.5 (15)
Alkaline Earth	Be	2	infinitely soluble	---
	Sr	2	0.011 (0), 0.012 (27)	0.41 (0), 21.83 (100)
	Ba	2	0.12(25), slightly soluble	5.6 (15), 94.7 (78)
	Ra	2	---	---
	La	3	---	insoluble
Lanthanides	Ce	4	insoluble	---
	Pr	3	---	---
	Nd	3	insoluble	---
	Pm	3	---	---
	Sm	3	insoluble	insoluble
	Eu	3	insoluble	---
	Gd	3	insoluble	---
	Tb	3	insoluble	---
	Dy	3	insoluble	---
	Ho	3	insoluble	---
	Er	3	insoluble	---
	Tm	3	insoluble	---
	Yb	3	insoluble	---
	Actinides	Ac	3	insoluble
Th		4		insoluble
Pa		5	+4 insoluble	---
Np		6	decomposes	---
Pu		4		---
Am		4	---	---
Cm			---	---
Cf			---	---
Transition Metals and Other	Zn	2	1.62 (20), soluble (hot)	very slightly soluble
	Ga	3	0.002 (cold), insoluble (hot)	insoluble
	Y	3	insoluble	insoluble
	Zr	4	1.388 (25), decomposes (hot)	0.02 (cold), insoluble (hot)
	Ru	4	---	---
	Rh	4	---	---
	Pd	2	slightly soluble, decompose (cold)	---
	Ag	2	decomposes	---
	Cd	2	4.35 (25)	0.00026 (26)
	In	3	0.040 (25)	insoluble
	Sn	4	very soluble (cold), decomposes (hot)	---
	Pb	4	---	---
	Bi	4	---	---

**Table 2.3 - Solubilities of Multi-Component Systems
(Linke, 1958; Linke, 1965)**

**Solubility of Barium Fluoride in Aqueous Solutions of NaF and
KF at 25°C (mol/L)**

KF	BaF₂	NaF	BaF₂
0	0.00923	0.0334	0.00236
0.0005002	0.0091	0.03902	0.00208
0.001233	0.00871	0.0502	0.00164
0.005028	0.00775	0.05281	0.00142
0.007031	0.00713	0.1023	0.00081
0.01087	0.0062	0.1521	0.0005
0.02081	0.00436	0.2563	0.00039
0.0248	0.00343	0.3076	0.00031
0.05011	0.0016	0.423	0.00027
0.07256	0.00113	0.603	0.00016
0.1001	0.00075		
0.1096	0.00067		
0.1507	0.00054		
0.2008	0.0004		
0.2571	0.0003		

**Solubility of Strontium Fluoride in Aqueous Solutions of NaF
and KF at 25°C (mol/L)**

KF	SrF₂	NaF	SrF₂
0	0.000962	0	0.000926
0.0004987	0.000837	0.0009974	0.00065
0.0009974	0.000656	0.001995	0.000451
0.001496	0.000538	0.003447	0.000253
0.001995	0.000446	0.00399	0.0002
0.002494	0.000367	0.004987	0.00014
0.002992	0.000292	0.005985	0.000119
0.003421	0.000236	0.006982	0.000093
0.00399	0.000205	0.00798	0.000066
0.004488	0.000164	0.008982	0.000064
0.004987	0.000144	0.009978	0.00006
0.005487	0.000119	0.01096	0.00005
0.005985	0.000109		
0.006485	0.000091		
0.007982	0.000068		
0.00848	0.000064		
0.008948	0.000056		
0.009877	0.000051		

dissolved in solution. The solubility of a substance can be calculated from its solubility product. The literature values for the available solubility product constants are shown in Table 2.4.

2.3.3 *Common Ion Effect*

The concentrations of ions in solution are affected by all equilibria and all species present in the solution. The simplest and most significant such effect is called the common ion effect. The common ion effect is observed whenever an ion in solution is common to two different salts which serve as its source. Addition of the second salt adds the common ion, which is a product of the dissolution of the first and drives equation 2.1 to the left. The effect of adding the product ion is to decrease the solubility of the first salt.

The common ion effect is an application of LeChatelier's Principle. If a soluble salt, containing ions common with a slightly soluble salt, is added to a slightly soluble salt equilibrium, then the position of the equilibrium of the slightly soluble salt system is strongly affected. According to LeChatelier's Principle, the addition of the common ion places a stress upon the slightly soluble salt equilibrium. The equilibrium responds so as to undo the stress of the added common ion, which means the equilibrium shifts so that the common ion is reduced meaning a shift to the unionized form, thus reducing the solubility of the slightly soluble salt system.

The common ion effect causes the solubility of soluble substances to be suppressed by the presence of a common ion. In the case of this study, fluoride is the common ion. The common ion effect may cause a slightly soluble fluoride, such as SrF_2 , to become less soluble because of the fluoride ions in solution.

Table 2.4 - Solubility Product Constants for Fluoride Residues

Species	Single Component Solubility (2)	K_{sp} @ 25°C	Reference
BaF₂	slightly soluble	1.84E-07	1, 2
CdF₂	slightly soluble	6.44E-03	1, 2
LaF₃	insoluble	7.00E-17	3, 4, 5
LiF	slightly soluble	1.84E-03	2
SrF₂	soluble	4.33E-09	1, 2
YF₃	insoluble	8.62E-21	2
ZnF₂	slightly soluble	3.04E-02	1, 2

1) Weast, Robert C., Ed., CRC Handbook of Chemistry and Physics, 70th ed., CRC Press, Inc., Boca Raton, Florida, (1989).

2) Lide, David R., Ed., CRC Handbook of Chemistry and Physics, 78th ed., CRC Press, Inc., Boca Raton, Florida, (1997).

3) <http://intro.chem.okstate.edu/1515F01/Database/SolKs.pdf>

4) <http://bilbo.chm.uri.edu/CHM112/tables/KspTable.htm>

5) <http://www.geocities.com/teacherchem/ksp.html>

3. Chemical Process Development and Modeling

3.1 Simulation Software

Two software packages were used in this project; HSC Chemistry 5.0 and OLI Systems Inc Stream Analyzer 1.2.

3.1.1 HSC Chemistry 5.0

The HSC Chemistry 5.0 program (HSC website) was used throughout this project. From this point forward this model will be referred to as HSC. HSC was designed to simulate various kinds of chemical reactions and equilibria calculations. The current version contains fourteen calculation modules (listed below) displayed as fourteen options in the HSC main menu:

- | | |
|-------------------------------|-----------------------------|
| 1. Reaction Equations | 8. H, S, C and G Diagrams |
| 2. Heat and Material Balances | 9. Phase Stability Diagrams |
| 3. Heat Loss Calculations | 10. Mineralogy Iterations |
| 4. Equilibrium Compositions | 11. Composition Conversions |
| 5. Electrochemical Equilibria | 12. Elements |
| 6. Formula Weights | 13. Water (Steam Tables) |
| 7. Eh - pH – Diagrams | 14. Units |

One feature of HSC is that all fourteen-calculation options automatically utilize the same extensive thermochemical database, which contains enthalpy (H), entropy (S) and heat capacity (Cp) data for more than 17,000 chemical compounds. HSC offers calculation methods for studying the effects of different variables on a chemical system at equilibrium. HSC enables the user to simulate chemical reactions and processes on a thermochemical basis. HSC does not take into account all the necessary factors, such as rates of reactions, heat and mass transfer issues, etc. HSC makes it possible to calculate chemical equilibria between pure substances and in ideal solutions, and to some extent, non-ideal solutions. For these calculations only enthalpy (H), entropy (S) and heat

capacity (C_p) data for all prevailing compounds or pure substances is needed. A number of solution models are available in the literature to describe the non-ideality of mixture phases. The practical problem is quite often a lack of valid data for solution parameters. Although solution models are not included in HSC, the non-ideality of solutions can be taken into account in the equilibrium calculations to a certain extent by including constant activity coefficients or simple activity coefficient formulae in the Gibbs equilibrium solver. In many cases, the calculated results may simulate the real chemical reactions and processes at sufficient accuracy for practical applications. One important advantage is that specification of the chemical system, data retrieval, and final calculations may be carried out in normal Intel Pentium-based personal computers within a few minutes.

Modules 1, 4, and 9 were used almost exclusively in this research. Module 1, Reaction Equations, calculates the heat capacity (C_p), enthalpy (H), entropy (S) and Gibbs energy (G) values for a single species, as well as for specified reactions between pure substances.

Module 4, Equilibrium Compositions, easily calculates multi-component equilibrium compositions in heterogeneous systems. The user must specify the substances and potentially stable phases to be taken into account in the calculations, as well as the amounts of raw materials and the temperature. The program calculates the amounts of products at equilibrium in isothermal and isobaric conditions. The equilibrium composition is calculated using the GIBBS or SOLGASMIX solvers, which use the Gibbs energy minimization method.

Module 9, Phase Stability Diagrams, shows stability (predominance) areas of condensed phases in a ternary system as a function of temperature or in isothermal conditions with the remaining constraints as the other axis. These diagrams are very useful when a fast estimation of the prevailing phases is needed. The module assumes that all phases are pure substances. Mixture phases are not taken into account in basic phase stability diagrams. HSC draws two types of phase stability diagrams. The Tpp Diagram module calculates the diagrams on the basis of minimum Gibbs energy (area graphics) and the Lpp Diagram module calculates the phase stability boundaries as lines

based on the reaction equations (vector graphics). The Tpp diagram module draws temperature partial pressure diagrams (Tpp-diagrams) as well as p-p-diagrams with partial pressures on both axes. The Lpp module draws only diagrams with selected partial pressures on both axes. A common limitation for both the diagram modules is that only three elements can be selected simultaneously in the calculation system. Another basic feature is that only two variables can be selected for the diagram.

3.1.2 OLI Systems Inc Stream Analyzer 1.2

The OLI Systems Inc Stream Analyzer 1.2 (OLI website) was also used throughout this project. The OLI Stream Analyzer 1.2 program is the result of over 30 years of effort and represents the state-of-the-art technology in aqueous simulation. From this point forward this model will be referred to as OLI.

OLI allows the user to perform single point and survey calculations. Single point calculations are listed as: isothermal, isenthalpic, bubble points, dew points, vapor amount, vapor fraction, set pH, precipitation point, composition point, set oxidation/reduction potential, and custom. Survey calculations include temperature, pressure, pH, and composition. The user creates a stream that contains the system information including: inflow amounts of each species, inflow amount of water, temperature, and pressure. Single point or survey calculations can be performed on the stream.

OLI provides a predictive thermodynamic framework for calculating the physical and chemical properties of multi-phase, aqueous-based systems. This framework is applicable to most multi-component mixtures of chemicals in water, and is predictive over almost any conceivable temperature, pressure, and concentration of interest. The OLI Engine, supported by a very large, in-place databank, allows the prediction of chemical and phase behavior (including aqueous, vapor, nonaqueous liquid, and multiple solids), of most mixtures of inorganic or organic chemicals in water. The resulting phase separation into aqueous, vapor, organic liquid, and multiple solids is performed automatically.

The OLI Databank contains proprietary coefficients for the prediction of thermodynamic, transport, and physical properties for 80 inorganic elements of the periodic table, and their associated aqueous species, as well as over 5000 organic species. Therefore, most mixtures of chemicals in water can be modeled. The OLI Thermodynamic Framework provides accurate prediction of multi-component aqueous systems including aqueous liquid, vapor, organic liquid, and multiple solid phases over the general range of 0 to 30 molal, -50 to 300°C, and 0 to 1500 bar. Computed thermodynamic properties such as pH, ionic strength, enthalpy, density, osmotic pressure, and transport properties such as viscosity and self-diffusivity, are supplied automatically. The aqueous model can incorporate redox chemistry, co-precipitation, and reaction kinetics. Surface phenomena such as ion exchange, complexation, and molecular adsorption are also available. Transport properties such as electrical conductivity, viscosity, and diffusivity are also available.

3.2 Definition of Chemical System

3.2.1 Estimation of Fluoride Residues and Quantities

A representative SNF system from a PWR with an average fuel burnup of 33,000 MWd/MTIHM and cooled for 10 years was used. The assay of the elemental and radionuclide components of the SNF is detailed in a report by Croff (1980) using a basis of 1.0 metric tonne heavy metal (MTHM). The elemental assay for the SNF used in this study is shown in Table A.1. Negligible carryover of SNF in the cladding was assumed. In order to simplify the mathematical modeling, materials insoluble in water were not initially considered in the model.

Material balances, along with HSC predominance studies, were performed on the voloxidation and fluorination steps (refer to Figure 1.2) to determine the species and composition of the exit streams. Croff (1980) was used to determine what elements and what quantities were fed to the voloxidizer. Voloxidation was modeled at conditions of 450°C in 20%-vol oxygen in air (Mailen and Cathers, 1969, Levitz et al, 1969, and Steindler et al, 1969). Calculations indicated the known volatile oxides and gases were removed from solid oxide fuel. These included: Br₂, CO₂, H₂O, He, I₂, Kr, Rn, and Xe,

as well as some SeO_2 , Tc_2O_7 and RuO_4 . Volatile species were based on literature values for melting and boiling points of the predominant species (Lide, 1997). Components initially present in SNF in quantities less than 10^{-10} g/MTIHM were considered zero. These components were removed from further consideration. The remaining components were considered in the fluorination model. Fluorination calculations assumed a temperature of 500°C in pure fluorine gas (Kamoshida et al, 2000). Using the HSC Phase Stability Diagrams module, phase stability diagrams were produced to determine which form of each component would predominate after fluorination. Uranium was removed as volatile UF_6 . Other volatile fluorides include: AsF_3 , GeF_2 , MoF_6 , NbF_5 , SbF_5 , SeF_4 , TcF_6 , and TeF_6 . Volatile species were based on literature values for melting and boiling points of the predominant species (Lide, 1997). Uranium hexafluoride was assumed to be purified by well-known chemisorption or distillation methods. The remaining components were classified as primary or trace in order to simplify the initial modeling efforts. Primary components were defined as any element present in quantities greater than 0.01 wt-% of the total mass, and trace components were defined as any element less than or equal to 0.01 wt-% down to 10^{-10} g. Table 3.1 shows the literature values for the melting and boiling points of the volatile species. The composition of the volatile stream leaving the voloxidizer is shown in Table 3.2. These values were calculated based on the material balances performed on the voloxidizer. Table 3.3 shows the composition of the volatile stream leaving the fluorinator. These values were calculated based on the material balances performed on the fluorinator. The composition of the fluoride solid residues is shown in Table 3.4. These values were also calculated based on the material balances performed on the fluorinator.

