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System Design Description and Requirements for Modeling the Off-Gas Systems for Fuel Recycling Facilities

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ACRONYMS

AtC	Atomistic-to-Continuum
AFCF	Advanced Fuel Cycle Facility
CETE	coupled end-to-end (pilot plant facility at Oak Ridge)
COG	cell off-gas
CT	Capability Transfer
DF	decontamination factor
DOG	dissolver off-gas
EAS	Engineering Alternative Studies
ECT	Enabling Computational Technologies
FCR&D	Fuel Cycle Research and Development
FMM	Fundamental Methods and Models
GCMD	Grand Cononical Molecular Dynamics
GWd/MT	giga-watt days per metric ton
HWC	Hazardous Waste Combustor
ICPP	Idaho Chemical Processing Plant
IPSC	Integrated Performance and Safety Codes
LWR	light water reactor
MACT	Maximum Achievable Control Technology
MOF	metal organic framework
MTU	metric tons uranium
NEAMS	Nuclear Energy Advanced Modeling and Simulation
NESHAPS	National Emission Standards for Hazardous Air Pollutants
NRC	Nuclear Regulatory Commission
PFD	process flow diagram
SafeSep	Safeguard and Separations
VOG	vessel off-gas
VU	Verification, Validation and Uncertainties Quantification
WAK	Wiederaufarbeitungsanlage Karlsruhe, refers to WAK operation company
WOG	waste processing off-gas

NEAMS CAMPAIGN/SAFESEP IPSC
SYSTEM DESIGN DESCRIPTION AND REQUIREMENTS FOR MODELING THE OFF-GAS SYSTEMS FOR FUEL RECYCLING FACILITIES, REV 1

1. INTRODUCTION

1.1 Background

The Department of Energy's Nuclear Energy Advanced Modeling and Simulation (NEAMS) Program has been established to rapidly create, and deploy next generation, verified and validated nuclear energy modeling and simulation capabilities for the design, implementation, and operation of future nuclear energy systems to improve the U.S. energy security future. The program elements of the NEAMS Program are described below.

1.1.1 Integrated Performance and Safety Codes (IPSC)

The IPSC's are end-to-end codes developed to understand the detailed integrated performance of new nuclear processes. The four IPSC areas include Safeguards and Separations, Reactors, Fuels and Waste Forms.

1.1.2 Fundamental Methods and Models (FMM)

Includes smaller length scale material modeling work, and Atomistic-to-Continuum (AtC) multi-scale simulation. This modeling provides understanding and improved properties and models for integrated codes. This element also identifies and drives small scale experimentation necessary to generate the data needed for physical and engineering models.

1.1.3 Verification, Validation and Uncertainties Quantification (VU)

The purpose is to develop and implement the methodologies required to understand and document the boundaries and uncertainties. This process will ensure the modeling work is performed with the proper pedigree to meet requirements for use in future facility design. This element provides a principal interface to the Nuclear Regulatory Commission (NRC).

1.1.4 Capability Transfer (CT)

NEAMS success depends on use of capabilities by the nuclear energy industry and licensing bodies. This includes strategies such as turning scientific codes into engineering tools to be used by industry. This element also includes working to improving the "usability" of high performance computer codes and systems.

1.1.5 Enabling Computational Technologies (ECT)

An essential element of NEAMS is to ensure that the enabling technologies are available to make the first four program elements possible. This includes computational science supporting technologies that include programming tools, model setup, and results analysis (e.g. visualization). This element also includes development of the platforms required to support the code development and the application work

Development of the requirements for off-gas modeling falls under the Safeguard and Separations (SafeSep) IPSC. The vision of the Safeguards SafeSep IPSC effort is the development of integrated plant models that allow dynamic simulations of the performance of separations plants and integrated safeguards of various configurations and operating conditions. The codes will be developed on modern, expandable architecture with flexibility to explore and evaluate a wide range of process options. Plant-level models will initially incorporate relatively simple models for each process. Codes will incorporate the capability to bridge to subscale models to provide required fidelity in chemical and physical processes. Several "challenge problems" have been proposed for the SafeSep IPSC including:

- ***Enable a significant advance in modeling of separations processes: Multiphysics modeling of unit operations in separations processes, informed by experimental data:***
    - Aqueous: Enable prediction of stage efficiency in a contactor for given conditions and a means of up scaling to plant-level unit operations models.
    - E-chem: electrorefiner including thermodynamics and kinetics; electrode current efficiency; contamination effects.
    - Dry processes: Fundamental models of gas-solid systems characteristic of voloxidation and halide volatility.
- ***Demonstration of end-to-end dynamic plant modeling capability***
    - The capability will be demonstrated first for the PUREX plant, because of the relative abundance of data for the PUREX process.
- ***Agent Design to Process Design - Extend capability of molecular level modeling to separations systems***
    - Solvent extraction – predict distribution coefficients and interfacial transport.
- ***Off-gas Modeling – Develop molecular level models of phenomena of importance in gas-treatment systems***
    - Iodine Capture – fundamental mechanisms of capture and mass transport in silver-based and novel sorbents.
- ***Develop performance models for advanced monitoring technologies including those under development in the Materials Protection, Accounting, and Control Technologies Campaign***
    - Performance of Hybrid K-Edge Densitometry, Lead Slowing Down Spectroscopy, Ultra-High Resolution Spectrometry/Microcalorimetry.

Development of the modeling requirements for the separations off-gas system clearly is part of the Off-Gas Modeling Challenge Problem.

1.2 Overview of Plant Level Toolkit

An integrated reprocessing plant is envisioned as a collection of all physico-chemical processes needed to transform spent nuclear fuel into new fuel and waste forms matching the stringent specifications of the product and waste processes. While existing reprocessing technology options deliver high quality products efficiently and robustly, they do not meet the challenges of minimizing waste, effluents, proliferation risk, environmental impact, and cost. Hence here lies the opportunity for modeling and simulation to play a role in the future design of a US reprocessing plant.

The 10-year vision for this IPSC is the development of a fully integrated, dynamic, plant-level simulator able to design, optimize, control, operate and safeguard a reprocessing plant in a similar way flight simulators operate in the aircraft industry. In view of the breadth of processes involved in a reprocessing plant it is advantageous to begin the task of implementing integrated performance and safety codes (IPSC) by considering a dynamic plant-level simulation capability that spans the entire plant. This capability would enable early feasibility analysis of existing and emerging reprocessing technology, and more importantly would help identify areas of research and development needed to improve the simulation tool. To assure the longevity of the simulation capability, models should be modular, extensible, hierarchal and aligned with a long term vision to operate, control, and protect the reprocessing plant. In order to help prioritize and organize the task of designing modules and implementing corresponding codes, a plant can be viewed as a three-tier set of modules as illustrated by Figure 1.

The top tier is a collection of discrete event models that provides throughput analysis, scheduling impacts, and output compositions. Models at this level generally summarize significant sections of the separations plant or collection of sections. These high-level models (i.e. zero-dimensional models for which elapsed time is the principal variable) can use the simulation environment to call supporting simulations at other levels of (finer) detail not captured in discrete event simulations, such as those described by rigorous chemical process models. Depending on the level of detail in the sub models selected, discrete event models require the least amount of computer cycles from the pool of computers attached to the problem solving environment; say a few processors to several dozens of processors.

In the middle tier, macroscopic process models are designed to represent a specific unit operation or group of operations within the facilities. Models at this level are modular and may actually consist of several interchangeable models for the same separations plant section at varying levels of detail. For instance, modules for a space-time averaged one-dimensional versus a two-dimensional fluid flow model of a chemical reactor. The models are typically based on well-founded physical approximations that meet the accuracy requirements of the analysis. For example, a well-mixed chemical reactor might be represented by a point calculation to determine output composition. Macroscopic models can also use decision logic in the simulation environment to call other process models or models at other levels of detail. The requirement for computing power at this level may be on the order of tens to hundreds or thousands of processors depending on the sub models chosen.