3.2.2 Characterization of Fluoride Residues

The predominant species of the fluoride residues were calculated as: rare earth fluorides, PuF_4 , and ZrF_4 . Even though cesium and strontium are the short-term high heat emitters, they were estimated to constitute only 6.2 mol% of the total fluoride residues. The stability of the fluoride residues in water was determined using the HSC

Table 3.1 - Literature Values for the Melting and Boiling Points of the Volatile Species (Lide, 1997)

Species	mp (°C)	bp (°C)
AsF ₃	-5.9	57.8
Br ₂	-7.2	58.8
CO ₂	-56.57 tp	-78.4 sp
GeF ₂	110	dec 130
H ₂ O	0	100
He	-272.2	-268.934
I ₂	113.7	184.4
Kr	-156.6	-152.3
MoF ₆	17.5	34
NbF ₅	80.00	229.00
Rn	-71	-61.8
SbF ₅	8.3	141
SeF ₄	-10	106
TcF ₆	37.4	55.3
TeF ₆	-37.6 tp	-38.9 sp
UF ₆	56.2	64.5
Xe	-111.9	-107.1

Table 3.2 - Composition of Off-Gas Stream Leaving Voloxidizer

Volatile Oxides	mol %
Br ₂	1.098
CO ₂	1.312E-05
H ₂ O	0.138
He	0.421
I ₂	7.481
Kr	8.642
Rn	7.534E-14
Xe	82.220

Table 3.3 - Composition of Volatile Fluoride Stream from Fluorinator

Volatile Fluorides	mol %
AsF ₃	3.755E-05
GeF ₂	9.586E-05
MoF ₆	0.856
NbF ₅	9.808E-07
SbF ₅	3.388E-03
SeF ₄	0.013
TcF ₆	0.194
TeF ₆	0.093
UF ₆	98.841

**Table 3.4 - Composition of Solid Fluoride Residues
Leaving Fluorinator**

Primary Species	mol %	Trace Species	mol %
AgF ₂	0.211	AcF ₃	9.968E-11
AmF ₄	1.183	BeF ₂	4.889E-06
BaF ₂	3.742	BiF ₄	1.577E-12
CdF ₂	0.286	Cf	4.984E-11
CeF ₄	8.386	DyF ₃	3.383E-03
Cm ₂ O ₃	0.027	ErF ₃	1.336E-04
CsF	3.562	GaF ₃	4.927E-09
EuF ₃	0.345	HoF ₃	3.424E-04
GdF ₃	0.029	InF ₃	8.657E-03
LaF ₃	3.479	LiF	5.489E-06
NdF ₃	11.091	PaF ₅	9.155E-07
NpF ₆	1.312	PbF ₄	3.963E-08
PdF ₂	3.840	RaF ₂	4.951E-10
Pm ₂ O ₃	0.036	TbF ₃	6.457E-03
PrF ₄	3.935	ThF ₄	1.634E-05
PuF ₄	17.696	TmF ₃	1.310E-07
RbF	0.820	YbF ₃	4.118E-08
RhF ₄	2.256	ZnF ₂	1.723E-10
RuF ₄	10.711		
SmF ₃	2.275		
SnF ₄	0.377		
SrF ₂	2.628		
YF ₃	2.040		
ZrF ₄	19.715		

* Database did not contain information about fluoride forms of Cf, Cm, and Pm . It is predicted that Cf would be CfF₃, Cm would be CmF₃, and Pm would be PmF₃.

Reaction Equation module. In this module, the potential reaction equation was input along with a temperature range. The module returned equilibrium constants for the specified temperature range. The stability of the fluoride residues was tested by modeling of reaction of fluoride species with water to produce hydrogen fluoride. For the process studied, it was necessary to determine whether or not HF would be produced. Hydrogen fluoride production would make the separation of the fluoride residues difficult because many metal fluorides are soluble in aqueous HF. The reactions and equilibrium constants at 25°C for potential HF producing reactions are tabulated in Table 3.5. The reactions and equilibrium constants at the upper and lower temperature bounds for all reactions of fluoride residues with water are tabulated in Table A.2.

3.3 Modeling Approach

3.3.1 Modeling using HSC Chemistry 5.0

The HSC Equilibrium Compositions Module was used to model the system and determine which components would dissolve and which would remain insoluble.

Testing of single-component systems with known literature values for solubility (Lide, 1997) was used to validate the HSC Chemistry Equilibrium module. For each component, 1 kmol of compound was added to 100 mL of water. The model returned the concentration as a function of temperature, which indicated the solubility of each component. Compounds with only known qualitative data were also run to determine if HSC would return a reasonable value compared to the literature information. Multi-component testing was also performed using the HSC Chemistry Equilibrium module. For each system, 1 kmol of compound; BaF₂ or SrF₂, depending on the system used, was added to 1000L of water. Each system studied the response to the addition of KF or NaF. The model returned the concentration of one component as a function of the concentration of the other component. The results of the modeling were compared to the literature values for each system.

The HSC Equilibrium Compositions module was used to model the system response to an increase in temperature. The temperature was increased from 0 to 100°C

Table 3.5 - Potential HF-Forming Reactions

Species	Potential Reaction	log K @ 25°C
AgF ₂	AgF ₂ + H ₂ O(l) = AgO + 2HF(a)	6.980
	2AgF ₂ + 2H ₂ O(l) = Ag ₂ O ₂ + 4HF(a)	14.236
NpF ₆	NpF ₆ + 2H ₂ O(l) = NpO ₂ F ₂ (a) + 4HF(a)	45.341
PbF ₄	PbF ₄ + 2H ₂ O(l) = 4HF(a) + PbO ₂	16.511
PdF ₂	PdF ₂ + H ₂ O(l) = PdO + 2HF(a)	3.222
PuF ₄	PuF ₄ + 2H ₂ O(l) = PuO ₂ + 4HF(a)	4.581
RuF ₄	RuF ₄ + 2H ₂ O(l) = RuO ₂ + 4HF(a)	15.175
SnF ₄	SnF ₄ + 2H ₂ O(l) = SnO ₂ + 4HF(a)	26.144
	SnF ₄ (ia) + 2H ₂ O(l) = SnO ₂ + 4HF(a)	21.100
	SnF ₄ + 4H ₂ O(l) = Sn(OH) ₄ + 4HF(a)	19.532
	SnF ₄ + 4H ₂ O(l) = Sn(OH) ₄ (a) + 4HF(a)	19.210
	SnF ₄ (ia) + 4H ₂ O(l) = Sn(OH) ₄ + 4HF(a)	14.488
	SnF ₄ (ia) + 4H ₂ O(l) = Sn(OH) ₄ (a) + 4HF(a)	14.166
TmF ₃	2TmF ₃ + 3H ₂ O(l) = 6HF(a) + Tm ₂ O ₃	1.709

in 5-degree increments, and 1 kmol of water was used. Table 3.6 lists the quantities of the expected components input for the calculation by the HSC Equilibrium Compositions Module. Output for HSC is discussed in Section 4.1.3. For modeling the second dissolution with water, all soluble species; including, AgF₂, BeF₂, CsF, CdF₂, LiF, PuF₄, RaF₂, RbF, SnF₄, and ZnF₂, were removed from the input list. Use of HSC was discontinued once the OLI was utilized. OLI appeared to have greater functional capabilities than HSC, including the ability to survey over two variables at one time.

3.3.2 Modeling using OLI System Inc Stream Analyzer

Testing of single component systems with known literature values for solubility was used to validate the OLI Systems Stream Analyzer model. For each component, a precipitation point calculation was performed. In the precipitation calculation, the species to be studied was listed as an inflow stream but 0 mol was entered, and 5.5508 mol water was also listed as an inflow. The precipitant and adjuster were both set as the

Table 3.6 - HSC Input

Species	Input (kmol)	Species	Input (kmol)
AgF ₂	6.416E-05	PuF ₄	5.385E-03
BaF ₂	1.139E-03	RaF ₂	1.507E-13
BeF ₂	1.488E-09	RbF	2.494E-04
CdF ₂	8.707E-05	SnF ₄	1.146E-04
CsF	1.084E-03	SrF ₂	7.998E-04
InF ₃	2.635E-06	ZnF ₂	5.242E-14
LiF	1.670E-09	ZrF ₄	5.999E-03
PdF ₂	1.169E-03		

species in question. The model returned the amount of adjuster added until precipitation began, which would be the saturation point, and therefore, the solubility of the species. Compounds with only known qualitative data were also run to determine if OLI would return a reasonable value compared to the literature information. Multi-component testing was also performed in the same manner.

OLI was used to model each process of the conceptual flow sheet shown in Figure 1.2. Surveys were performed to determine the optimum temperature and amount of water for each process step. For each step, the inflow streams, including water, were entered in molar quantities. These molar quantities were from the above described material balances. The pressure was set as 1 atm. Table 3.7 lists the input concentrations used for the first process step modeling on OLI. Output for OLI is discussed in Section 4.2.3. The model output included the compositions of the species in the solid, aqueous, and vapor phases. These outputs were used as the feed to model the downstream processes.

Table 3.7 - OLI Input

Species	Input (mol)	Species	Input (mol)
BaF ₂	1.139	PuF ₄	5.385
CdF ₂	0.087	RaF ₂	1.507E-10
CsF	1.084	RbF	0.249
DyF ₃	1.029E-03	SmF ₃	0.692
ErF ₃	4.067E-05	SrF ₂	0.800
EuF ₃	0.105	TbF ₃	1.965E-03
GdF ₃	8.889E-03	ThF ₄	4.973E-06
HoF ₃	1.042E-04	TmF ₃	3.986E-08
LaF ₃	1.059	YbF ₃	1.253E-08
LiF	1.670E-06	YF ₃	0.621
NdF ₃	3.375	ZnF ₂	5.242E-11
NpF ₆	0.399	ZrF ₄	5.999

4. Results and Discussion

4.1 Results from HSC Chemistry 5.0

4.1.1 Single Component Solubility

HSC was able to qualitatively predict the solubility of the single component systems. For BaF_2 , CsF , and RbF , HSC predicted solubility values within 10% of the literature value. However, for CdF_2 , GaF_3 , InF_3 , SrF_2 , and ZnF_2 , HSC predicted values with errors greater than 100%; however, each of these species were in small quantities in this system and the error may not effect the model results. Table 4.1 shows the HSC Single Component Validation results for selected species. A complete listing of the HSC Single Component Validation results can be found in Table A.3. HSC accurately predicted the qualitative solubility of each species tested. However, the distinction between slightly soluble and insoluble was not clear.

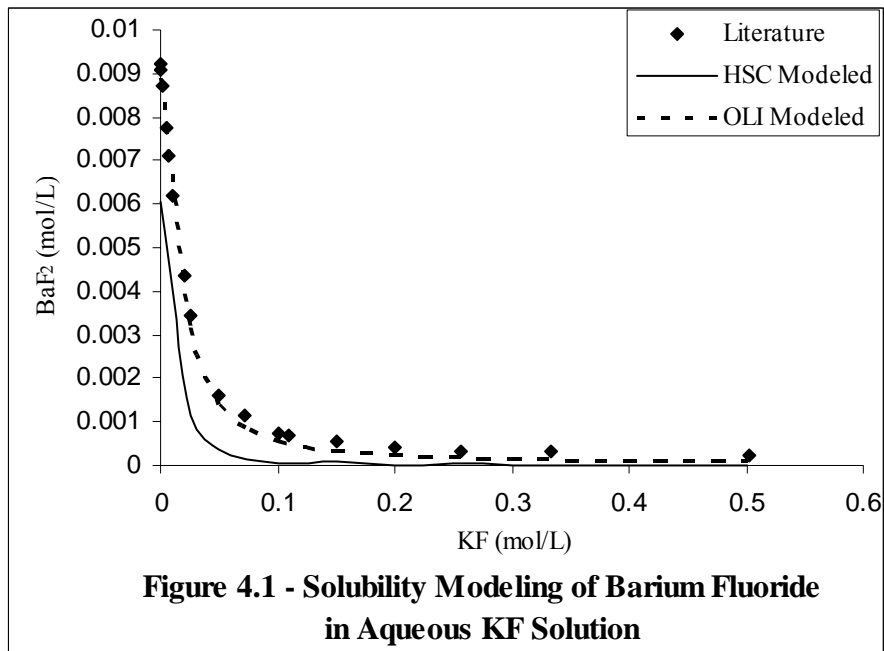
4.1.2 Multi-Component Solubility

HSC accurately modeled multi-component systems containing BaF_2 , which HSC accurately predicted the single component solubility, as shown in Figures 4.1 and 4.2. Figures 4.1 and 4.2 show the multi-component solubility modeling of BaF_2 in aqueous KF solution and aqueous NaF solution, respectively.

HSC did not accurately model multi-component systems containing SrF_2 , which HSC did not accurately predict the single component solubility, as shown in Figures 4.3 and 4.4. Figures 4.3 and 4.4 show the multi-component solubility modeling of SrF_2 in aqueous KF solution and aqueous NaF solution, respectively. This lead to a need for activity coefficients for each of the components. However, information for fluorides was not readily available. Strontium fluoride was never in the presence of KF or NaF in the system studied. The higher percentage of error in part of the solubility calculations was a problem. HSC greatly over predicts the solubility of strontium, which was an important component in this research. There are possibilities that the literature values are incorrect

Table 4.1 - HSC Single Component Solubility Validation

Species	Qualitative Solubility of Fluoride in Water (Weast, 1989)	Quantitative Solubility of Fluoride in Water (grams per 100mL water (°C)) (Lide, 1997)	Expected kmol (per 100mL water)	HSC (kmol/.0055509 kmol water)	% Error
BaF ₂	Slightly Soluble	0.12(25), Slightly Soluble	6.84E-07	6.42E-07	6.22
CdF ₂	Slightly Soluble	4.35 (25)	2.89E-05	1.18E-04	-309.32
CsF	Very Soluble	367 (18)	2.42E-03	2.42E-03	-0.21
GaF ₃	Insoluble	0.002 (cold), Insoluble (hot)	1.58E-08	7.18E-08	-355.13
InF ₃	Slightly Soluble	0.040 (25)	2.33E-07	3.72E-14	100.00
LiF	Slightly Soluble	0.27 (18)	1.04E-05	5.48E-06	47.33
RbF	Very Soluble	130.6 (18)	1.25E-03	1.25E-03	-0.15
SrF ₂	Soluble	0.011 (0), 0.012 (27)	9.55E-08	4.24E-07	-343.99
ZnF ₂	Slightly Soluble	1.62 (20), Soluble (hot)	1.57E-05	5.07E-05	-223.56
ZrF ₄	Slightly Soluble	1.388 (25), Decomposes (hot)	8.30E-06	1.33E-09	99.98



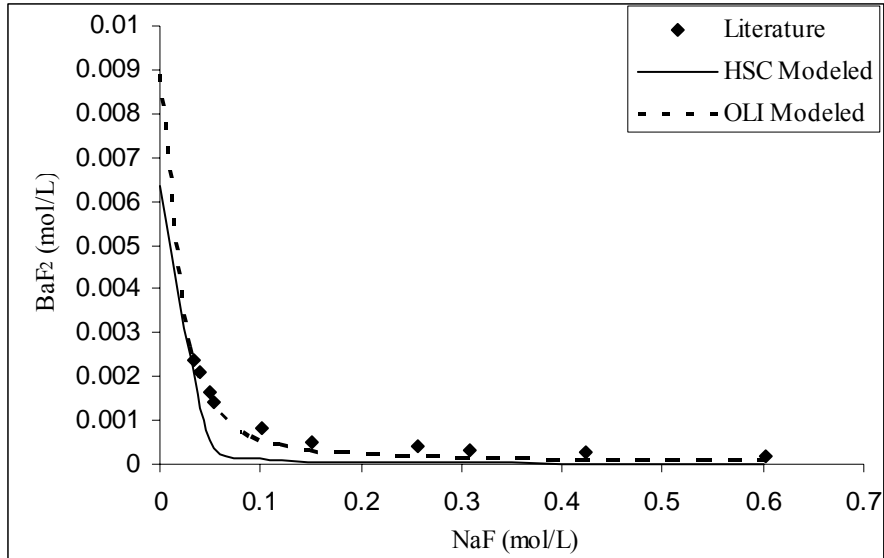


Figure 4.2 - Solubility Modeling of Barium Fluoride in Aqueous NaF Solution

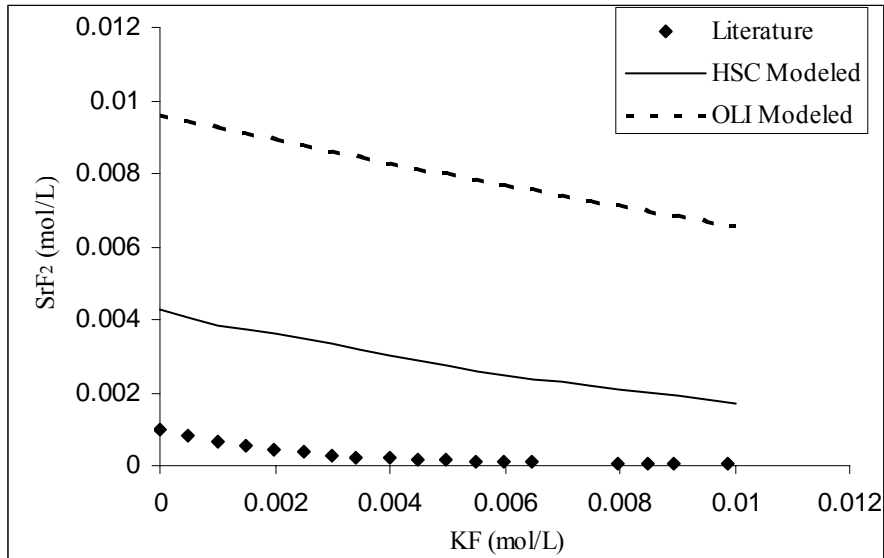
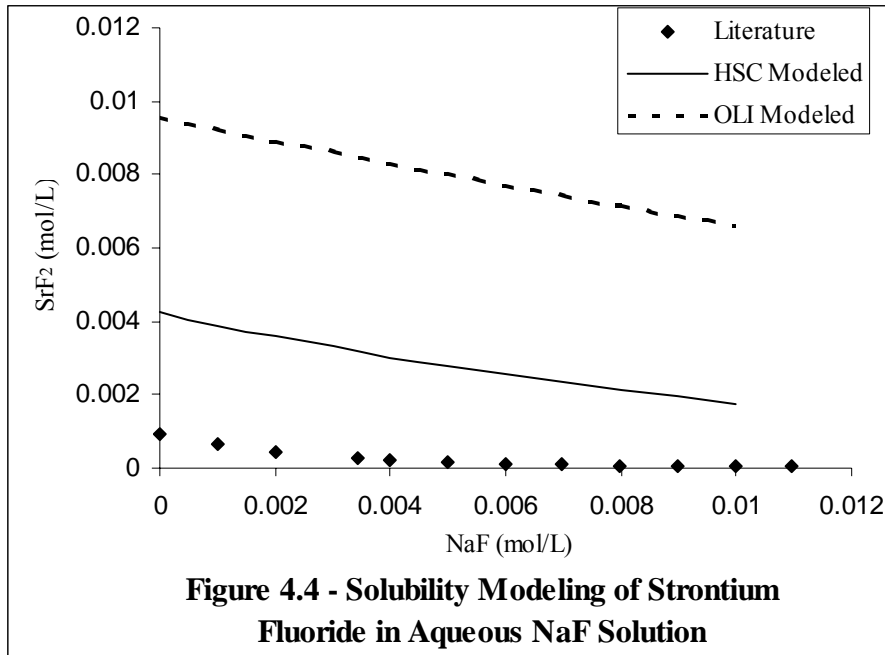


Figure 4.3 - Solubility Modeling of Strontium Fluoride in Aqueous KF Solution



due to impurities or other factors. HSC does not consider reaction rates; therefore, the residence time of the reaction was not relevant to this calculation. OLI results are discussed in Section 4.2.

4.1.3 Fluoride Residue System Results

HSC modeling of the first dissolution with water showed that AgF_2 , BeF_2 , CsF , CdF_2 , LiF , PuF_4 , RaF_2 , RbF , SnF_4 , and ZnF_2 were soluble, that is 43.4% of the initial feed stream. HSC predicted that Pu would be soluble in this system. As a single component in water, CsF is very soluble in water (367 g/100 mL H_2O at 18°C); however, SrF_2 is only slightly soluble in water (0.012 g/100 mL H_2O at 27°C). Due to the common ion effect of CsF , as well as the other ions in solution, the solubility of SrF_2 was suppressed. HSC predicted the solubility of strontium in water containing fluoride residues to be 0.00058 g/100 mL. Figure 4.5 shows the HSC Chemistry result for the separation of Cs/Sr from fluoride residues via dissolution in water. The composition of each species determined the solubility. In Figure 4.5, SrF_2 and $\text{Cs}(+a)$ are the largest components. Strontium

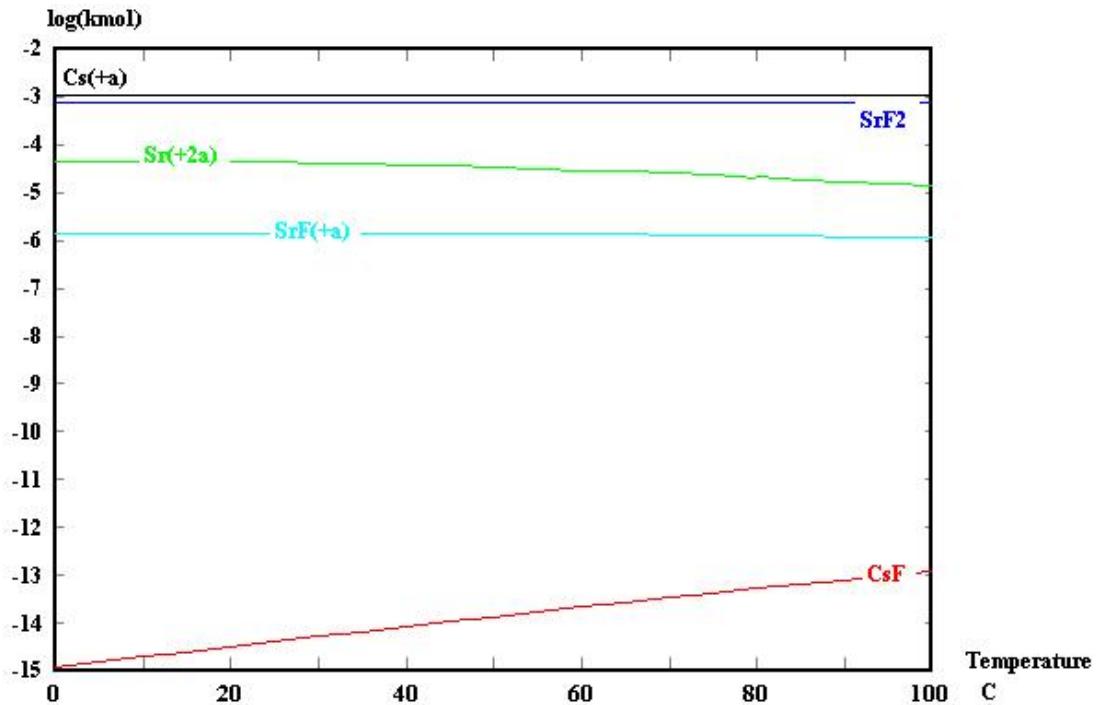


Figure 4.5 - HSC Modeled Separation of Cs/Sr from Fluoride Residues in Water

fluoride, as shown in Figure 4.5, was in the solid form; Cs(+a) was the aqueous form of the cesium ion. The first dissolution with water was effective for the removal of cesium from SNF, although strontium appeared to be insoluble.

Figure 4.6 shows the HSC result for the separation of strontium from SNF via dissolution in water after removal of species that solubilized during the first dissolution. A second dissolution with water did cause adequate separation of strontium from SNF, and the highest degree of separation occurred at 20°C.

The separation of cesium from strontium by water dissolution could be desirable if disposal required separation. It is reasonable to dispose of Cs/Sr together because these are the largest short-term heat producers in the waste. Based on literature values, the solubility of Group 1 and 2 of the periodic table increases upon conversion to hydroxide (refer to Table 2.2), which leads to the possible advantage of converting all fluorides to hydroxides without a water washing process. The separation of PuF₄ during the first

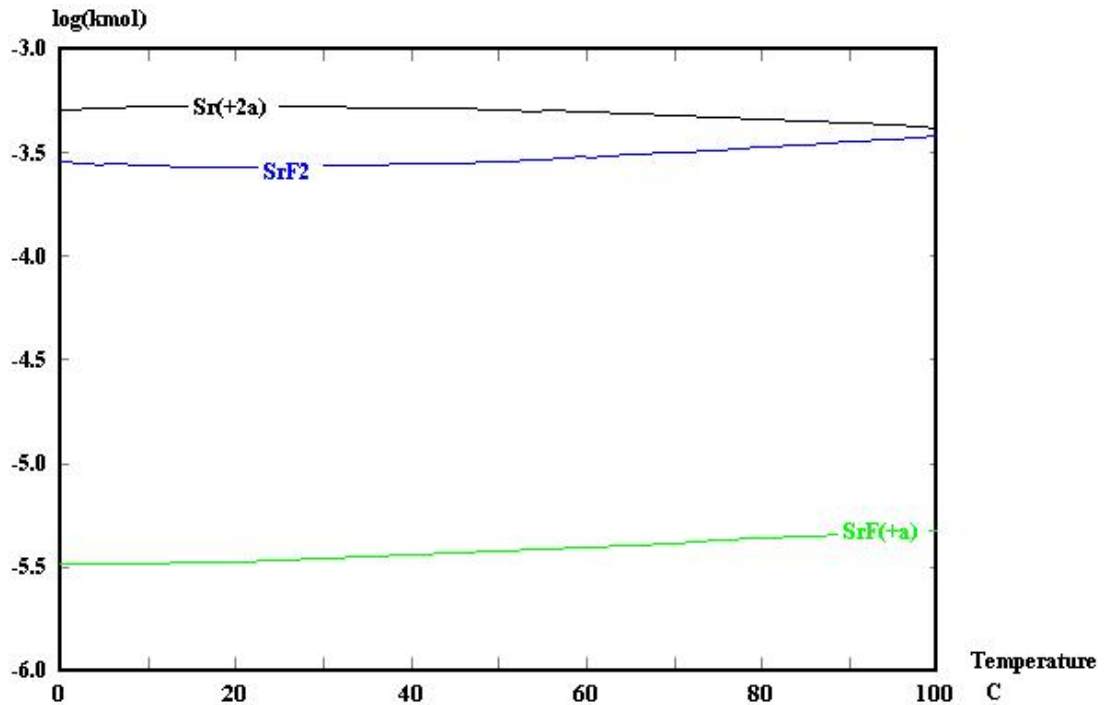


Figure 4.6 - HSC Separation of Sr in Water after Removal of Soluble Species

dissolution with water was not expected. However, an initial conversion to hydroxide could make it insoluble or separation could be performed during the purification of the cesium containing stream.

SNF after a 10-year cooling period contains 772.5 g/MTIHM of strontium. Assuming a reprocessing plant would treat 2000 MTIHM/yr with 200 operating days/yr, 14660 gal of water/hr would be required to separate the 322g Sr/hr according to HSC. Under the same conditions when the common ion effect is not considered, only 700 gal water would be needed based on the solubility of strontium listed in Lide (1997).

4.2 Results from OLI System Inc Stream Analyzer

4.2.1 Single Component Solubility

OLI was able to qualitatively predict the solubility of the single component systems. For CdF₂, OLI predicted solubility values within 10% of the literature value. However, for CsF, RbF, and SrF₂, OLI predicted values with errors greater than 100%

over the literature value; however, each of these species was in small quantities in this system and the error may not affect the model results. Also, SrF_2 was never in the presence of KF or NaF in the system studied. Table 4.2 shows the OLI Single Component Validation results for selected species. A complete listing of the OLI Single Component Validation results is in Table A.4. OLI over estimated the qualitative solubility of each species tested. However, the distinction between slightly soluble and insoluble was not clear.

4.2.2 Multi-Component Solubility

OLI predicted the solubility of BaF_2 in aqueous KF and NaF solutions, as shown in Figures 4.1 and 4.2, very accurately. However, OLI did not accurately predict the solubility of SrF_2 in KF or NaF, as shown in Figures 4.3 and 4.4, respectively.

The higher percentage of error in part of the solubility calculations, like HSC, was also a problem with OLI. OLI was a better predictor than HSC for BaF_2 . However, OLI predicted the solubility of SrF_2 as even higher than the HSC model prediction. There are possibilities that the literature values are incorrect due to impurities or other factors. OLI, like HSC, does not consider reaction rates; therefore, the required residence time for the reaction is not known. Due to the information included in the database and the extent of calculates performed, OLI is most likely the better model.