In the bottom tier, first-principles models can be developed to address specific computer-intensive calculations needed to accurately describe time-dependent, three-dimensional (or higher dimensional) systems. For example, these models could include solid thermo-mechanics with microstructure, turbulent fluid flow, micro-nano flows, molecular dynamics, molecular mechanics, quantum mechanics calculations, and radiation transport if it is necessary to adequately model the system of interest. Computing power requirements at this level could be the highest available; up to hundreds of thousands of processors.

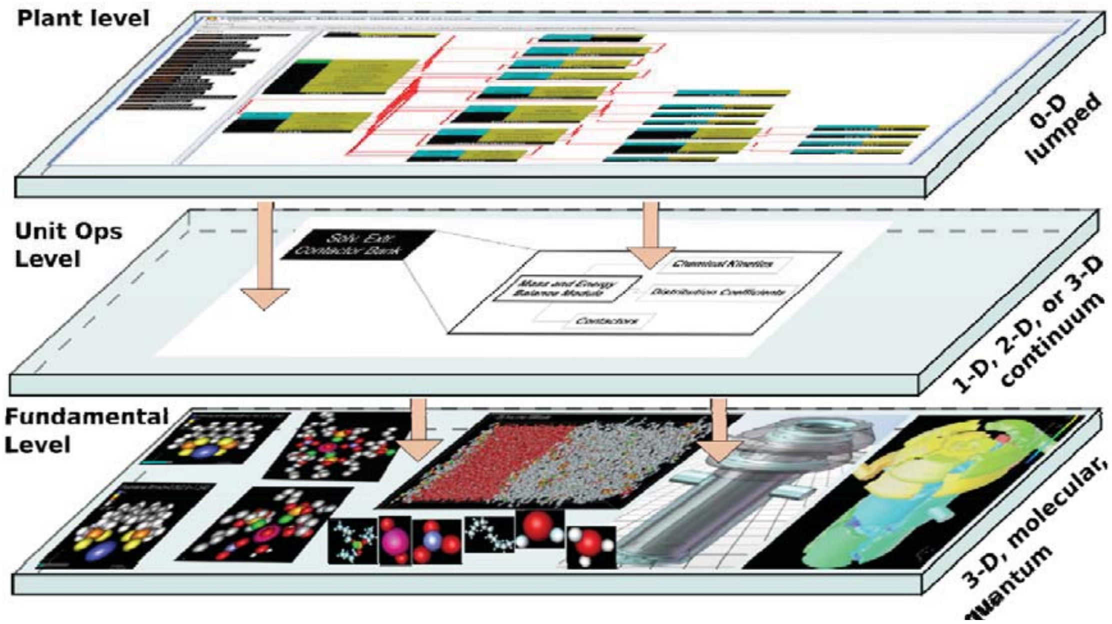

Figure 1. Tiered grouping of models and codes for a reprocessing plant. Top-down implementation approach guides development and determines research priority on lower tiers.

1.3 Overview of Separations Campaign Off-gas Sigma Team

The Fuel Cycle Research and Development (FCR&D) Separations and Waste Form Campaign is focused on goal-oriented, science-based R&D of separation and waste form processes to support development of sustainable nuclear fuel cycles. This includes evolutionary and transformational research that supports simplification of aqueous separation schemes to reduce cost of the fuel recycle, continued improvement and feasibility testing of electrochemical fuel recycle methods, on-line processing monitoring methods to provide real-time process information, transformational sampling methods to reduce waste and sampling uncertainties, development of glass and metal waste forms, and evaluation of glass and metal waste form performance . This effort includes research being performed by the Sigma Team for Off-Gas Capture and Immobilization. The scope of the Off-Gas Sigma Team is to perform fundamental studies to examine the pretreatment methods, chemical mechanisms of retention, stability, regeneration, in-situ aging, and immobilization issues applicable to available materials for treatment of off-gas streams arising from head-end operations of a used nuclear fuel processing facility. Starting with the highest priority elements, materials for capture and immobilization of iodine, tritium and krypton are being evaluated for implementation across the entire head-end processing operation. These studies are being conducted using cold and/or traced simulant off-gas streams in a small scale system. The Off-Gas Sigma Team is being led by Oak Ridge National Laboratory with support from the Idaho National Laboratory, Sandia National Laboratories, and Pacific Northwest Laboratory.

1.4 Scope of Off-Gas Modeling Effort

One of the proposed Challenge Problems of the SafeSep IPSC is “Off-gas Modeling.” To that end, an effort is being initiated for modeling the off-gas system of used fuel recycling processes. Modeling of the off-gas system will be integrated with the separation process models being developed separate from this effort. This will support the IPSC’s goal of the development of an end-to-end code for evaluation of the detailed integrated performance of proposed separation processes, as well as integrated performance of proposed off-gas systems independent of separations processes. Detailing the requirements of the off-gas modeling effort, prior to initiation of modeling efforts, is the primary purpose of this document.

The FCR&D Separations Campaign and the Off-Gas Sigma Team within this campaign will be one of the primary users of off-gas modeling. Therefore, the SafeSep IPSC team members worked closely with the Separations Campaign and Sigma Team in developing the requirements of this effort. The modeling effort will initially focus on development of individual unit operation models that can be incorporated into an overall plant-level model. Efforts will focus on the development of a dynamic plant level model as opposed to steady-state modeling of the system. This will allow for evaluation of the response of the system to startup, shutdown, step changes to operating conditions, and system response to upset conditions. Fundamental modeling to support these unit operation models is also considered very important in the overall modeling efforts for the off-gas system and will be developed and integrated into the plant level model. Immobilization of the captured off-gas products into an appropriate waste form is considered outside of the scope of the SafeSep IPSC and models should be developed as part of the Waste Forms IPSC.

The scope of this document is to develop the requirements for this modeling effort and obtain input/agreement from the Separations Campaign prior to the initiation of model development. Specifically, the scope includes:

- Identification of the off-gas unit operations to model. This includes off-gas unit operations for aqueous and electrochemical processing. It is understood that specific unit operations are under development and it is unknown at this time what unit operations may be required to support off-gas treatment of a used nuclear fuel recycling process. The framework for the overall modeling effort will, therefore, allow for various unit operations to be incorporated for comparison.
- Identification of the major components to be modeled, initial source term for the off-gas feed, and decontamination requirements for off-gas treatment. Again, the off-gas model must be flexible to allow for variation in these parameters to be evaluated.
- Recommendation of initial modeling efforts for each of the unit operations to support development of the plant-level model. These recommendations will be based on the priorities of the Off-gas Sigma Team and the data gaps identified by the Sigma Team.

1.5 Major Gaseous Emissions of Interest

The primary concern with airborne radionuclides is their mobility in the environment and the potential to deliver a dose to the general public. After a relatively short cooling period (several months), the list of gaseous radionuclides of concern is usually limited to H-3, C-14, Kr-85 and I-129. Ruthenium (Ru-106) is also known to form gaseous species (RuO_4) and may also require emission control. In addition, releases of semi-volatiles like cesium (Cs-137) and particulate radionuclides must also be limited.

DOE and other federal facilities are regulated for radioactive emissions under 40 CFR 61, National Emission Standards for Hazardous Air Pollutants (NESHAPS). Two limits exist, one for total radionuclide emissions, and one for iodine emissions. 40 CFR 61 Subpart H and Subpart I limit the estimated effective dose equivalent received by any member of the public from those emissions to less than 10 mRem/yr for total radionuclides, and 3 mRem/yr for iodine. Pollutant dispersion after the emissions leave the stack and prior to potential human exposure is considered in addition to the actual amounts and kinds of radionuclides emitted.