4.2.3 Fluoride Residue System Results

The final process flow sheet for the separation of fluoride residues is shown in Figure 4.7. The dashed line shows the steps covered by this study. Activity coefficients calculated by OLI for each of the process steps in Figure 4.7 are tabulated in Tables A.5, A.6, and A.7. A temperature survey on the dissolution with water resulted in the optimal temperature of 30°C to produce the desired separation. The composition survey on water resulted in the optimal water to solids ratio of 4:1 (molar basis) to produce the desired separation. Optimum being defined as the amount of water to provide the separation without increasing the solubility of additional species. The calculated pH of this step was 3.0742 and was not adjusted. These conditions provided adequate separation of desired

Table 4.2 - OLI Single Component Solubility Validation

Species	Qualitative Solubility of Fluoride in Water (Weast, 1989)	Quantitative Solubility of Fluoride in Water (grams per 100mL water (°C)) (Lide, 1997)	OLI (mol/100mL water)	OLI (g/100mL water)	% Error
BaF ₂	Slightly Soluble	0.12(25), Slightly Soluble	8.92E-04	0.156	-30.35
CdF ₂	Slightly Soluble	4.35 (25)	3.02E-02	4.549	-4.57
CsF	Very Soluble	367 (18)	7.7871	1182.890	-222.31
LiF	Slightly Soluble	0.27 (18)	0.0050	0.129	52.11
RbF	Very Soluble	130.6 (18)	7.9202	827.393	-533.53
SrF ₂	Soluble	0.011 (0), 0.012 (27)	9.64E-04	0.121	-908.91
ZrF ₄	Slightly Soluble	1.388 (25), Decomposes (hot)	5.55E-06	9.28E-04	99.93

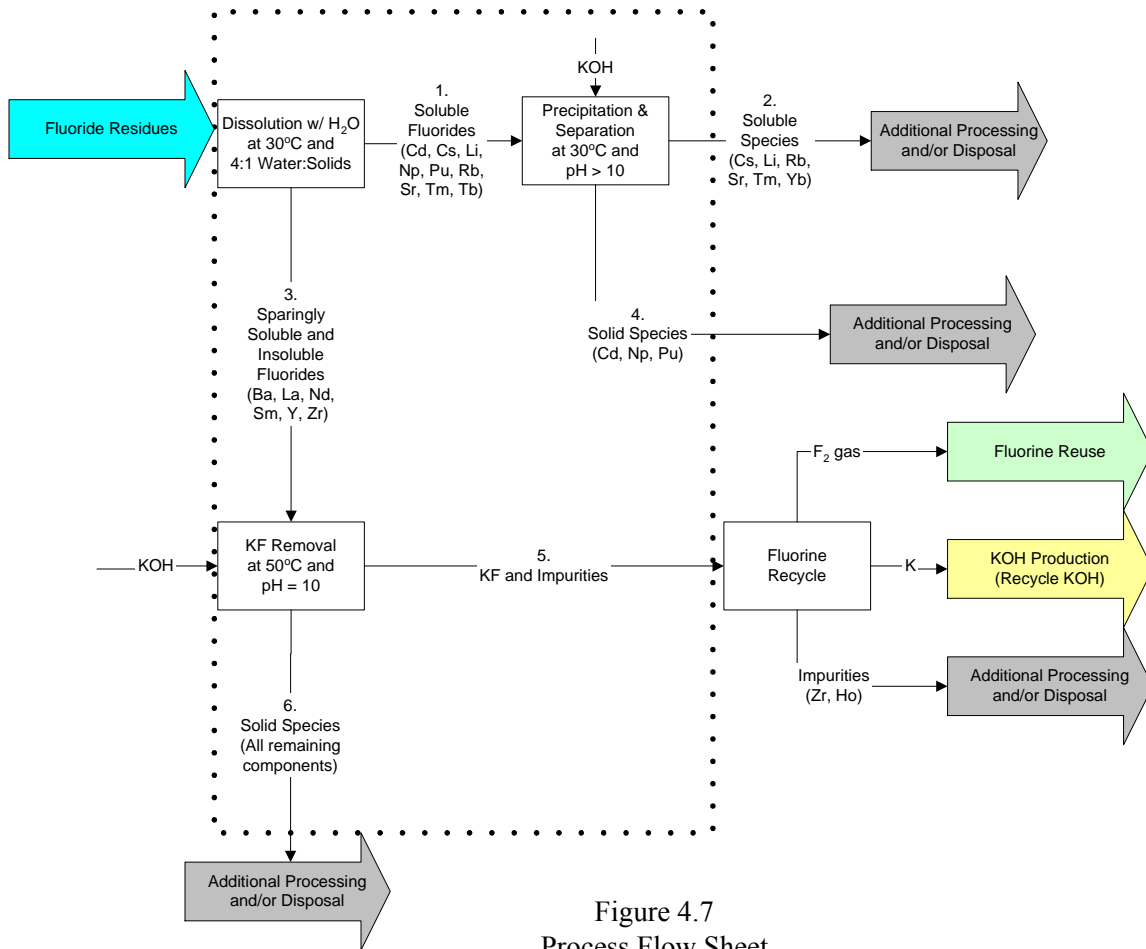


Figure 4.7
Process Flow Sheet
for the Separation of Fluoride
Residues

species (CsF, LiF, and RbF) from fluoride residues without excess contamination of the soluble fluoride stream. Higher temperatures and increased water to solids ratios increased the solubility of most species which would cause contamination of the soluble fluoride stream. Table 4.3 shows the compositions of the streams leaving the first process step. In addition, 77.224 mol of water and 1.11 mol of HF are in the aqueous phase leaving the first step. Strontium fluoride was removed during the first dissolution with water making a second dissolution with water unnecessary.

A study of pH effect, using the pH survey calculation in OLI, on the precipitation and separation of soluble fluorides in water with potassium hydroxide resulted in the optimal pH of 10 or higher to produce the desired separation. The temperature was maintained at 30°C and the water was carried over from the first process step. These conditions provided adequate separation of desired species (CsF, LiF, RbF, and SrF₂) from precipitated Pu and Np. After precipitation of Pu and Np, 99% of the initial CsF, LiF, RbF, SrF₂, TmF₃, and YbF₃ were removed in the aqueous phase. These soluble ions may be sent for additional processing if necessary and ultimately, disposal. The precipitated Pu and Np stream was a desired product stream. Table 4.4 shows the compositions of the streams leaving the KOH precipitation step.

A study of pH effect on KF removal from the insoluble fluorides from the dissolution with water resulted in the optimal pH of 10 to produce the desired conversion. A temperature survey on the same stream resulted in the optimal temperature of 50°C. These conditions were adequate for removal of potassium and fluoride ions. This process step was necessary to remove fluorine from the system prior to any further treatment of the waste and for recovery of fluorine. Table 4.5 shows the compositions of the streams leaving the KF removal step. Soluble ions, including K⁺ and F⁻, leave the KF removal step and were assumed to be treated to recover potassium and fluoride by known techniques. The soluble stream contained trace amounts of several components; the largest was 1.78% of the initial amount of HoF₃ and 0.99% of the initial ZrF₄ feed. Potassium and fluoride ions, along with impurities, were routed to fluorine recycle. During fluorine recycle, fluorine gas is recovered and then recycled as input for the

**Table 4.3 - Output Concentrations from
Dissolution with Water**

Aqueous Phase (Stream 1)		Solid Phase (Stream 3)	
Species	mol %	Species	mol %
Ba ⁺²	4.82E-04	BaF ₂	8.76
BaF ⁺¹	1.92E-05	DyF ₃	7.91E-03
Cd ⁺²	0.50	ErF ₃	3.13E-04
CdF ₊₁	0.53	EuF ₃	0.81
CdF ₂	5.47E-02	GdF ₃	6.84E-02
CdOH ⁺¹	2.21E-08	HoF ₃	8.01E-04
Cs ⁺¹	13.54	LaF ₃	8.15
ErF ₄ ⁻¹	4.26E-09	NdF ₃	25.96
EuF ₄ ⁻¹	1.54E-08	RaF ₂	1.12E-09
GdF ₄ ⁻¹	3.49E-09	SmF ₃	5.32
HoF ₃	4.49E-09	TbF ₃	1.51E-02
HoF ₄ ⁻¹	1.26E-06	ThF ₄ ·2.5H ₂ O	3.83E-05
HZrF ₆ ⁻¹	1.24E-06	YF ₃	4.78
Li ⁺¹	2.09E-05	ZrF ₄ ·1H ₂ O	46.13
NdF ₄ ⁻¹	1.90E-08		
NpO ₂ ⁺²	5.08E-07		
NpO ₂ F ⁺¹	8.11E-03		
NpO ₂ F ₂	4.98		
NpO ₂ OH ⁺¹	2.51E-09		
PuF ₂ ⁺²	3.55E-06		
PuF ₃ ⁺¹	0.26		
PuF ₄	67.01		
Rb ⁺¹	3.11		
SmF ₄ ⁻¹	3.67E-08		
Sr ⁺²	9.03		
SrF ⁺¹	0.96		
TbF ₃	1.40E-09		
TbF ₄ ⁻¹	3.93E-07		
TmF ₃	1.47E-09		
TmF ₄ ⁻¹	4.96E-07		
YbF ₄ ⁻¹	1.56E-07		
YF ₃	2.21E-08		
ZrF ₃ ⁺¹	2.14E-07		
ZrF ₄	5.56E-03		
ZrF ₅ ⁻¹	1.22E-06		
ZrF ₆ ⁻²	7.80E-03		

**Table 4.4 - Output Concentrations from
Precipitation with Hydroxide**

Aqueous Phase (Stream 2)		Solid Phase (Stream 4)	
Species	mol %	Species	mol %
Ba ⁺²	1.97E-05	BaF ₂	6.75E-04
BaF ⁺¹	1.61E-07	CdF ₂	1.48
Cd(OH) ₂	5.28E-08	YF ₃	2.97E-08
Cd(OH) ₃ ⁻¹	8.92E-09	NpO ₂ (OH) ₂	6.78
Cd ⁺²	8.48E-08	Pu(OH) ₄	91.74
CdF ₊₁	6.16E-03		
CdF ₂	3.59E-03		
CdOH ⁺¹	6.79E-06		
Cs ⁺¹	50.69		
ErF ₄ ⁻¹	1.60E-08		
EuF ₄ ⁻¹	5.77E-08		
GdF ₄ ⁻¹	1.31E-08		
HoF ₄ ⁻¹	4.74E-06		
Li ⁺¹	7.84E-05		
NdF ₄ ⁻¹	7.13E-08		
NpO ₂ F ⁺¹	6.60E-06		
NpO ₂ F ₂	2.29E-02		
NpO ₂ OH ⁺¹	5.71E-08		
PuF ₄	3.98E-08		
Rb ⁺¹	11.69		
SmF ₄ ⁻¹	1.38E-07		
Sr ⁺²	36.15		
SrF ⁺¹	1.40		
SrOH ⁺¹	2.70E-06		
TbF ₄ ⁻¹	1.48E-06		
TmF ₄ ⁻¹	1.86E-06		
YbF ₄ ⁻¹	5.87E-07		
ZrF ₄	2.06E-08		
ZrF ₅ ⁻¹	4.32E-08		
ZrF ₆ ⁻²	5.02E-02		

Table 4.5 - Output Concentrations from KF Removal

Aqueous Phase (Stream 5)		Solid Phase (Stream 6)	
Species	mol %	Species	mol %
Ba ⁺²	5.53E-04	BaF ₂	8.80
BaF ⁺¹	9.13E-06	DyF ₃	7.96E-03
DyF ₄ ⁻¹	4.37E-06	ErF ₃	3.14E-04
ErF ₄ ⁻¹	1.25E-05	EuF ₃	0.81
EuF ₄ ⁻¹	4.92E-05	GdF ₃	6.87E-02
GdF ₄ ⁻¹	1.54E-05	HoF ₃	7.89E-04
HoF ₄ ⁻¹	3.12E-03	LaF ₃	8.18
NdF ₄ ⁻¹	6.30E-05	NdF ₃	26.08
SmF ₄ ⁻¹	1.17E-04	RaF ₂	1.13E-09
TbF ₄ ⁻¹	1.03E-03	SmF ₃	5.35
Zr(OH) ₅ ⁻¹	2.29E-06	TbF ₃	1.52E-02
ZrF ₄	1.57E-04	ThF ₄ ·2.5H ₂ O	3.84E-05
ZrF ₅ ⁻¹	1.28E-04	YF ₃	4.80
ZrF ₆ ⁻²	99.99	ZrO ₂	45.89

fluorination step. Potassium was also recovered and could be used for KOH production and then recycled for the conversion of fluorides to hydroxides. The impurities were also removed during fluorine recycle.

Table 4.6 shows the percentage of initial species in each of the numbered streams in Figure 4.7. Stream 1, the soluble fluoride output stream from the dissolution with water, contained all the initial Cd, Cs, Li, Np, Pu, Rb, Sr, Tm, and Yb, as well as small amounts of other components. Stream 2, the aqueous output stream from the precipitation step, contained all the initial Cs, Li, Rb, Sr, Tm, and Yb, as well as small amounts of other components. Stream 3, the insoluble fluoride output stream from the dissolution with water, contained all the initial Ba, Dy, Er, Eu, Gd, Ho, La, Nd, Ra, Sm, Tb, Th, Y, and Zr. Stream 4, the solid output stream from the precipitation step, contained 100% of the initial Pu, 99.7% of the initial Cd, and 99.8% of the initial Np, as well as small amounts of Ba and Y. Stream 5, the aqueous output stream from the

Table 4.6 - Percent of Initial Species in Process Streams

Species	Initial Conc (mol)	% of Initial Species					
		Stream 1	Stream 2	Stream 3	Stream 4	Stream 5	Stream 6
BaF ₂	1.139	3.52E-03	3.72E-05	100.00	3.48E-03	2.93E-05	100.00
CdF ₂	0.087	99.92	0.24		99.68		
CsF	1.084	100.00	99.64				
DyF ₃	1.029E-03			99.97		2.52E-04	100.00
ErF ₃	4.067E-05	8.38E-04	8.38E-04	100.00		0.02	99.98
EuF ₃	0.105	1.17E-06	1.17E-06	100.00		2.78E-05	100.00
GdF ₃	8.889E-03	3.14E-06	3.14E-06	100.00		1.03E-04	100.00
HoF ₃	1.042E-04	0.10	0.10	99.90		1.78	98.22
LaF ₃	1.059			100.00			100.00
LiF	1.670E-06	99.99	99.99				
NdF ₃	3.375	4.50E-08	4.50E-08	100.00		1.11E-06	100.00
NpF ₆	0.399	99.93	0.12		99.80		
PuF ₄	5.385	100.00	1.57E-08		100.00		
RaF ₂	1.507E-10			97.03			99.97
RbF	0.249	99.83	99.83				
SmF ₃	0.692	4.25E-07	4.25E-07	99.95		1.00E-05	100.00
SrF ₂	0.800	100.00	100.00				
TbF ₃	1.965E-03	1.61E-03	1.61E-03	100.00		0.03	99.97
ThF ₄	4.973E-06			100.00			100.00
TmF ₃	3.986E-08	100.00	99.61				
YbF ₃	1.253E-08	99.67	99.74				
YF ₃	0.621	2.85E-07		100.00	2.82E-07		100.00
ZnF ₂	5.242E-11						
ZrF ₄	5.999	0.02	0.02	99.98		0.99	99.01

fluorine recovery step, contained only trace amounts of the initial components with Zr and Ho as the largest components. Stream 6, the solid output stream from the fluorine recovery step, contained nearly all the initial Ba, Dy, Er, Eu, Gd, Ho, La, Nd, Ra, Sm, Tb, Th, Y, and Zr.

5. Conclusions and Recommendations

As stated in the Introduction, the overall objective of this work was to support an alternative hybrid process to meet the AFCI goals using fluorination and aqueous processing techniques for treatment of SNF, and the specific goal was to develop a simple aqueous process for partitioning the residue from the fluorination stage of the fluoride volatility process. Figure 1.2 shows the conceptual flow diagram which provided a starting point for modeling. This flow diagram was modified as the modeling was completed for each step. The final flow diagram is shown in Figure 4.7. These two diagrams are very different. It was determined that the second dissolution with water in Figure 1.2 was not necessary if the temperature of the first dissolution with water was increased from 25°C to 30°C and a 4:1 water to solids molar ratio was used. As shown in Figure 4.7, Pu and Np were removed during the first process step and then precipitated. According to Figure 1.2, Pu and Np were not to be removed until the conversion of solid fluorides to hydroxides. In the final flow diagram, the conversion of fluoride residues to hydroxides was performed as a method to recover fluorine for recycle and to prepare solid residues vitrification. The final process step of Figure 1.2, acidification with HNO₃, was not necessary in the final process.