Commercial operations that are part of a nuclear fuel cycle are regulated for radionuclide emissions under 40 CFR 190, “Environmental Radiation Protection Standards for Nuclear Power Operations.” 40 CFR 190.10(a) limits annual dose equivalents to any member of the public from these operations to 25 mRem to the whole body, 75 mRem to the thyroid, and 25 mRem to any other organ. 40 CFR 190.10(b) limits emissions to the environment during the entire uranium fuel cycle, per gigawatt-year of electrical energy produced by the fuel cycle, to less than 50,000 Ci of krypton-85, 5 mCi of iodine-129, and 0.5 mCi combined plutonium-239 and other alpha-emitting transuranic radionuclides with half-lives greater than one year.

Dose calculations have been performed to estimate the capture efficiency required to meet the regulatory requirements outlined above. Several assumptions were necessary to make the calculations manageable. Significant among these is the conservative assumption that each radionuclide is captured to the extent that it contributes less than 0.1 mrem/yr to a maximally exposed individual. With this approach, the decontamination factor (DF) for individual radionuclides is a function of the reprocessing plant size – the larger the fuel throughput, the higher the DF must be. For example, it was estimated that a plant processing 100 metric tons/yr would require an I-129 system DF of about 10^3, while a 1000 MT/yr plant would require a DF of about 10^4. Similar estimates were made for H-3, C-14, and Kr-85 and appear in Table 1. These values are considered rough guidelines since several assumptions including the fuel type, plant design, and local meteorological conditions will affect the dose calculations. For more information on the calculation approach and assumptions, the reference source should be consulted (Soelberg 2008).

Table 1. Estimated DFs required for selected gaseous radionuclides.

Radionuclide	Target DF
I-129	10^3 to 10^4
H-3	10^2 to 10^3
Kr-85	10 to 10^2
C-14	none to <10

NO_x will likely be generated in significant quantities from dissolving spent fuel as well as any thermal operations (evaporators, calciners, steam reformers, melters, etc.) involving nitrate-bearing streams. It is anticipated that NO_x will be captured and recombined as HNO_3, and then recycled back to the process. Not only is this due to the potential emission restrictions on NO_x, but also to the cost benefit of recycling HNO_3. An emission limit on NO_x for a reprocessing plant is not clearly defined – for example 40 CFR 61, National Emission Standards for Hazardous Air

Pollutants (NESHAPS), Subpart EEE, Final Standards for Hazardous Air Pollutants for Hazardous Waste Combustors, also known as the Hazardous Waste Combustor (HWC) Maximum Achievable Control Technology (MACT) does not regulate NO_x emissions. In the absence of a federal standard, a state limit is assumed to apply. For the state of Idaho, an emission rate above 40 tons/yr for total nitrogen oxides (as NO_2) is deemed to be "significant" (IDAPA 1994). Although not an emission limit, this value can be used to determine a target emission value. Using conservative assumptions including: (1) a total off-gas flow rate of 1700 dry m^3/yr and (2) 100% operating time per year (8,760 hrs/yr), a target emission value of about 1000 ppm NO_x was estimated (Haefner 2007a).

Emission rates for other air pollutants such as Cl_2, H_2S, SO_2, mercury, hydrocarbons, particulate matter, semi-volatile metals (Cd, Pb), and low volatility metals (As, Cr) are regulated under federal and/or state regulations. These air pollutant species are either not expected to be emitted in significant amounts or their generation rates are not known well enough to be useful for modeling at the present time.

1.6 Reference Cases

Reference cases were chosen for both aqueous and electrochemical processing. There currently are no baseline off-gas processes since off-gas treatment is in the research and development phase. The reference cases presented below are, therefore, one potential method for off-gas treatment and are used to establish a starting point for development of a plant-level model. It is expected that the reference case for the model will evolve as data become available, the model will be used for comparison of the integration of various unit operations, and the model will ultimately be used to aid in the development of a baseline flowsheet.

1.6.1 Aqueous Processing

The block flow diagram of Figure 2 shows the significant off-gas streams associated with aqueous fuel reprocessing. The voloxidation and dissolver off-gases (DOG) contain most of the gaseous fission products of concern. However, depending on the removal efficiency required for iodine, streams relatively low in iodine concentration may also be targeted for emission control. These could include the vessel off-gas (VOG), waste processing off-gas (WOG), and even the cell off-gas (COG).

The process information presented below is accumulated from several sources and significant variability in the process conditions exist. The most complete information is from the Advanced Fuel Cycle Facility (AFCF) preliminary design, which assumed a process throughput of 25 metric tons of LWR fuel in 240 days (AFCF 2007b). The AFCF design admittedly used an unrealistic fuel source to provide an upper bounding limit for its gaseous radionuclide source term. More realistic information was obtained in the literature for actual processing facilities such as the reprocessing plant at Karlsruhe (WAK).

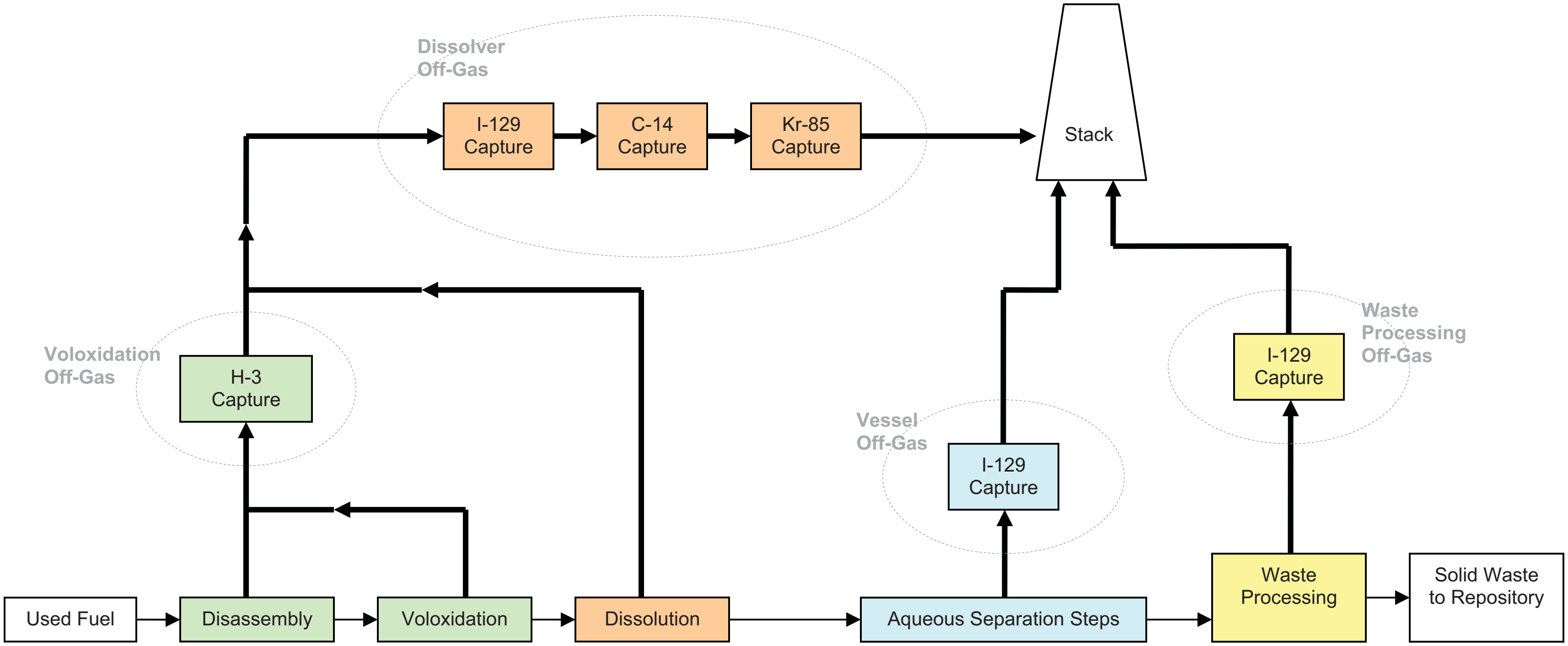

Figure 2. Bounding the Off-Gas Problem for Aqueous Reprocessing (modified from Jubin 2010).