The original objectives stated that the work was designed to examine the separation of high-heat fission products (Cs/Sr) from fluoride residues using simple dissolution methods. This was accomplished with greater than 99% recovery of cesium and strontium after only two process steps. Cesium and Sr were completely recovered during the dissolution with water, but the Pu/Np required that a precipitation step be added before Cs/Sr could be processed further for disposal. The objectives also mentioned the potential further processing to recover Pu/Np and/or Am/Cm. Plutonium and Np were recovered as solid in the precipitation with KOH. This solid stream could be used for fabrication of MOX fuel after removal of the Cd. Data for Am/Cm were not available; therefore further study of the potential to separate these components is still needed, which is outside the scope of this study. This study showed that the process shown in Figure 4.7 is thermodynamically possible.

5.1 Conclusions from HSC Chemistry 5.0

The HSC model was valid for the prediction of qualitative solubilities. Currently, HSC assumes an ideal solution. Activity coefficients are needed to improve the capabilities of HSC or another model must be developed.

The HSC model predicted that CsF can be readily separated from SNF using water, while SrF₂ cannot be practically separated from SNF using water. Cesium and strontium can be disposed of together; hence, separation of these two nuclides is not necessary. Initially, the process seemed reasonable; however, it was predicted that the common ion effect would prevent dissolution and separation of the strontium with the cesium in one step. Cesium fluoride is highly soluble and does not appear to be suppressed by any ions.

Because Sr(OH)₂ is more soluble (0.41 g/100 mL H₂O at 0°C and 21.83 g/100 mL H₂O at 100°C) than SrF₂ (0.012 g/100 mL H₂O at 27°C), conversion to hydroxide and separation is another possibility. There are possible advantages to having strontium separate from cesium for disposal. Strontium only has one radioactive isotope, which has a half-life of 30 years. Cesium has one isotope with a 30-year half-life (¹³⁷Cs) and another with a much longer half-life, ¹³⁵Cs has a half-life of 3x10⁶ years. Cesium would therefore require geologic disposal, while strontium could be allowed to decay outside the repository until possible disposal as low-level waste. Therefore, more research is needed to examine the possibility of converting fluoride residues to hydroxides, after removal of the Group 1 ions, to improve the solubility of strontium. Group 2 ions are also soluble hydroxides; therefore, cesium and strontium could potentially be separated together if desired.

5.2 Conclusions from OLI System Inc Stream Analyzer

The OLI model predicts that the separation of fluoride residues by a simplified, alternative aqueous process is practical. For the process shown in Figure 4.7, atmospheric pressure was used throughout with temperature ranging from 30-50°C. Separation of cesium and strontium was possible with only one dissolution with water, in contrast to HSC predictions which required two dissolutions. Plutonium and Np were

removed with the Cs and Sr but were precipitated by adjusting the pH. A pH of 8 would selectively precipitate Pu, but a pH of 10 or greater would precipitate Np with Pu, which would maintain the proliferation resistance. Initial dissolution with water and then precipitation with hydroxide, provided the desired separation of the fluoride residues: 1) an aqueous stream containing Cs/Sr, 2) a solids stream containing Pu/Np that could be used in MOX fuel fabrication, and 3) a final waste stream after recovery of fluorine. The fluorine containing stream carried some contaminants, which could easily be removed and returned to the solid stream or processed further if necessary. The solid stream leaving the fluorine recovery step contained all the rare earth species (REs) and could potentially be processed further to recover Am and Cm for transmutation. However, the OLI database did not contain information for Am or Cm. The separation of Am/Cm from REs needs to be investigated.

Figure 5.1 shows an alternative process to the one described in this paper. This alternative process could potentially simplify the partitioning process. It is recommended that the alternatives be studied, as well.

Because this research was based solely computer modeling, follow-on laboratory experiments would be necessary to validate the results and to improve the process flow diagram. Experiments are needed to determine the actual solubility of the components in solution, as well as the effects of temperature on the solubility. More data is especially needed for CdF_2 , CsF , RbF , SrF_2 , and ZrF_4 , as well as Am and Cm. Hydroxides, other than KOH, should be investigated, such as, NaOH and NH_4OH . Further development of the process diagram, with equipment design and cost estimation, is also recommended.

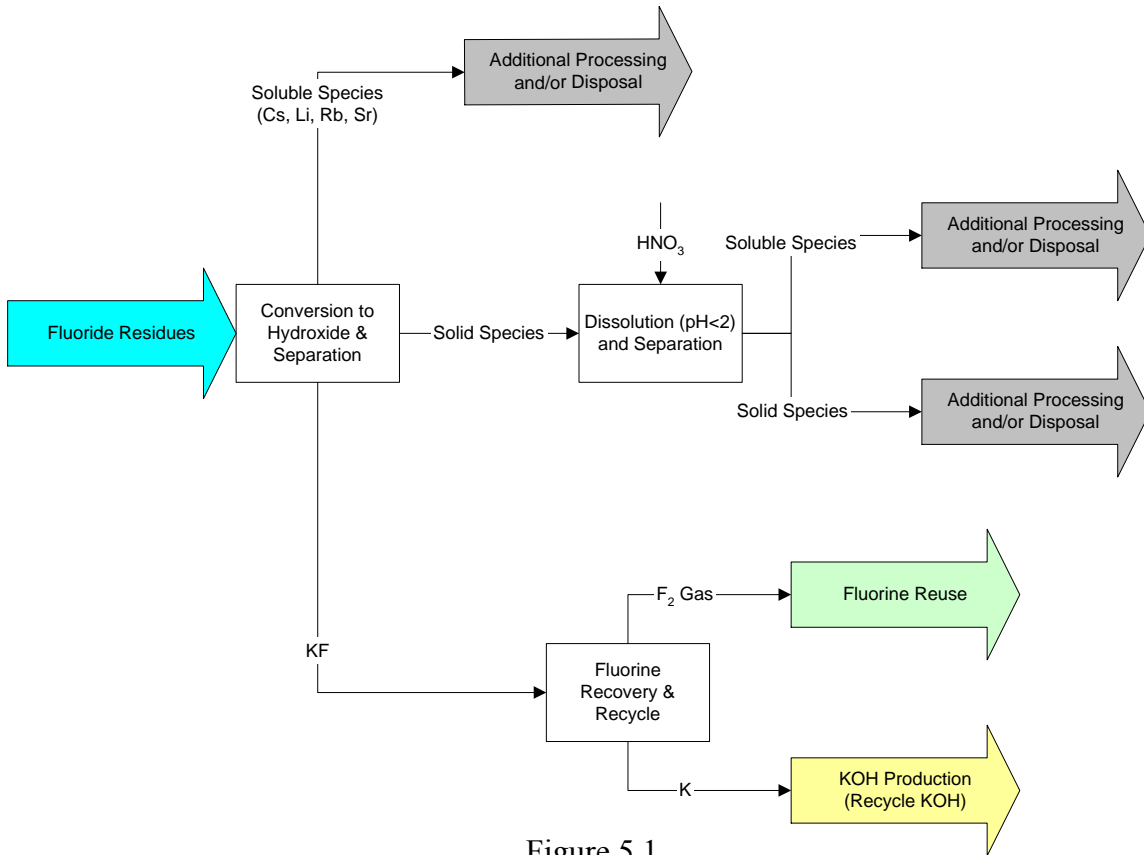


Figure 5.1
 Alternative Potential Process
 Flow Sheet for Separation of
 Fluoride Residues

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Appendix

Table A.1 - Elemental Assay after 10-year Cooling Period from Croff (1980)

Element	Grams of Actinide Elements in SNF (1)	Grams of Fission Product Elements in SNF (2)	Total Grams in SNF (1+2)	Grams of Actinide Elements in Cladding (3)	Grams of Fission Product Elements in Cladding (4)	Total Grams in Cladding (3+4)	Actual Feed to Figure 1.1
AC	5.693E-08		5.693E-08	2.962E-11		2.962E-11	5.69E-08
AG		7.629E+01	7.629E+01		3.815E-02	3.815E-02	7.63E+01
AM	5.786E+02		5.786E+02	2.970E-01		2.970E-01	5.78E+02
AS		2.001E-01	2.001E-01		1.000E-04	1.000E-04	2.00E-01
AT	4.344E-20		4.344E-20	2.208E-23		2.208E-23	4.34E-20
BA		1.724E+03	1.724E+03		8.672E-01	8.672E-01	1.72E+03
BE		1.478E-04	1.478E-04		7.390E-08	7.390E-08	1.48E-04
BI	6.634E-10		6.634E-10	3.393E-13		3.393E-13	6.63E-10
BK	3.768E-11		3.768E-11	1.332E-14		1.332E-14	3.77E-11
BR		2.168E+01	2.168E+01		1.165E-05	1.165E-05	2.17E+01
C		2.595E-05	2.595E-05		6.500E-13	6.500E-13	2.59E-05
CD		1.079E+02	1.079E+02		5.395E-02	5.395E-02	1.08E+02
CE		2.365E+03	2.365E+03		1.183E+00	1.183E+00	2.36E+03
CF	1.259E-07		1.259E-07	6.275E-11		6.275E-11	1.26E-07
CM	1.330E+01		1.330E+01	6.541E-03		6.541E-03	1.33E+01
CO		0.000E+00	0.000E+00			0.000E+00	0.00E+00
CS		2.382E+03	2.382E+03		1.186E+00	1.186E+00	2.38E+03
CU		0.000E+00	0.000E+00		0.000E+00	0.000E+00	0.00E+00
DY		1.383E+00	1.383E+00		6.914E-04	6.914E-04	1.38E+00
ER		5.624E-02	5.624E-02		2.812E-05	2.812E-05	5.62E-02
ES	1.678E-17		1.678E-17	5.624E-21		5.624E-21	1.68E-17
EU		1.318E+02	1.318E+02		6.551E-02	6.551E-02	1.32E+02
FR	1.864E-15		1.864E-15	9.648E-19		9.648E-19	1.86E-15
GA		8.643E-07	8.643E-07		4.322E-10	4.322E-10	8.64E-07
GD		1.161E+01	1.161E+01		5.844E-02	5.844E-02	1.16E+01
GE		6.601E-01	6.601E-01		3.301E-04	3.301E-04	6.60E-01
H		3.229E-02	3.229E-02		9.453E-03	9.453E-03	2.28E-02
HE	8.318E-01		8.318E-01	2.609E-04		2.609E-04	8.32E-01
HO		1.421E-01	1.421E-01		7.106E-05	7.106E-05	1.42E-01
I		2.345E+02	2.345E+02		4.629E-04	4.629E-04	2.34E+02
IN		2.501E+00	2.501E+00		1.252E-03	1.252E-03	2.50E+00
KR		3.578E+02	3.578E+02		7.011E-06	7.011E-06	3.58E+02
LA		1.216E+03	1.216E+03		6.081E-01	6.081E-01	1.22E+03

Table A.1 - Cont.

LI		1.917E-04	1.917E-04		9.587E-08	9.587E-08	1.92E-04
MO		3.337E+03	3.337E+03		1.669E+00	1.669E+00	3.34E+03
NB		4.441E-03	4.441E-03		2.292E-06	2.292E-06	4.44E-03
ND		4.025E+03	4.025E+03		2.013E+00	2.013E+00	4.02E+03
NI		0.000E+00	0.000E+00			0.000E+00	0.00E+00
NP	4.471E+02		4.471E+02	2.237E-01		2.237E-01	4.47E+02
PA	3.548E-04		3.548E-04	1.791E-07		1.791E-07	3.55E-04
PB	1.653E-05		1.653E-05	8.761E-09		8.761E-09	1.65E-05
PD		1.371E+03	1.371E+03		6.858E-01	6.858E-01	1.37E+03
PM		1.058E+01	1.058E+01		4.714E-03	4.714E-03	1.06E+01
PO	8.762E-12		8.762E-12	4.845E-15		4.845E-15	8.76E-12
PR		1.116E+03	1.116E+03		5.580E-01	5.580E-01	1.12E+03
PU	8.691E+03		8.691E+03	4.338E+00		4.338E+00	8.69E+03
RA	3.754E-07		3.754E-07	2.002E-10		2.002E-10	3.75E-07
RB		3.525E+02	3.525E+02		1.709E-01	1.709E-01	3.52E+02
RH		4.673E+02	4.673E+02		2.337E-01	2.337E-01	4.67E+02
RN	8.267E-12		8.267E-12	4.234E-15		4.234E-15	8.26E-12
RU		2.179E+03	2.179E+03		1.090E+00	1.090E+00	2.18E+03
SB		1.956E+01	1.956E+01		9.720E-03	9.720E-03	1.96E+01
SE	1.056E-05	5.633E+01	5.633E+01	5.434E-09	2.817E-02	2.817E-02	5.63E+01
SM		8.607E+02	8.607E+02		4.309E-01	4.309E-01	8.60E+02
SN		8.998E+01	8.998E+01		4.499E-02	4.499E-02	8.99E+01
SR		7.725E+02	7.725E+02		3.841E-01	3.841E-01	7.72E+02
TB		2.582E+00	2.582E+00		1.291E-03	1.291E-03	2.58E+00
TC		7.709E+02	7.709E+02		3.855E-01	3.855E-01	7.71E+02
TE		4.836E+02	4.836E+02		2.419E-01	2.419E-01	4.83E+02
TH	7.633E-03		7.633E-03	3.958E-06		3.958E-06	7.63E-03
TL	6.864E-12		6.864E-12	3.456E-15		3.456E-15	6.86E-12
TM		5.567E-05	5.567E-05		2.783E-08	2.783E-08	5.56E-05
U	9.562E+05		9.562E+05	4.782E+02		4.782E+02	9.56E+05
XE		5.333E+03	5.333E+03		1.398E-04	1.398E-04	5.33E+03
Y		4.563E+02	4.563E+02		2.281E-01	2.281E-01	4.56E+02
YB		1.793E-05	1.793E-05		8.966E-09	8.966E-09	1.79E-05
ZN		3.779E-08	3.779E-08		1.890E-11	1.890E-11	3.78E-08
ZR		3.620E+03	3.620E+03		1.812E+00	1.812E+00	3.62E+03

Table A.2 - Potential HF-Forming Reactions for all Fluoride Residues

Species	Rxn to possibly form HF	log K @ 25°C	log K @ 300°C
AcF3	$2AcF_3 + 3H_2O(l) = Ac_2O_3 + 6HF(a)$	-94.754	-47.684
	$AcF_3 + 3H_2O(l) = Ac(OH)_3 + 3HF(a)$	-47.844	-27.015
AgF2	$AgF_2 + H_2O(l) = AgO + 2HF(a)$	6.980	4.457
	$2AgF_2 + 2H_2O(l) = Ag_2O_2 + 4HF(a)$	14.236	9.079
AmF4	$AmF_4 + 2H_2O(l) = AmO_2 + 4HF(a)$	-6.827	-0.967
BaF2	$BaF_2 + H_2O(l) = BaO + 2HF(a)$	-49.351	-24.531
	$BaF_2(ia) + H_2O(l) = BaO + 2HF(a)$	-42.371	-17.350
	$BaF_2 + 2H_2O(l) = Ba(OH)_2 + 2HF(a)$	-32.455	-16.799
	$BaF_2(ia) + 2H_2O(l) = Ba(OH)_2 + 2HF(a)$	-25.475	-9.618
	$BaF_2 + 10H_2O(l) = Ba(OH)_2 \cdot 8H_2O + 2HF(a)$	-24.844	-25.421
	$BaF_2(ia) + 10H_2O(l) = Ba(OH)_2 \cdot 8H_2O + 2HF(a)$	-17.864	-18.240
BeF2	$BeF_2 + H_2O(l) = BeO + 2HF(a)$	-7.540	-3.182
	$BeF_2 + H_2O(l) = BeO(a) + 2HF(a)$	-14.882	-9.740
	$BeF_2(a) + H_2O(l) = BeO + 2HF(a)$	-29.879	-22.477
	$BeF_2(a) + H_2O(l) = BeO(a) + 2HF(a)$	-37.221	-29.036
	$BeF_2(a) + 2H_2O(l) = Be(OH)_2 + 2HF(a)$	-30.110	-23.627
	$BeF_2 + 2H_2O(l) = Be(OH)_2 + 2HF(a)$	-7.771	-4.332
CdF2	$CdF_2 + H_2O(l) = CdO + 2HF(a)$	-11.131	-4.787
	$CdF_2(a) + H_2O(l) = CdO + 2HF(a)$	-11.104	-1.292
	$CdF_2 + H_2O(l) = CdO(a) + 2HF(a)$	-16.488	-9.933
	$CdF_2(a) + H_2O(l) = CdO(a) + 2HF(a)$	-16.462	-6.437
	$CdF_2 + 2H_2O(l) = Cd(OH)_2 + 2HF(a)$	-9.920	-5.291
	$CdF_2(a) + 2H_2O(l) = Cd(OH)_2 + 2HF(a)$	-9.893	-1.796
CeF4	$CeF_4 + 2H_2O(l) = CeO_2 + 4HF(a)$	-2.414	-0.068
CsF	$2CsF + H_2O(l) = Cs_2O + 2HF(a)$	-68.870	-35.068
	$2CsF(ia) + H_2O(l) = Cs_2O + 2HF(a)$	-83.487	-43.017
	$CsF + H_2O(l) = CsOH + HF(a)$	-17.119	-8.605
	$CsF(ia) + H_2O(l) = CsOH + HF(a)$	-24.427	-12.579
	$CsF + H_2O(l) = CsOH(a) + HF(a)$	-5.314	-2.760
	$CsF(ia) + H_2O(l) = CsOH(a) + HF(a)$	-12.623	-6.735
DyF3	$2DyF_3 + 3H_2O(l) = Dy_2O_3 + 6HF(a)$	-68.010	-32.257
	$2DyF_3(a) + 3H_2O(l) = Dy_2O_3 + 6HF(a)$	-52.584	-11.849
	$DyF_3(a) + 2H_2O(l) = DyO_2H(a) + 3HF(a)$	-27.654	-9.143
	$DyF_3 + 2H_2O(l) = DyO_2H(a) + 3HF(a)$	-35.367	-19.346
	$DyF_3 + 3H_2O(l) = Dy(OH)_3 + 3HF(a)$	-13.142	-7.642
	$DyF_3(a) + 3H_2O(l) = Dy(OH)_3 + 3HF(a)$	-5.429	2.562
ErF3	$2ErF_3 + 3H_2O(l) = Er_2O_3 + 6HF(a)$	-62.107	-29.115
	$2ErF_3(a) + 3H_2O(l) = Er_2O_3 + 6HF(a)$	-48.124	-7.867
	$ErF_3(a) + 2H_2O(l) = ErO_2H(a) + 3HF(a)$	-27.197	-8.275
	$ErF_3 + 2H_2O(l) = ErO_2H(a) + 3HF(a)$	-34.188	-18.899
EuF3	$2EuF_3 + 3H_2O(l) = Eu_2O_3 + 6HF(a)$	-65.503	-30.699
	$2EuF_3(a) + 3H_2O(l) = Eu_2O_3 + 6HF(a)$	-56.970	-12.761
	$EuF_3 + 2H_2O(l) = EuO_2H(a) + 3HF(a)$	-31.908	-17.170
	$EuF_3(a) + 2H_2O(l) = EuO_2H(a) + 3HF(a)$	-27.641	-8.201
	$EuF_3 + 3H_2O(l) = Eu(OH)_3 + 3HF(a)$	-21.766	-11.392
	$EuF_3(a) + 3H_2O(l) = Eu(OH)_3 + 3HF(a)$	-17.500	-2.423

Table A.2 - Cont.

GaF ₃	2GaF ₃ + 3H ₂ O(l) = Ga ₂ O ₃ + 6HF(a)	-23.096	-9.460
	GaF ₃ + 3H ₂ O(l) = Ga(OH) ₃ + 3HF(a)	-20.373	-10.187
	GaF ₃ + 2H ₂ O(l) = Ga(OH)O(a) + 3HF(a)	-19.311	-11.889
	GaF ₃ + 2H ₂ O(l) = GaOOH + 3HF(a)	-9.936	-4.713
GdF ₃	2GdF ₃ + 3H ₂ O(l) = Gd ₂ O ₃ + 6HF(a)	-74.204	-35.257
	2GdF ₃ (a) + 3H ₂ O(l) = Gd ₂ O ₃ + 6HF(a)	-55.273	-12.650
	GdF ₃ + 2H ₂ O(l) = GdO ₂ H(a) + 3HF(a)	-37.344	-19.859
	GdF ₃ (a) + 2H ₂ O(l) = GdO ₂ H(a) + 3HF(a)	-27.879	-8.555
	GdF ₃ + 3H ₂ O(l) = Gd(OH) ₃ + 3HF(a)	-13.702	-7.252
GdF ₃ (a) + 3H ₂ O(l) = Gd(OH) ₃ + 3HF(a)	-4.237	4.052	
HoF ₃	2HoF ₃ + 3H ₂ O(l) = Ho ₂ O ₃ + 6HF(a)	-66.419	-31.199
	2HoF ₃ (a) + 3H ₂ O(l) = Ho ₂ O ₃ + 6HF(a)	-53.249	-11.526
	HoF ₃ (a) + 2H ₂ O(l) = HoO ₂ H(a) + 3HF(a)	-27.523	-8.773
	HoF ₃ + 2H ₂ O(l) = HoO ₂ H(a) + 3HF(a)	-34.108	-18.610
InF ₃	2InF ₃ + 3H ₂ O(l) = In ₂ O ₃ + 6HF(a)	-58.370	-28.091
	InF ₃ + 3H ₂ O(l) = In(OH) ₃ + 3HF(a)	-30.962	-17.798
	InF ₃ + 2H ₂ O(l) = In(OH)O(a) + 3HF(a)	-34.587	-19.197
LaF ₃	2LaF ₃ + 3H ₂ O(l) = La ₂ O ₃ + 6HF(a)	-82.404	-39.688
	2LaF ₃ (a) + 3H ₂ O(l) = La ₂ O ₃ + 6HF(a)	-67.342	-18.488
	LaF ₃ + 2H ₂ O(l) = LaO ₂ H(a) + 3HF(a)	-36.170	-19.207
	LaF ₃ (a) + 2H ₂ O(l) = LaO ₂ H(a) + 3HF(a)	-28.639	-8.607
	LaF ₃ + 3H ₂ O(l) = La(OH) ₃ + 3HF(a)	-28.855	-15.088
	LaF ₃ (a) + 3H ₂ O(l) = La(OH) ₃ + 3HF(a)	-21.325	-4.488
LiF	2LiF + H ₂ O(l) = Li ₂ O + 2HF(a)	-45.496	-22.785
	2LiF(ia) + H ₂ O(l) = Li ₂ O + 2HF(a)	-39.718	-18.962
	LiF + H ₂ O(l) = LiOH + HF(a)	-15.324	-7.932
	LiF + H ₂ O(l) = LiOH(a) + HF(a)	-13.491	-8.002
	LiF(ia) + H ₂ O(l) = LiOH + HF(a)	-12.435	-6.020
	LiF(ia) + H ₂ O(l) = LiOH(a) + HF(a)	-10.602	-6.090
	LiF + 2H ₂ O(l) = LiOH*H ₂ O + HF(a)	-14.458	-8.936
	LiF(ia) + 2H ₂ O(l) = LiOH*H ₂ O + HF(a)	-11.569	-7.024
NdF ₃	2NdF ₃ + 3H ₂ O(l) = Nd ₂ O ₃ + 6HF(a)	-72.933	-34.731
	2NdF ₃ (a) + 3H ₂ O(l) = Nd ₂ O ₃ + 6HF(a)	-62.522	-13.183
	NdF ₃ + 2H ₂ O(l) = NdO ₂ H(a) + 3HF(a)	-33.641	-18.122
	NdF ₃ (a) + 2H ₂ O(l) = NdO ₂ H(a) + 3HF(a)	-28.436	-7.348
	NdF ₃ + 3H ₂ O(l) = Nd(OH) ₃ + 3HF(a)	-9.152	-4.915
NdF ₃ (a) + 3H ₂ O(l) = Nd(OH) ₃ + 3HF(a)	-3.947	5.859	
NpF ₆	NpF ₆ + 2H ₂ O(l) = NpO ₂ F ₂ (a) + 4HF(a)	45.341	18.441
PaF ₅	2PaF ₅ + 5H ₂ O(l) = 10HF(a) + Pa ₂ O ₅	-80.564	-40.965
PbF ₄	PbF ₄ + 2H ₂ O(l) = 4HF(a) + PbO ₂	16.511	10.156
	PdF ₂ + H ₂ O(l) = PdO + 2HF(a)	3.222	2.117
PdF ₂	PdF ₂ + 2H ₂ O(l) = Pd(OH) ₂ + 2HF(a)	-0.518	-0.482
	PdF ₂ + 2H ₂ O(l) = Pd(OH) ₂ (a) + 2HF(a)	-5.836	-5.954
PrF ₄	PrF ₄ + 2H ₂ O(l) = PrO ₂ + 4HF(a)	-51.505	-23.445
PuF ₆	PuF ₆ + 2H ₂ O(l) = PuO ₂ F ₂ (a) + 4HF(a)	75.161	31.976
RaF ₂	RaF ₂ + H ₂ O(l) = 2HF(a) + RaO	-52.594	-26.385
	RaF ₂ + 2H ₂ O(l) = 2HF(a) + Ra(OH) ₂	-29.117	-15.096
	RaF ₂ + 2H ₂ O(l) = 2HF(a) + Ra(OH) ₂ (a)	-26.745	-19.781

Table A.2 - Cont.

	$2\text{RbF} + \text{H}_2\text{O}(\text{l}) = \text{Rb}_2\text{O} + 2\text{HF}(\text{a})$	-70.802	-35.824
	$2\text{RbF}(\text{a}) + \text{H}_2\text{O}(\text{l}) = \text{Rb}_2\text{O} + 2\text{HF}(\text{a})$	-85.204	-44.526
RbF	$\text{RbF} + \text{H}_2\text{O}(\text{l}) = \text{RbOH} + \text{HF}(\text{a})$	-16.855	-8.344
	$\text{RbF}(\text{a}) + \text{H}_2\text{O}(\text{l}) = \text{RbOH} + \text{HF}(\text{a})$	-24.056	-12.695
	$\text{RbF} + \text{H}_2\text{O}(\text{l}) = \text{RbOH}(\text{a}) + \text{HF}(\text{a})$	-5.312	-2.652
	$\text{RbF}(\text{a}) + \text{H}_2\text{O}(\text{l}) = \text{RbOH}(\text{a}) + \text{HF}(\text{a})$	-12.513	-7.004
		$\text{RhF}_4 + 2\text{H}_2\text{O}(\text{l}) = \text{RhO}_2(\text{g}) + 4\text{HF}(\text{a})$	-58.172
RuF4	$\text{RuF}_4 + 2\text{H}_2\text{O}(\text{l}) = \text{RuO}_2 + 4\text{HF}(\text{a})$	15.175	8.967
	$2\text{SmF}_3 + 3\text{H}_2\text{O}(\text{l}) = \text{Sm}_2\text{O}_3 + 6\text{HF}(\text{a})$	-65.902	-31.178
	$2\text{SmF}_3(\text{a}) + 3\text{H}_2\text{O}(\text{l}) = \text{Sm}_2\text{O}_3 + 6\text{HF}(\text{a})$	-57.646	-10.646
SmF3	$\text{SmF}_3 + \text{H}_2\text{O}(\text{l}) = \text{SmOF} + 2\text{HF}(\text{a})$	-24.454	-11.523
	$\text{SmF}_3(\text{a}) + \text{H}_2\text{O}(\text{l}) = \text{SmOF} + 2\text{HF}(\text{a})$	-20.326	-1.257
	$\text{SmF}_3(\text{a}) + 2\text{H}_2\text{O}(\text{l}) = \text{SmO}_2\text{H}(\text{a}) + 3\text{HF}(\text{a})$	-27.951	5.346
	$\text{SmF}_3 + 2\text{H}_2\text{O}(\text{l}) = \text{SmO}_2\text{H}(\text{a}) + 3\text{HF}(\text{a})$	-32.079	-4.920
		$\text{SnF}_4 + 2\text{H}_2\text{O}(\text{l}) = \text{SnO}_2 + 4\text{HF}(\text{a})$	26.144
	$\text{SnF}_4(\text{ia}) + 2\text{H}_2\text{O}(\text{l}) = \text{SnO}_2 + 4\text{HF}(\text{a})$	21.100	23.804
SnF4	$\text{SnF}_4 + 4\text{H}_2\text{O}(\text{l}) = \text{Sn}(\text{OH})_4 + 4\text{HF}(\text{a})$	19.532	7.276
	$\text{SnF}_4 + 4\text{H}_2\text{O}(\text{l}) = \text{Sn}(\text{OH})_4(\text{a}) + 4\text{HF}(\text{a})$	19.210	-0.893
	$\text{SnF}_4(\text{ia}) + 4\text{H}_2\text{O}(\text{l}) = \text{Sn}(\text{OH})_4 + 4\text{HF}(\text{a})$	14.488	16.694
	$\text{SnF}_4(\text{ia}) + 4\text{H}_2\text{O}(\text{l}) = \text{Sn}(\text{OH})_4(\text{a}) + 4\text{HF}(\text{a})$	14.166	8.526
		$\text{SrF}_2 + \text{H}_2\text{O}(\text{l}) = \text{SrO} + 2\text{HF}(\text{a})$	-43.395
SrF2	$\text{SrF}_2 + 2\text{H}_2\text{O}(\text{l}) = \text{Sr}(\text{OH})_2 + 2\text{HF}(\text{a})$	-28.752	-14.936
	$2\text{TbF}_3 + 3\text{H}_2\text{O}(\text{l}) = 6\text{HF}(\text{a}) + \text{Tb}_2\text{O}_3$	-72.274	-34.208
	$2\text{TbF}_3(\text{a}) + 3\text{H}_2\text{O}(\text{l}) = 6\text{HF}(\text{a}) + \text{Tb}_2\text{O}_3$	-52.681	-11.366
TbF3	$\text{TbF}_3(\text{a}) + 2\text{H}_2\text{O}(\text{l}) = 3\text{HF}(\text{a}) + \text{TbO}_2\text{H}(\text{a})$	-27.846	-9.007
	$\text{TbF}_3 + 2\text{H}_2\text{O}(\text{l}) = 3\text{HF}(\text{a}) + \text{TbO}_2\text{H}(\text{a})$	-37.642	-20.427
	$\text{TbF}_3 + 3\text{H}_2\text{O}(\text{l}) = 3\text{HF}(\text{a}) + \text{Tb}(\text{OH})_3$	-53.509	-28.005
	$\text{TbF}_3(\text{a}) + 3\text{H}_2\text{O}(\text{l}) = 3\text{HF}(\text{a}) + \text{Tb}(\text{OH})_3$	-43.712	-16.584
		$\text{ThF}_4 + 2\text{H}_2\text{O}(\text{l}) = 4\text{HF}(\text{a}) + \text{ThO}_2$	-21.603
	$\text{ThF}_4(\text{a}) + 2\text{H}_2\text{O}(\text{l}) = 4\text{HF}(\text{a}) + \text{ThO}_2$	-11.454	2.894
ThF4	$\text{ThF}_4(\text{a}) + \text{H}_2\text{O}(\text{l}) = 2\text{HF}(\text{a}) + \text{ThOF}_2$	-0.210	7.960
	$\text{ThF}_4 + \text{H}_2\text{O}(\text{l}) = 2\text{HF}(\text{a}) + \text{ThOF}_2$	-10.360	-4.690
	$\text{ThF}_4 + 4\text{H}_2\text{O}(\text{l}) = 4\text{HF}(\text{a}) + \text{Th}(\text{OH})_4$	-29.336	-17.328
	$\text{ThF}_4(\text{a}) + 4\text{H}_2\text{O}(\text{l}) = 4\text{HF}(\text{a}) + \text{Th}(\text{OH})_4$	-19.187	-4.678
	$\text{ThF}_4(\text{a}) + 4\text{H}_2\text{O}(\text{l}) = 4\text{HF}(\text{a}) + \text{Th}(\text{OH})_4(\text{a})$	-21.044	-11.747
	$\text{ThF}_4 + 4\text{H}_2\text{O}(\text{l}) = 4\text{HF}(\text{a}) + \text{Th}(\text{OH})_4(\text{a})$	-31.194	-24.398
		$2\text{TmF}_3 + 3\text{H}_2\text{O}(\text{l}) = 6\text{HF}(\text{a}) + \text{Tm}_2\text{O}_3$	1.709
	$2\text{TmF}_3(\text{a}) + 3\text{H}_2\text{O}(\text{l}) = 6\text{HF}(\text{a}) + \text{Tm}_2\text{O}_3$	-50.738	-9.577
TmF3	$\text{TmF}_3(\text{a}) + 2\text{H}_2\text{O}(\text{l}) = 3\text{HF}(\text{a}) + \text{TmO}_2\text{H}(\text{a})$	-27.189	-8.295
	$\text{TmF}_3 + 2\text{H}_2\text{O}(\text{l}) = 3\text{HF}(\text{a}) + \text{TmO}_2\text{H}(\text{a})$	-0.966	-1.560
		$2\text{YbF}_3 + 3\text{H}_2\text{O}(\text{l}) = 6\text{HF}(\text{a}) + \text{Yb}_2\text{O}_3$	-34.382
	$2\text{YbF}_3(\text{a}) + 3\text{H}_2\text{O}(\text{l}) = 6\text{HF}(\text{a}) + \text{Yb}_2\text{O}_3$	-52.637	-10.085
YbF3	$\text{YbF}_3(\text{a}) + 2\text{H}_2\text{O}(\text{l}) = 3\text{HF}(\text{a}) + \text{YbO}_2\text{H}(\text{a})$	-26.941	-7.766
	$\text{YbF}_3 + 2\text{H}_2\text{O}(\text{l}) = 3\text{HF}(\text{a}) + \text{YbO}_2\text{H}(\text{a})$	-17.814	-10.284
		$2\text{YF}_3 + 3\text{H}_2\text{O}(\text{l}) = \text{Y}_2\text{O}_3 + 6\text{HF}(\text{a})$	-70.500
YF3	$\text{YF}_3 + 3\text{H}_2\text{O}(\text{l}) = \text{Y}(\text{OH})_3 + 3\text{HF}(\text{a})$	-32.815	-17.655