1.6.1.1 Voloxidation Off-gas and Capture System

Voloxidation is a thermal processing step to condition the fuel prior to dissolution. Although conditions may vary, the basic operation involves heating chopped fuel pieces (with cladding) to 450 to 650°C in air or oxygen-enriched atmosphere. The fuel is oxidized from UO_2 to U_3O_8, which causes the fuel to undergo significant structural changes and results in the fuel crumbling into small particles with the simultaneous release of volatile fission products. Tritium is effectively removed (>99.9% release at 480°C in 3 to 4 hours) by this process and reacts in the hot volox atmosphere to form water vapor. Other volatiles are also released but to a lesser extent than tritium; their fractional release dependent on the specific operating conditions (AFCF 2007a). Representative parameters for the reference case voloxidation off-gas are the following:

- Voloxidizer temperature: 480°C (although AFCF design assumed 350°C per PFD[*])
- Atmosphere/feed gas: air (although AFCF design assumed 98.5% O_2/1.5% N_2 per PFD[*])
- Sweep gas/infiltration rate: 2.64 kg/hr air – assumes 50% excess oxygen above that required for the reaction UO_2 to U_3O_8. Note the stoichiometric oxygen rate is 0.409 kg/hr O_2 for a UO_2 feed rate of 10.354 kg/hr. (AFCF design assumed 0.487 kg/hr of oxygen mixture noted above, per PFD[*])
- Solids feed rate: 11.87 kg/hr total solids (9.128 kg/hr U or 10.354 kg/hr UO_2)
- Release fraction: tritium – 100%
- Capture technology: adsorption on molecular sieve 3A

For the reference case, tritiated water is captured prior to the volox off-gas being combined with the dissolver off-gas. This concept is illustrated in the block flow diagram shown in Figure 3. Any fractional amounts of krypton, C-14, or iodine released during voloxidation would presumably be carried to the more extensive capture system associated with the dissolver off-gas. Additional options to be considered for modeling the voloxidation off-gas could include:

- Ru release (presumably as RuO_4) and capture
- Particulate capture

1.6.1.2 Dissolver Off-gas(DOG) and Capture System

Dissolution is carried out by submerging the solids (spent fuel and cladding) discharged from the voloxidizer in a solution of hot nitric acid. The primary constituents in the off-gas are air, steam, and NO_x. In addition, essentially all xenon, krypton, and C-14 (evolved as CO_2) entering the dissolver are released to the DOG. Most of the iodine is also liberated, with release percentages of 94 to 99% being reported. Iodine in the DOG is primarily I_2, although organic iodides may also be present if nitric acid is recycled from throughout the plant.

Downstream of the dissolver, the off-gas is passed through a condenser and/or ambient temperature absorber to cool the gas and to capture, recombine, and recycle NO and NO_2. NO_x

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[*] From process flow diagram (PFD) 220-21-001-sht1-Rev. A of the 30% conceptual design report.

levels are reportedly reduced to 1000 ppm or lower using a downdraft condenser and ambient temperature scrub (Benedict 1981, Henrich 1980).

The flow diagram of Figure 3 shows one possible sequence of unit operations for capturing the gaseous radionuclides. In this diagram the volox and dissolver off-gases are combined prior to the technologies to remove I-129, C-14, and Kr-85. Other unit operations will be also be required for the process to function properly and allow efficient capture of the targeted nuclides. This includes the "Drier" which removes water vapor prior to the cold temperature operations associated with Kr capture. Another is the capture/separation of Xe, which is itself not a radiological concern, but is problematic because it will hinder the separation of Kr, particularly since Xe will have a concentration about 10 times higher than Kr. Further NO_x removal beyond that achieved by the condenser and scrubber will also presumably be necessary prior to the Kr/Xe capture step.

Representative operating parameters for the reference case DOG are the following:

- Dissolver temperature: 85°C (per AFCF PFD[*])
- NO_x absorber: water (dilute acid) scrub at ~20°C, gas to liquid flow ratio ~50 (Henrich 1980)
- Nitric acid molarity in dissolver: 5-10 M HNO_3
- Sparge/carrier gas rate: 5.03 kg/hr air, equivalent to 3.9 m^3/hr STP (per AFCF PFD[*]). By comparison the WAK used a batch dissolver with an average dissolver gas rate of 80-120 m^3/hr STP (Herrmann 1996).
- Release fractions:
  - Iodine – 96%
  - C-14 (as CO_2) – 100%
  - Xenon – 100%
  - Krypton – 100%
- Capture technologies: Iodine adsorption on Ag-mordenite
  - CO_2 absorption with alkali scrub solution
  - Xe adsorption on Ag-mordenite
  - Kr adsorption on H-mordenite

Additional options to be considered for modeling the DOG could include:

- Modeling the NO/NO_2 recombination to HNO_3 in a downdraft condenser
- Modeling NO/NO_2 in a scrubber
- Removal of water vapor prior to Xe/Kr capture, presumably by adsorption
- Destruction of NO_x prior to Xe/Kr capture, possibly by a selective catalytic reduction process

1.6.1.3 Streams Containing Dilute Levels of Iodine

Iodine not partitioned to the dissolver off-gas will be carried off in the undissolved solids discharged from the dissolver or in the liquid phase with the dissolved fuel. The liquid phase is

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[*] From process flow diagram 220-21-001-sht1-Rev. A of the 30% conceptual design report