Table A.2 - Cont.

ZnF2	$\text{ZnF}_2 + \text{H}_2\text{O}(\text{l}) = 2\text{HF}(\text{a}) + \text{ZnO}$	-6.419	-2.346
	$\text{ZnF}_2(\text{ia}) + \text{H}_2\text{O}(\text{l}) = 2\text{HF}(\text{a}) + \text{ZnO}$	-4.878	5.016
	$\text{ZnF}_2 + \text{H}_2\text{O}(\text{l}) = 2\text{HF}(\text{a}) + \text{ZnO}(\text{l})$	-13.348	-5.677
	$\text{ZnF}_2 + \text{H}_2\text{O}(\text{l}) = 2\text{HF}(\text{a}) + \text{ZnO}(\text{a})$	-13.129	-7.632
	$\text{ZnF}_2(\text{ia}) + \text{H}_2\text{O}(\text{l}) = 2\text{HF}(\text{a}) + \text{ZnO}(\text{l})$	-11.807	1.686
	$\text{ZnF}_2(\text{ia}) + \text{H}_2\text{O}(\text{l}) = 2\text{HF}(\text{a}) + \text{ZnO}(\text{a})$	-11.588	-0.27
	$\text{ZnF}_2 + 2\text{H}_2\text{O}(\text{l}) = 2\text{HF}(\text{a}) + \text{Zn}(\text{OH})_2$	-7.108	-3.930
	$\text{ZnF}_2(\text{ia}) + 2\text{H}_2\text{O}(\text{l}) = 2\text{HF}(\text{a}) + \text{Zn}(\text{OH})_2$	-5.567	3.433
ZrF4	$\text{ZrF}_4 + 2\text{H}_2\text{O}(\text{l}) = \text{ZrO}_2 + 4\text{HF}(\text{a})$	-9.537	-2.767
	$\text{ZrF}_4 + 2\text{H}_2\text{O}(\text{l}) = \text{ZrO}_2(\text{a}) + 4\text{HF}(\text{a})$	-21.118	-13.503
	$\text{ZrF}_4 + 4\text{H}_2\text{O}(\text{l}) = \text{Zr}(\text{OH})_4 + 4\text{HF}(\text{a})$	-4.285	-3.517
	$\text{ZrF}_4 + 3\text{H}_2\text{O}(\text{l}) = \text{ZrO}(\text{OH})_2 + 4\text{HF}(\text{a})$	-6.307	-3.058

Table A.3 - HSC Single Component Solubility Validation

	Species	Qualitative Solubility of Fluoride in Water	Quantitative Solubility of Fluoride in Water (grams per 100mL water (°C))	Expected kmol (per 100mL water)	HSC (kmol/.0055509 kmol water)	% Error
Alkali	LiF	Slightly Soluble	0.27 (18)	1.04E-05	5.48E-06	47.33
	RbF	Very Soluble	130.6 (18)	1.25E-03	1.25E-03	-0.15
	CsF	Very Soluble	367 (18)	2.42E-03	2.42E-03	-0.21
Alkaline Earth	BeF ₂	Very Soluble	Infinite in both		Infinite	
	SrF ₂	Soluble	0.011 (0), 0.012 (27)	9.55E-08	4.24E-07	-343.99
	BaF ₂	Slightly Soluble	0.12(25), sl s	6.84E-07	6.42E-07	6.22
	RaF ₂		---		2.41E-06	
Lanthanides	LaF ₃	Insoluble	---	Insoluble	3.98E-09	
	CeF ₄	Insoluble	Insoluble	Insoluble	1.25E-06	
	PrF ₄		---	Assumed insoluble	5.21E-09	
	NdF ₃	Insoluble	Insoluble	Insoluble	5.51E-09	
	Pm ₂ O ₃	---	---	Assumed insoluble	1.00E-06	
	SmF ₃	Reactive	Insoluble	Insoluble	2.05E-08	
	EuF ₃	Insoluble	Insoluble	Insoluble	1.89E-08	
	GdF ₃		Insoluble	Insoluble	3.98E-10	
	TbF ₃	---	Insoluble	Insoluble	3.16E-10	
	DyF ₃		Insoluble	Insoluble	1.00E-09	
	HoF ₃	Soluble	Insoluble	Insoluble	1.62E-09	
	ErF ₃	Insoluble	Insoluble	Insoluble	1.27E-09	
	TmF ₃	Soluble	Insoluble	Insoluble	1.00E-07	
YbF ₃	Insoluble	Insoluble	Insoluble	1.00E-07		
Actinides	AcF ₃	Insoluble	Insoluble	Insoluble	1.00E-15	
	ThF ₄			Assumed insoluble	3.16E-11	
	PaF ₅	---	---	Assumed insoluble	7.94E-06	
	NpF ₆	---	Decomposes	Assumed insoluble	3.09E-06	
	PuF ₄			Assumed insoluble	1.58E-05	
	AmF ₄		---	Assumed insoluble	1.26E-10	
	Cm ₂ O ₃	---	---	Assumed insoluble	1.00E-06	
	Cf	---	---	Assumed insoluble	No Cf ions in database	

Table A.3 - Cont.

Species	Qualitative Solubility of Fluoride in Water	Quantitative Solubility of Fluoride in Water (grams per 100mL water (°C))	Expected kmol (per 100mL water)	HSC (kmol/.0055509 kmol water)	% Error
ZnF ₂	Slightly Soluble	1.62 (20), Soluble (hot)	1.57E-05	5.07E-05	-223.56
GaF ₃	Insoluble	0.002 (cold), Insoluble (hot)	1.58E-08	7.18E-08	-355.13
YF ₃	Insoluble	Insoluble	Insoluble	4.68E-10	
ZrF ₄	Slightly Soluble	1.388 (25), Decomposes (hot)	8.30E-06	1.33E-09	99.98
RuF ₄	Reactive	---		No Ru ions in database	
RhF ₄	---	---	Assumed insoluble	1.00E-06	
PdF ₂	Reactive	Slightly Soluble, Decompose (cold)	Slightly Soluble	6.31E-07	
AgF ₂	Reactive	Decomposes		3.37E-05	
CdF ₂	Slightly Soluble	4.35 (25)	2.89E-05	1.18E-04	-309.32
InF ₃	Slightly Soluble	0.040 (25)	2.33E-07	3.72E-14	100.00
SnF ₄	Reactive	Very soluble (cold), Decomposes (hot)		Infinite in cold, Decomposes to Sn(+2a) above 25°C	
PbF ₄		---	Assumed insoluble	1.00E-06	
BiF ₄	---	---	Assumed insoluble	1.00E-06	

Transition Metals

Table A.4 - OLI Single Component Solubility Validation (FC = Failure to Converge, ND = Not in database)

	Species	Qualitative Solubility of Fluoride in Water	Quantitative Solubility of Fluoride in Water (grams per 100mL water (°C))	OLI (mol/100mL water)	OLI (g/100mL water)	% Error
Alkali	LiF	Slightly Soluble	0.27 (18)	0.0050	0.129	52.11
	RbF	Very Soluble	130.6 (18)	7.9202	827.393	-533.53
	CsF	Very Soluble	367 (18)	7.7871	1182.890	-222.31
Alkaline Earth	BeF ₂	Very Soluble	Infinite in both	ND		
	SrF ₂	Soluble	0.011 (0), 0.012 (27)	9.64E-04	0.121	-908.91
	BaF ₂	Slightly Soluble	0.12(25), sl s	8.92E-04	0.156	-30.35
	RaF ₂		---	4.04E-06	1.07E-03	
Lanthanides	LaF ₃	Insoluble	---	1.57E-06	3.07E-04	
	CeF ₄	Insoluble	Insoluble	ND		
	PrF ₄		---	ND		
	NdF ₃	Insoluble	Insoluble	2.80E-06	5.63E-04	
	Pm ₂ O ₃		---	ND		
	SmF ₃	Reactive	Insoluble	3.09E-06	6.41E-04	
	EuF ₃	Insoluble	Insoluble	2.26E-06	4.72E-04	
	GdF ₃		Insoluble	FC		
	TbF ₃		Insoluble	3.94E-06	8.50E-04	
	DyF ₃		Insoluble	FC		
	HoF ₃	Soluble	Insoluble	4.97E-06	1.10E-03	
	ErF ₃	Insoluble	Insoluble	FC		
	TmF ₃	Soluble	Insoluble	3.50E-05	7.92E-03	
	YbF ₃	Insoluble	Insoluble	8.26E-05	0.019	
Actinides	AcF ₃	Insoluble	Insoluble	ND		
	ThF ₄			2.22E+01	6839.228	
	PaF ₅		---	ND		
	NpF ₆		Decomposes	2.64E+01	9272.685	
	PuF ₄			FC		
	AmF ₄		---	FC		
	Cm ₂ O ₃		---	ND		
	Cf		---	ND		

Table A.4 - Cont.

Species	Qualitative Solubility of Fluoride in Water	Quantitative Solubility of Fluoride in Water (grams per 100mL water (°C))	OLI (mol/100mL water)	OLI (g/100mL water)	% Error	
ZnF ₂	Slightly Soluble	1.62 (20), Soluble (hot)	FC			
GaF ₃	Insoluble	0.002 (cold), Insoluble (hot)	ND			
YF ₃	Insoluble	Insoluble	9.40E-06	1.37E-03		
ZrF ₄	Slightly Soluble	1.388 (25), Decomposes (hot)	5.55E-06	9.28E-04	99.93	
RuF ₄	Reactive	---	ND			
RhF ₄	---	---	ND			
Transition Metals	PdF ₂	Reactive	Slightly Soluble, Decompose (cold)	ND		
	AgF ₂	Reactive	Decomposes	ND		
	CdF ₂	Slightly Soluble	4.35 (25)	3.02E-02	4.549	-4.57
	InF ₃	Slightly Soluble	0.040 (25)	ND		
	SnF ₄	Reactive	Very soluble (cold), Decomposes (hot)	ND		
	PbF ₄		---	ND		
	BiF ₄	---	---	ND		