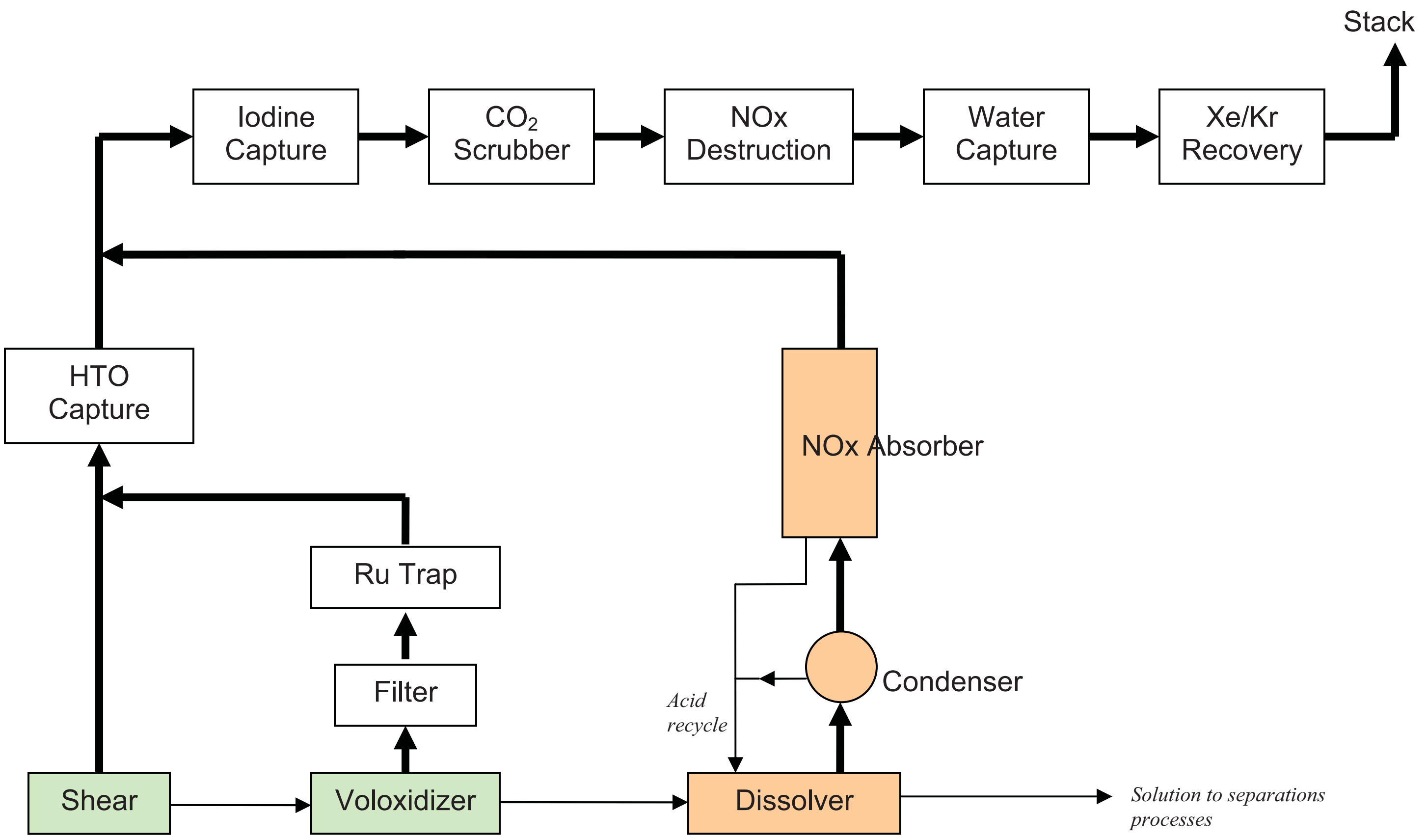

Figure 3. Notional Combined Voloxidation and Dissolver Off-gas Treatment System (modified from Jubin 2010).

used as feed to the extraction cascade where separation of U and transuranics from the fission and activation products is performed. Vigorous mixing with various organic solvents/diluents occurs in the extraction cascade. Although information is limited, low levels of iodine have been found in the vented gas from these and associated operations and is called the vessel off-gas (VOG). The WAK plant reported the iodine concentration in their PUREX VOG as 0.008 to 0.018 mg/m^3 (equivalent to 0.8 to 1.8 ppb I_2) using a vent flow rate of 270 to 330 m^3/hr (Herrmann 1996). The iodine emitted to the VOG may be bound as an organic compound.

The undissolved solids as well as other streams from reprocessing will likely undergo some type of thermal treatment prior to storage/disposal. Iodine present in the feed to these processes will potentially be emitted to the waste processing off-gas (WOG).

1.6.2 E-chem Process

The major processing steps used in the E-chem process are shown in Figure 4. This figure assumes oxide fuel as the spent fuel source and includes a voloxidation step after chopping. If metal fuel is being processed, voloxidation would be eliminated and the chopped fuel is sent directly to the electrolytic reduction step (AFCF 2007c). This is significant as the sequence of off-gas components and conditions will change slightly if voloxidation is performed. The processing rate is based on 1 metric ton of ABR fuel per year.

1.6.2.1 E-Chem using Voloxidation

The operations of chopping and voloxidizing the fuel will result in essentially complete release of tritium, which reacts in the oxidizing voloxidation atmosphere to form tritiated water. Other volatile constituents (carbon, krypton, xenon, iodine, etc.) will also be released, but possibly to a lesser extent than tritium depending on the specific operating conditions (AFCF 2007a).

Any Kr or Xe still in the fuel after voloxidation will be released during electrolytic reduction where the fuel is mixed with molten salt. However, residual iodine will **not** be liberated during reduction, but will most likely accumulate in the electrolytic reduction and electrorefining salts. Its eventual release (mostly as monomeric LiI) is likely downstream as a consequence of the electroreduction and electrorefining steps. Electroreduction produces oxygen as a by-product, including possible nascent oxygen, which may interact with iodine to produce other species which have a higher vapor pressure than LiI. This interaction of iodide-containing salt with an electroreducer requires further study. Electrolysis from U/TRU recovery (step 10 from figure 4) and U/TRU drawdown (step 16) can directly produce I_2. The primary electrorefining step to produce metallic uranium, however, is done at conditions not expected to produce I_2. The fate of any carbon not off-gassed during voloxidation is not known (Fortner 2010).

The reference off-gas system is based on the AFCF 30% conceptual design and is shown in Figure 5. For the case of oxide fuel, the first two unit operations are shown as light blue blocks, thereafter processing is the same for oxide and metal fuel. The reference case voloxidation off-gas process characteristics are the following (AFCF 2007c):

- Voloxidation operated at 700°C for 3 hours (batch processing)
- Assumes all H-3, C, Kr, and Xe is released during voloxidation, none during chopping[*]
- Voloxidation effluent gas rate broken down as follows (assumes O_2 feed gas to the voloxidizer at 4 L/hr)[†]:
    - Ar 0.002 g/hr
    - He 0.038 g/hr
    - O_2 3.01 g/hr
    - Xe 5.652 g/hr
    - Kr 0.276 g/hr
    - HTO 0.102 g/hr
    - I_2 0.42 g/hr[‡]
    - CO_2 0.038 g/hr[§]

For fuel undergoing voloxidation, the effluents are assumed to pass through a "fission product trap" consisting of a series of three beds. The first bed is composed of fly ash and operates at 800°C and captures Cs, Rb, and Cd. The second bed uses CaO as an active ingredient and operates at 600°C to trap Ru, Tc, and C-14 (as CO_2). The third bed is a silver zeolite adsorbent, identical in function to silver mordenite, to capture iodine. A prototype fission product trap has been designed and tested in a bench-scale system at the INL. The design specifications for that unit were the following (INL 2006):

- Fly ash filter
  Bed diameter = 2.0 cm
  Bed height = 3.6 cm
  Superficial gas vel. = 10 cm/sec
  Contact time = 0.36 sec

- CaO filter
  Bed diameter = 2.0 cm
  Bed height = 8.0 cm
  Superficial gas vel. = 10 cm/sec
  Contact time = 0.8 sec

- Ag zeolite
  Bed diameter = 2.0 cm
  Bed height = 5.0 cm
  Superficial gas vel. = 3.8 cm/sec
  Contact time = 1.3 sec

After the fission product trap, the gases are routed to a molecular sieve to capture tritiated water, then to a silver mordenite bed for Xe, and finally H-mordenite for Kr retention.

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[*] ACFC design assumed 50% release during chopping and 50% during voloxidation

[†] From process flow diagram 215-21-003 of the AFCF 30% conceptual design report

[‡] PFD 215-21-003 does not show iodine – this value estimated from 1-year aged ABR oxide fuel from the 30% CDR – Section 3.1

[§] PFD 215-21-003 does not show carbon – this value estimated from 1-year aged ABR oxide fuel from the 30% CDR – Section 3.1

1.6.2.2 E-Chem without Voloxidation

Oxide fuels can be directly fed into an electrolytic reduction step. A complete cost-benefit analysis of bypassing Volox has not been determined. Metal fuel will not undergo voloxidation, instead, the fuel is chopped and sent directly to the electrolytic reduction cell. Tritium, Kr, and Xe will be completely released during these two processing steps. Both operations are performed under an inert argon atmosphere, so tritium will presumably be liberated as a diatomic gas. In the AFCF design, this gas stream (containing tritium, Kr, and Xe in an argon carrier gas) is combined with oxygen and fed to a recombination unit where tritiated water is formed. The water is subsequently captured on molecular sieves (AFCF 2007c). Xe and Kr can be trapped on silver and hydrogen mordenite, respectively. The first two unit operations for the reference process for metal fuel are shown as the orange blocks in Figure 5.