Table A.5 - Activity Coefficients for Dissolution with Water Step of Figure 4.7

Speices	Activity Coeff.	Speices	Activity Coeff.	Speices	Activity Coeff.
H2O	0.86561	Gd(OH)2+1	0.66108	NpO2+2	0.28517
(HF)2 - Aq	1.5878	Gd(OH)3 - Aq	1.5878	NpO2F+1	0.66108
(NpO2)2(OH)2+2	0.28517	Gd(OH)4-1	0.47801	NPO2F2 - Aq	1.5878
(NpO2)3(OH)5+1	0.66108	Gd+3	0.077366	NpO2OH+1	0.66108
Ba+2	0.04063	GdF+2	0.28517	OH-1	0.62385
BaF+1	0.66108	GdF2+1	0.66108	Pu(OH)2+2	0.28517
BaOH+1	0.66108	GdF3 - Aq	1.5878	Pu(OH)3+1	0.66108
Cd(OH)2 - Aq	1.5878	GdF4-1	0.47801	Pu(OH)4 - Aq	1.59E+00
Cd(OH)3-1	0.49123	GdOH+2	0.28517	Pu+4	3.34E-04
Cd(OH)4-2	0.05327	H+1	0.55111	PuF2+2	0.28517
Cd+2	0.2166	H2ZrF6 - Aq	1.5878	PuF3+1	0.66108
CdF+1	0.66108	HF - Aq	1.6493	PuF3+3	0.077366
CdF2 - Aq	1.5878	HF2-1	0.84415	PuF4 - Aq	1.5878
CdOH+1	0.62725	Ho(OH)2+1	0.66108	PuOH+3	0.077366
Cs+1	0.66108	Ho(OH)3 - Aq	1.5878	Ra+2	0.28517
Dy(OH)2+1	0.66108	Ho(OH)4-1	0.47801	RaF+1	0.66108
Dy(OH)3 - Aq	1.5878	Ho+3	0.077365	RaF2 - Aq	1.5878
Dy(OH)4-1	0.47801	HoF+2	0.28517	RaOH+1	0.66108
Dy+3	0.077366	HoF2+1	0.66108	Rb+1	0.6457
DyF+2	0.28517	HoF3 - Aq	1.5878	Sm(OH)2+1	0.66108
DyF2+1	0.62725	HoF4-1	0.47801	Sm(OH)3 - Aq	1.5878
DyF3 - Aq	1.5878	HoOH+2	0.28517	Sm(OH)4-1	0.47801
DyF4-1	0.47801	HZrF6-1	0.47801	SM+3	0.077366
DyOH+2	0.28517	La(OH)2+1	0.66108	SmF+2	0.28517
Er(OH)2+1	0.66108	La(OH)3 - Aq	1.5878	SmF2+1	0.66108
Er(OH)3 - Aq	1.5878	La(OH)4-1	0.47801	SmF3 - Aq	1.5878
Er(OH)4-1	0.47801	La+3	0.077366	SmF4-1	0.47801
Er+3	0.077366	LaF+2	0.068673	SmOH+2	0.28517
ErF+2	0.28517	LaF2+1	0.66108	Sr+2	0.045941
ErF2+1	0.66108	LaF3 - Aq	1.5878	SrF+1	0.66108
ErF3 - Aq	1.5878	LaF4-1	0.47801	SrOH+1	0.66108
ErF4-1	0.47801	LaOH+2	0.28517	Tb(OH)2+1	0.66108
ErOH+2	0.28517	Li+1	0.44716	Tb(OH)3 - Aq	1.5878
Eu(OH)2+1	0.66108	LiOH - Aq	1.5878	Tb(OH)4-1	0.47801
Eu(OH)3 - Aq	1.5878	Nd(OH)2+1	0.66108	Tb+2	0.28517
Eu(OH)4-1	0.4779	Nd(OH)3 - Aq	1.5878	Tb+3	0.077366
Eu+3	0.077367	Nd(OH)4-1	0.47801	TbF2+1	0.66108
EuF+2	0.28517	Nd+3	0.077366	TbF3 - Aq	1.5878
EuF2+1	0.66108	NdF+2	0.28517	TbF4-1	0.47801
EuF3 - Aq	1.5878	NdF2+1	0.66108	TbOH+2	0.28517
EuF4-1	0.47801	NdF3 - Aq	1.5878	Th(OH)2+2	0.28517
EuOH+2	0.28517	NdF4-1	0.47801	Th(OH)3+1	0.66108
F-1	0.50957	NdOH+2	0.28517	Th(OH)4 - Aq	1.59E+00

Table A.5 - Cont.

Speices	Activity Coeff.	Speices	Activity Coeff.	Speices	Activity Coeff.
Th ₂ (OH) ₂ +6	8448.5	Y(OH) ₄ -1	0.47801	Zn(OH) ₄ -2	0.052162
ThF ₃	0.077365	Y ⁺³	0.077366	Zn ⁺²	0.072213
ThF ₂ +2	0.28517	Yb(OH) ₂ +1	0.66108	ZnF ⁺¹	0.62725
ThF ₃ +1	0.66108	Yb(OH) ₃ - Aq	1.5878	ZnOH ⁺¹	0.66108
ThF ₄ - Aq	1.5878	Yb(OH) ₄ -1	0.47801	Zr(OH) ₂ +2	0.28526
ThOH ₃	0.077366	Yb ⁺³	0.077366	Zr(OH) ₃ +1	0.66109
Tm(OH) ₂ +1	0.66108	YbF ⁺²	0.28517	Zr(OH) ₄ - Aq	1.5878
Tm(OH) ₃ - Aq	1.5878	YbF ₂ +1	0.66108	Zr(OH) ₅ -1	4.78E-01
Tm(OH) ₄ -1	0.47801	YbF ₃ - Aq	1.5878	Zr ⁺⁴	5.98E-03
Tm ⁺³	0.077366	YbF ₄ -1	0.47801	ZrF ⁺³	0.077213
TmF ⁺²	0.28517	YbOH ⁺²	0.28517	ZrF ₂ +2	0.28526
TmF ₂ +1	0.66108	YF ⁺²	0.28517	ZrF ₃ +1	0.66109
TmF ₃ - Aq	1.5878	YF ₂ +1	0.66108	ZrF ₄ - Aq	1.5878
TmF ₄ -1	0.47801	YF ₃ - Aq	1.5878	ZrF ₅ -1	0.47801
TmOH ₂	0.28517	YOH ⁺²	0.28517	ZrF ₆ -2	0.052162
Y(OH) ₂ +1	0.66108	Zn(OH) ₂ - Aq	1.5878	ZrOH ⁺³	0.07742
Y(OH) ₃ - Aq	1.5878	Zn(OH) ₃ -1	0.47801		

Table A.6 - Activity Coefficients for Precipitation with KOH Step of Figure 4.7

Speices	Activity Coeff.	Speices	Activity Coeff.	Speices	Activity Coeff.
H2O	0.23791	H2ZrF6 - Aq	133.85	SmF+2	885.6
(HF)2 - Aq	133.85	HF - Aq	133.85	SmF2+1	3.5288
(NpO2)2(OH)2+2	885.61	HF2-1	4.1198	SmF3 - Aq	133.85
(NpO2)3(OH)5+1	3.5288	Ho(OH)2+1	3.5288	SmF4-1	0.3767
Ba+2	4.97E-04	Ho(OH)3 - Aq	133.85	SmOH+2	885.61
BaF+1	3.5288	Ho(OH)4-1	0.3767	Sr+2	9.96E-04
BaOH+1	3.5288	Ho+3	5.93E+05	SrF+1	3.5288
Cd(OH)2 - Aq	133.85	HoF+2	885.61	SrOH+1	3.5288
Cd(OH)3-1	0.3767	HoF2+1	3.5288	Tb(OH)2+1	3.5289
Cd(OH)4-2	0.020135	HoF3 - Aq	133.85	Tb(OH)3 - Aq	133.85
Cd+2	885.57	HoF4-1	0.3767	Tb(OH)4-1	0.3767
CdF+1	3.5288	HoOH+2	885.61	Tb+2	885.61
CdF2 - Aq	133.85	HZrF6-1	0.3767	Tb+3	5.93E+05
CdOH+1	3.5288	K+1	4.8949	TbF2+1	3.5288
Cs+1	3.5288	Li+1	0.1643	TbF3 - Aq	133.85
Er(OH)2+1	3.5288	LiOH - Aq	133.85	TbF4-1	0.3767
Er(OH)3 - Aq	133.85	Nd(OH)2+1	3.5288	TbOH+2	885.61
Er(OH)4-1	0.3767	Nd(OH)3 - Aq	133.85	Tm(OH)2+1	3.5288
Er+3	5.93E+05	Nd(OH)4-1	0.3767	Tm(OH)3 - Aq	133.85
ErF+2	885.61	Nd+3	5.93E+05	Tm(OH)4-1	0.3767
ErF2+1	3.5288	NdF+2	885.61	Tm+3	5.93E+05
ErF3 - Aq	133.85	NdF2+1	3.5288	TmF+2	885.61
ErF4-1	0.3767	NdF3 - Aq	133.85	TmF2+1	3.5288
ErOH+2	885.61	NdF4-1	0.3767	TmF3 - Aq	133.85
Eu(OH)2+1	3.5288	NdOH+2	885.61	TmF4-1	0.3767
Eu(OH)3 - Aq	133.85	NpO2+2	885.6	TmOH+2	885.6
Eu(OH)4-1	0.3767	NpO2F+1	3.5288	Y(OH)2+1	3.5288
Eu+3	5.93E+05	NPO2F2 - Aq	133.85	Y(OH)3 - Aq	133.85
EuF+2	885.61	NpO2OH+1	3.5288	Y(OH)4-1	0.3767
EuF2+1	3.5289	OH-1	10.178	Y+3	5.93E+05
EuF3 - Aq	133.85	Pu(OH)2+2	885.61	Yb(OH)2+1	3.5289
EuF4-1	0.3767	Pu(OH)3+1	3.5288	Yb(OH)3 - Aq	133.85
EuOH+2	885.61	Pu(OH)4 - Aq	133.85	Yb(OH)4-1	0.3767
F-1	3.9344	Pu+4	78.103	Yb+3	5.93E+05
Gd(OH)2+1	3.5288	PuF2+2	885.61	YbF+2	885.61
Gd(OH)3 - Aq	133.85	PuF3+1	3.5288	YbF2+1	3.5288
Gd(OH)4-1	0.3767	PuF3+3	5.93E+05	YbF3 - Aq	133.85
Gd+3	5.93E+05	PuF4 - Aq	133.85	YbF4-1	0.3767
GdF+2	885.61	PuOH+3	5.93E+05	YbOH+2	885.61
GdF2+1	3.5289	Rb+1	2.8002	YF+2	885.61
GdF3 - Aq	133.85	Sm(OH)2+1	3.5288	YF2+1	3.5289
GdF4-1	0.3767	Sm(OH)3 - Aq	133.85	YF3 - Aq	133.85
GdOH+2	885.6	Sm(OH)4-1	0.3767	YOH+2	885.61
H+1	0.71535	SM+3	5.93E+05	Zr(OH)2+2	885.76
Zr(OH)3+1	3.5288	ZrF+3	5.92E+05	ZrF5-1	0.3767
Zr(OH)4 - Aq	133.85	ZrF2+2	885.75	ZrF6-2	0.020135
Zr(OH)5-1	0.3767	ZrF3+1	3.5288	ZrOH+3	5.94E+05
Zr+4	1.73E+12	ZrF4 - Aq	133.85		

Table A.7 - Activity Coefficients for KF Removal Step of Figure 4.7

Speices	Activity Coeff.	Speices	Activity Coeff.	Speices	Activity Coeff.
H2O	0.3026	H2ZrF6 - Aq	63.811	SmF3 - Aq	63.811
(HF)2 - Aq	6.38E+01	HF - Aq	63.811	SmF4-1	0.36942
Ba+2	7.46E-04	HF2-1	2.5882	SmOH+2	240.57
BaF+1	2.5631	Ho(OH)2+1	2.5631	Tb(OH)2+1	2.5631
BaOH+1	2.5631	Ho(OH)3 - Aq	63.811	Tb(OH)3 - Aq	63.811
Dy(OH)2+1	2.5631	Ho(OH)4-1	0.36942	Tb(OH)4-1	0.36942
Dy(OH)3 - Aq	63.811	Ho+3	49266	Tb+2	240.57
Dy(OH)4-1	0.36942	HoF+2	240.57	Tb+3	49269
Dy+3	49269	HoF2+1	2.5631	TbF2+1	2.5631
DyF+2	240.57	HoF3 - Aq	63.811	TbF3 - Aq	63.811
DyF2+1	2.5631	HoF4-1	0.36942	TbF4-1	0.36942
DyF3 - Aq	6.38E+01	HoOH+2	240.57	TbOH+2	240.57
DyF4-1	3.69E-01	HZrF6-1	0.36942	Th(OH)2+2	240.57
DyOH+2	240.57	K+1	3.3431	Th(OH)3+1	2.5631
Er(OH)2+1	2.56E+00	La(OH)2+1	2.5631	Th(OH)4 - Aq	63.811
Er(OH)3 - Aq	6.38E+01	La(OH)3 - Aq	63.811	Th+4	3.52E-13
Er(OH)4-1	0.36942	La(OH)4-1	0.36942	Th2(OH)2+6	0
Er+3	49263	La+3	49265	ThF+3	49266
ErF+2	240.57	LaF+2	0.018626	ThF2+2	240.57
ErF2+1	2.5631	LaF2+1	2.5631	ThF3+1	2.5631
ErF3 - Aq	6.38E+01	LaF3 - Aq	63.811	ThF4 - Aq	63.811
ErF4-1	0.36942	LaF4-1	0.36942	ThOH+3	49266
ErOH+2	2.41E+02	LaOH+2	240.57	Y(OH)2+1	2.5631
Eu(OH)2+1	2.56E+00	Nd(OH)2+1	2.5631	Y(OH)3 - Aq	63.811
Eu(OH)3 - Aq	63.811	Nd(OH)3 - Aq	63.811	Y(OH)4-1	0.36942
Eu(OH)4-1	0.36942	Nd(OH)4-1	0.36942	Y+3	49265
Eu+3	49269	Nd+3	4.93E+04	YF+2	240.57
EuF+2	240.57	NdF+2	240.57	YF2+1	2.5631
EuF2+1	2.56E+00	NdF2+1	2.5631	YF3 - Aq	63.811
EuF3 - Aq	6.38E+01	NdF3 - Aq	63.811	YOH+2	240.57
EuF4-1	3.69E-01	NdF4-1	0.36942	Zr(OH)2+2	243.46
EuOH+2	2.41E+02	NdOH+2	240.57	Zr(OH)3+1	2.5634
F-1	3.38E+00	OH-1	7.4819	Zr(OH)4 - Aq	63.811
Gd(OH)2+1	2.5631	Ra+2	240.57	Zr(OH)5-1	0.36942
Gd(OH)3 - Aq	63.811	RaF+1	2.5631	Zr+4	3.46E+10
Gd(OH)4-1	0.36942	RaF2 - Aq	63.811	ZrF+3	44727
Gd+3	49266	RaOH+1	2.5631	ZrF2+2	243.46
GdF+2	240.57	Sm(OH)2+1	2.5631	ZrF3+1	2.5634
GdF2+1	2.5631	Sm(OH)3 - Aq	63.811	ZrF4 - Aq	63.811
GdF3 - Aq	63.811	Sm(OH)4-1	0.36942	ZrF5-1	0.36942
GdF4-1	0.36942	SM+3	49265	ZrF6-2	0.018624
GdOH+2	240.57	SmF+2	240.57	ZrOH+3	51275
H+1	0.66068	SmF2+1	2.5631		

Vita

Jennifer LeAnn Ladd was born in Knoxville, TN on February 25, 1980. She was raised in Roane County, TN and went to elementary school at Dyllis Elementary School in Harriman. She attended Oliver Springs Elementary School for junior high school. Jennifer graduated as valedictorian from Oliver Springs High School in 1998. From there, she received an A.S. in Chemical Engineering from Roane State Community College in 2000. After receiving her A.S., Jennifer transferred to Tennessee Technological University in Cookeville, TN where she received a B.S. in Chemical Engineering in 2002 with a minor in chemistry and mathematics. Upon graduation from TTU, she received a graduate fellowship from the US DOE AFCI program. Jennifer pursued graduate studies at the University of Tennessee, Knoxville and received a M.S. in Chemical Engineering in 2004. Jennifer was married in May 2003. Currently, Jennifer L. Ladd-Lively is working at ORNL and pursuing her doctorate in chemical engineering at the University of Tennessee, Knoxville.