Reference case flow rates based on the AFCF 30% design and assuming the chopper and electrolytic reduction gases are combined gives the following (AFCF 2007c)[**]:

- Ar 0.004 g/hr
- H-3 0.030 g/hr
- He 0.036 g/hr
- Xe 5.64 g/hr
- Kr 0.276 g/hr

No information is given for oxygen flow rate to the recombiner, but 0.08 grams of O_2 will be required to stoichiometrically convert diatomic tritium to T_2O. Assuming a 500% excess gives the following rate: O_2 0.40 g/hr

Iodine is not off-gassed with tritium and the noble gases, but will likely accumulate in the electrolytic reduction and electrorefining salts. The release path for the iodine is the waste form production steps, where iodine as salt vapor will likely be released to the sweep/purge gas from these processes. Although not included in the AFCF design, this sweep gas can presumably be combined and routed to a silver mordenite column for iodine capture. This is illustrated in the lower portion of Figure 5. The fate of C-14 is not clear at the present time (Fortner 2010).

[**] See PDFs 210-21-002 and 210-21-003

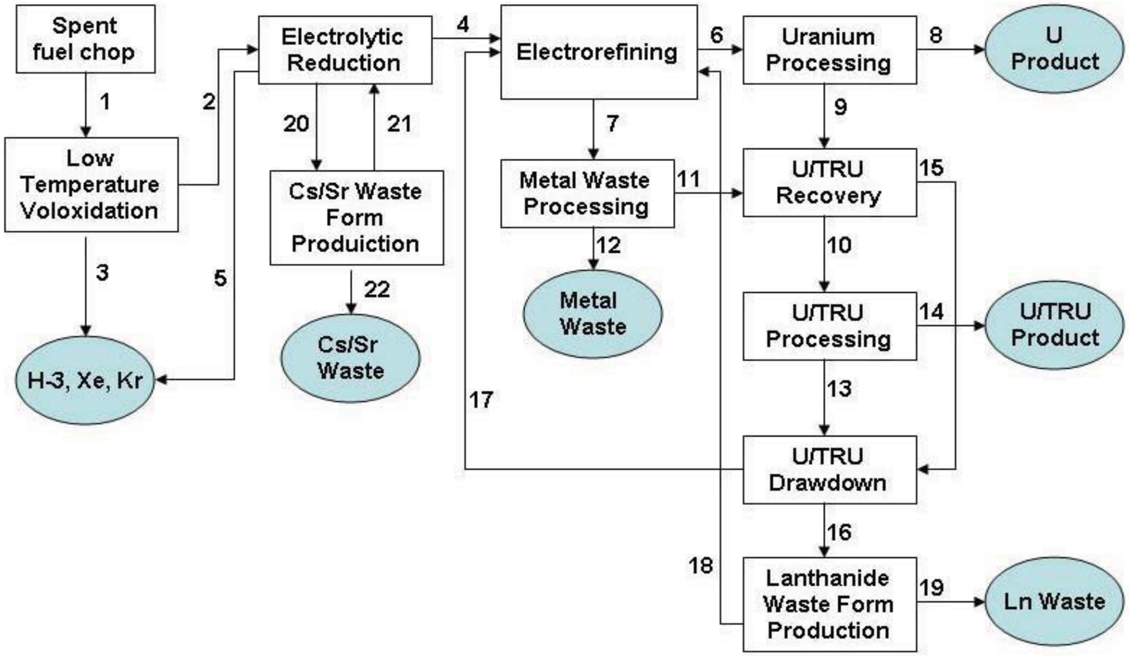

Figure 4. E-chem Block Flow Diagram for Oxide Fuel (Fortner 2010, after Wigeland *et al*., 2009).

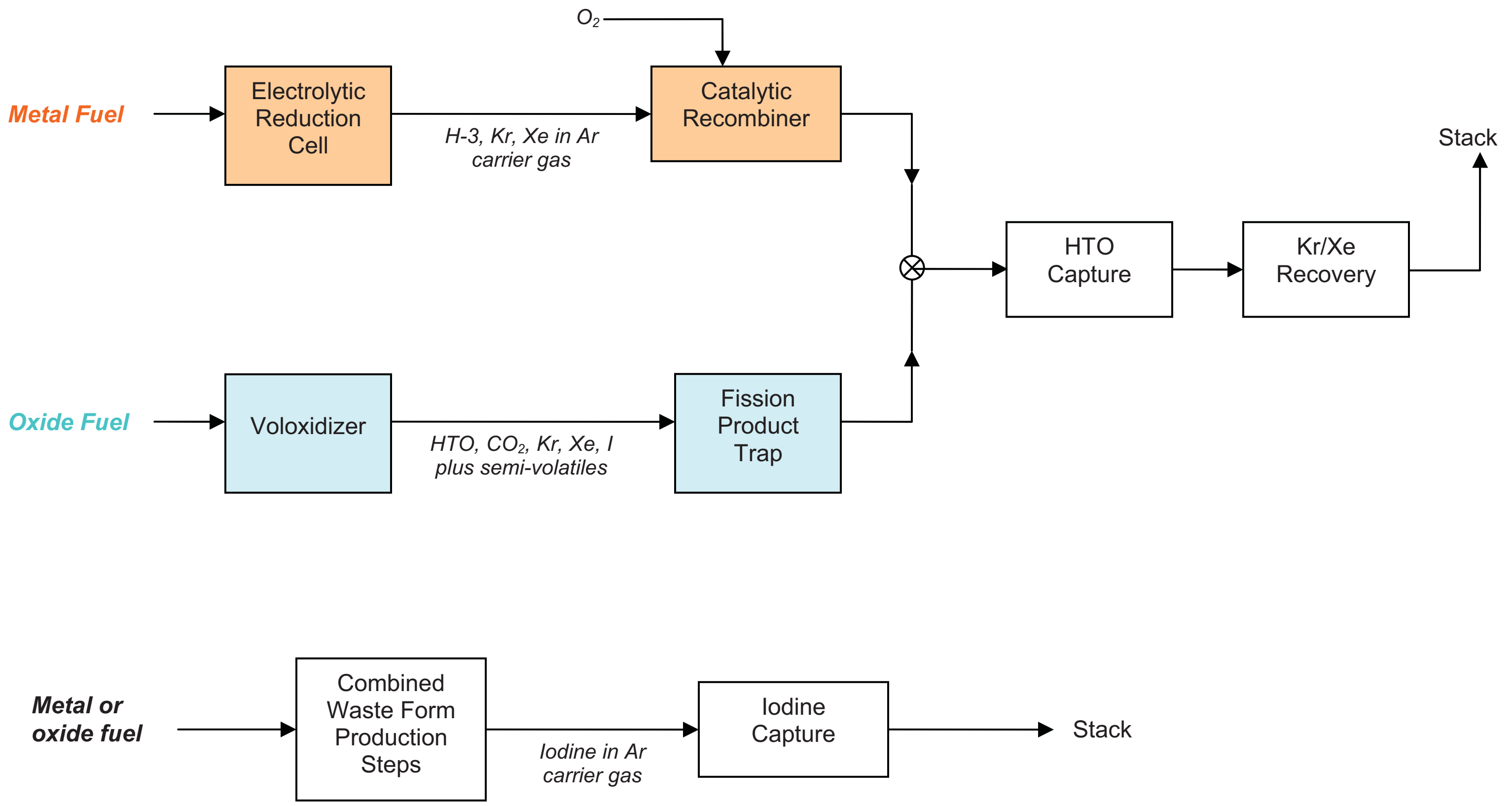

Figure 5. Notional Block Flow Diagram to Capture Gaseous Radionuclides from the E-chem Process.

1.7 Source Terms

1.7.1 Aqueous Processing

The 30% conceptual design report for the Advanced Fuel Cycle Facility (AFCF) project presented bounding conditions for LWR fuel as a basis for a robust reprocessing system design. To assure an upper bounding fission-product composition, the designers assumed 12% uranium enrichment, 100 GWd/MT burn-up, and a 5 year cooling period for the fuel. Table 2 shows the fission product yields (per metric ton of uranium initially present) for the key gas constituents as estimated by ORIGEN-S code (AFCF 2007b). The ORIGEN code predicts very little C-14 which is probably an underestimate. This is due to the formation of C-14, which is primarily generated by neutron activation of nitrogen impurities in the fuel and fuel cladding (Goossens 1991). Also shown in Table 2 is a more realistic fuel type based on 4.3% enrichment and a burn-up of 51 GWd/MT.

Table 2. Mass of gaseous fission products generated per metric ton of uranium for LWR oxide fuel.

Fission product	grams/MTU (bounding fuel type)[1]	Conc. from bounding fuel (ppm)[3]	grams/MTU (realistic fuel type)[2]	Conc. from realistic fuel (ppm)[3]
Tritium	0.153	6.7	0.0649	2.8
Carbon-14	8.27×10^{-3}		4.06×10^{-5}	
Krypton (total)	1184.	630	547	291
Xenon (total)	15,070.	5100	8040	2720
Iodine (total)	516.	89	359	62

1. Bounding fuel type: assumes 12% initial enrichment, 100 GWD/MTU, and 5 year cooling (AFCF 2007b).
2. Realistic fuel type: assumes 4.3% initial enrichment, 51 GWD/MTU, and 5 year cooling.
3. Concentrations based on a volox gas flow of 2.64 kg/hr and a DOG of 5.03 kg/hr.

The yields in Table 2 can be used with representative flow rates to estimate the concentrations of nuclides in the gas streams. For tritium (as HTO) in the voloxidation off-gas, a concentration of about 6.7 ppm is estimated from the upper bounding fuel type, and 2.8 ppm for the realistic fuel.

Using the fission yields in Table 2 for the bounding fuel type and a total combined air rate of 7.67 kg/hr air (2.64 from volox + 5.03 from DOG) the estimated concentrations are as follows: 89 ppm I_2, 630 ppm Kr, and 5100 ppm Xe. These are high but reasonable when compared to values from actual reprocessing plants. For example, at the WAK the dissolver iodine levels were reported as typically between 0.1 to 0.5 ppm, with an estimated peak value of 10 ppm (Herrmann 1996). The air flow rate at the WAK was about 100 m^3/hr STP (130 kg/hr) – a factor of 17 higher than used to get the 89 ppm estimated above. Similarly, typical commercial reprocessing facilities have ~70 ppm Kr and ~500 ppm Xe concentrations in the DOG with a gas rate of 100 to 500 m^3/hr STP (Hebel 1983). The level of CO_2 will likely be controlled by the amount of CO_2 entering with the process gases (volox sweep air, dissolver carrier gas, etc.) since the amount of C-14 generated in the fuel is believed to be relatively small. Assuming atmospheric CO_2 is not removed from entering air streams, the level may be as high as 350 to 400 ppm.

The volox and dissolver off-gases will contain most of the gaseous fission products of concern; however, other off-gases may also contain small, but significant quantities, of radiological and/or hazardous constituents. An obvious example of this is iodine, which may require a system capture efficiency of greater than 99.9%. However, if only 95% of the iodine is liberated to the DOG, the rest will be dispersed throughout the plant and may eventually be evolved in other off-gas streams. As mentioned earlier, the WAK plant's combined vessel off-gas had iodine levels of 0.8 to 1.8 ppb. Depending on the plant design and its associated off-gas systems, other emissions as noted in section 2.1 may require some level of control.

Table 3 presents operating/design characteristics for several recycling plants and shows the range of conditions that are encountered. The ICPP processed various types of fuel – the entries in the table are for aluminum clad, oxide fuel. Table 3 also lists information from the Engineering Alternative Studies (EAS) for design concepts for a full-scale reprocessing plant (EAS 2007a, EAS 2007b).

Table 3. Dissolver off-gas characteristics of some reprocessing facilities.

Facility	DOG flow rate (scfm)	Composition	Fuel throughput (MTHM/yr)
ICPP	9	2.1 vol% hydrogen (dry basis) 55 ppm Kr 330 ppm Xe 17.5 vol% N_2O (dry basis) 74.8 vol% N_2 (dry basis) 4.6 vol% O_2 (dry basis) 1.0 vol% combined NO, NO_2, N_2O_5, CO_2,and Ar (dry basis)	variable
Karlsruhe WAK	47 to 70	0.1 – 0.5 ppm iodine, peak value estimated at 10 ppm	30
AFCF	3.5†	62 - 89 ppm iodine (total) 2.8 - 6.7 ppm tritium* 290 - 630 ppm Kr (total) 5100 - 8000 ppm Xe (total)	25
EAS±	100	115 ppm iodine (assumed I_2) 125 ppm hydrogen (includes H-3) 500 ppm Kr 5000 ppm Xe 980 ppm CO_2	800

† = This is the combined voloxidation (1.2 scfm) plus dissolver (2.3 scfm) off-gases.
* = This is the concentration in the voloxidation off-gas.
± = The DOG flow rate and composition were presented in different documents, therefore consistency of this information maybe questionable.

1.7.2 E-Chem Process

The reference case fuels for E-chem processing are taken from the AFCF 30% conceptual design (AFCF 2007b). These are bounding fuels in that they set upper bounding levels for transuranics and fission product compositions. The fuel source is assumed to be ABR fuel with a burn-up of 250 GWd/MT, 1 year of cooling, and high beginning of life enrichment (>75%). Tables 4 and 5 show the prevalent gas species evolved from the fuels.

Table 4. Estimated masses of selected gaseous constituents for oxide ABR fuel. Basis: 250 GWd/MT, low conversion ratio, cooled 1 year.

Constituent	g/MT fuel
Tritium	0.448
Carbon (total)[1]	60.5
Krypton (total)[2]	1,610
Xenon	33,150
Iodine (total)[3]	2,480

1. Essentially all carbon is from cladding and about 1% is C-12 (activation product)
2. About 5.6% is Kr-85
3. About 73.4% is I-129

Table 5. Estimated masses of selected gaseous constituents for metal ABR fuel. Basis: 250 GWd/MT, low conversion ratio, cooled 1 year.

Constituent	g/MT fuel
Tritium	0.452
Carbon (total)	negligible
Krypton (total)[1]	1,610
Xenon	33,070
Iodine (total)[2]	2,470

1. About 5.7% is Kr-85
2. About 73.4% is I-129

1.8 Unit Operations

This section describes the system of unit operations used to capture the primary constituents of concern. This system represents the reference case and is composed of an interconnected series of adsorbers and scrubbers (absorbers). Heat exchangers will be used, as necessary, to condition the off-gas prior to entering an adsorber/absorber. Additionally, where known, alternative unit operations to be modeled outside of the reference case are described.

It is anticipated that a plant level model will be used to compare process alternatives to the reference case system. As such, the model must have the flexibility to allow a user to alter the sequencing of unit operations and/or to change-out unit operations (for example, replace an adsorber with a scrubber and vice versa). Process conditions, such as flow rates, constituent concentrations, temperatures, sorbent properties, etc., will also change from the reference case and the model must be able to accommodate these easily.

The computer generated output from the plant level model will be off-gas effluent concentrations and temperatures as a function of time for each unit operations. Sorbent concentration and temperature profiles should also be available as a function of time. Results should be conveniently presented in graphical display and in tabular form.

1.8.1 Tritium (as water vapor) Capture

1.8.1.1 Description of Reference Case Unit Operation

The reference unit operation for capturing tritium (as water vapor) is adsorption on a solid sorbent, such as molecular sieve 3A. Molecular sieves are preferred in this application because of their unique ability to produce extremely dry gases. Dew points as low as -120 to -150°F are achievable by molecular sieves, although it requires regeneration temperatures of 500 to 700°F (Kohl 1979). This technology is considered mature with commercial units readily available. Two locations in the unit operation sequence will have an adsorption drier: (1) the voloxidation off-gas "HTO Bed" and (2) the pretreatment "Drier" prior to the cryogenic capture of the noble gases.

The amount of H-3 in the spent fuel is small and will result in a relatively dry voloxidation off-gas if this is the only source of water vapor. This in turn may result in the amount of water in the off-gas being below the equilibrium vapor pressure of the sorbent – the equilibrium being dependent on the temperature used to regenerate the sorbent. Thus there may be a benefit (reduced process cost) to add normal water vapor to the off-gas to promote sorption (of both tritiated and normal water). For example, a water content of 6.7 ppm ($\sim 4.23\times10^{-6}$ g HTO/g air) is approximately equal to a dew point of -83°F, but adsorbing vapor from such a dilute stream will require higher temperatures and more frequent regeneration cycles than if a higher dew point could be used to capture H-3. This presumes that the 3A molecular sieve is regenerated and not disposed of as the final waste form.

A drying unit will also be required prior to the Kr/Xe recovery unit since temperatures approaching -112°F (-80°C) will be used for the noble gases. A dryer capable of producing an effluent with a low dew point is again required; however, the feed stream entering the dryer will essentially be saturated with water at ~25°C (the temperature of the CO_2 scrubber). With a significant amount of water in the gas stream, there may be an economic benefit in having a multi-stage drier in place. The first stage would provide partial removal of water, while the second would achieve the polishing (low dew point) required for the noble gas recovery unit. The first stage may be a simple chiller/condenser or other unit, while the polishing stage would be an adsorption bed with molecular sieves.

1.8.1.2 Current Research/Data Gaps

ORNL is conducting tests using a coupled end-to-end (CETE) pilot plant facility where actual fuel samples are undergoing voloxidation followed by dissolution. The off-gases from the CETE configuration are undergoing integrated off-gas treatment and include tritium capture on molecular sieve 3A.

Water vapor capture on solid sorbents is a relatively mature technology with adsorption isotherms and adsorbent physical data available in the open literature or from vendor data. However, in this application iodine vapor may co-adsorb on the molecular sieve and thereby complicate disposal of the final tritium waste form. Tests are being planned at Oak Ridge to evaluate the potential level of iodine retained by the molecular sieves. Additionally, understanding the adsorption isotherms at very dry conditions and the desorption isotherms with respect to the multiple waters of hydration is being evaluated.

1.8.2 Iodine Capture

1.8.2.1 Description of Reference Case Unit Operation

The reference unit operation for iodine capture is adsorption on silver mordenite. The flowing air stream from the dissolver and associated unit operations (down-draft condenser, absorber) carries the iodine onto a fixed bed of adsorbent where the iodine is retained. Although the carrier gas will contain significant levels of steam, NO, and NO_2, the iodine is efficiently captured - studies have shown decontamination factors of greater than 10,000 despite the co-constituents.

The adsorption mechanism is believed to be primarily chemisorption, with the iodine forming a chemical bond with the silver, although a fractional amount of iodine is probably physically adsorbed as well. Adsorption temperatures of about 150°C are typically used, although good performance has also been demonstrated at temperatures as low as 75 and as high as 200°C. A range of superficial gas velocities have also been used, ranging from 3 to 15 m/min (Haefner 2009, Jubin 1988, Scheele 1983, Thomas 1977).

1.8.2.2 Current Research/Data Gaps

Significant research efforts are being directed towards capturing iodine as well as developing stable waste forms for permanent disposal. Oak Ridge is using silver mordenite in its CETE demonstration unit to capture gaseous iodine resulting from dissolution of actual fuel samples. The INL is conducting column tests using silver mordenite to capture iodine (elemental and methyl iodine) from flowing gas streams that mimic the dissolver, vessel, and waste processing off-gases. Thin bed tests have been used to determine the capture efficiency (DFs) for various process conditions and deep bed tests are being conducted to obtain breakthrough behavior. Sandia Laboratories are studying the material properties of silver mordenite and developing robust iodine waste forms. In addition, Sandia has determined equilibrium sorption loadings of elemental and methyl iodine on silver mordenite. Researchers at Sandia and PNNL are independently developing novel adsorbents (metal organic framework, aero-gels, calco-gels, etc.) to capture iodine. Efforts are also underway to determine the loading mechanism at the pellet/particle level to provide the basic parameters for the differential mass transfer models. The impact of aging on the media and its performance is also being evaluated.

Silver mordenite is not a single, homogeneous material, but is a general term for an alumina-silica material containing ion exchanged or impregnated silver. The base mordenite may be a natural mineral obtained through mining or a synthetically manufactured material. Because of this, the physical and chemical properties of silver mordenite will vary somewhat and depend on the source of the material.

Limited loading information and dynamic column behavior on silver mordenite is available in the open literature. This information can be used to support development of an initial model of iodine sorption on silver mordenite. Given that silver mordenite currently used by the ORNL, INL and Sandia, may be somewhat different than that of the literature sources, data from these tests and from specific tests designed to generate modeling data will be required to support development of this model. Additionally, as data is generated with novel adsorbents, the iodine capture unit operation model can be modified for these adsorbents and utilized to compare various adsorbents, design experiments, and evaluate integrated operation with other unit operations as part of the plant-level model.

1.8.2.3 Alternative to the Reference Case Unit Operation

In addition to adsorption on solids, various wet scrub solutions have been used in actual operations or pilot plant studies. Caustic solution (1 to 2 M NaOH) has been extensively used at reprocessing plants, but is not effective for organic iodine compounds. Various nitric acid solutions have been proposed or tested at small scales. Included among these are: (1) the Mercurex process, which uses a solution of mercury nitrate and 14 M HNO_3, the (2) Iodox process, which uses hyperazeotropic (20-23 M) nitric acid, and (3) electrolytic scrubbing using 8 to 12 M HNO_3 containing a metal ion oxidant. Organic solvents have also been proposed and include fluorocarbons (R-12) and polymethylsiloxane (Haefner 2007b).

1.8.3 Carbon-14 (as CO_2) Capture

1.8.3.1 Description of Reference Case Unit Operation

The reference unit operation for capturing and separating C-14 (as CO_2) is a double alkali absorption/precipitation process. In the first step CO_2 is absorbed in a packed column using caustic (NaOH) solution, which retains the carbon dioxide as soluble Na_2CO_3. The scrub solution is then transferred to a batch mixing tank where $Ca(OH)_2$ is added, resulting in precipitation of $CaCO_3$, which is removed by filtration. NaOH solution is regenerated as a consequence of precipitation and is recycled back to the scrubber (Goossens 1991).

Pilot plant operations have show that 99% of CO_2 can be removed from a gas containing 330 ppm CO_2. The pilot plant used a column with a 10-cm diameter, 200-cm tall and packed with 15-mm stainless steel Pall rings. Flow was countercurrent using a scrub of 0.5 to 2.0 N caustic solution. Gas rates of 20-30 kg/hr were used with the scrub flowing at about 150 L/hr (Braun 1982).

1.8.3.2 Current Research/Data Gaps

Capture of CO_2 is receiving minimal attention since: (1) scrubbing technology for CO2 absorption is fairly mature, and (2) the required capture efficiency is expected to be very low or unnecessary.

1.8.3.3 Alternative to the Reference Case Unit Operation

In addition to wet scrubbing methods using alkaline solutions, studies using solid alkaline (LiOH, NaOH, KOH, etc.) and alkaline earth ($Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$, etc) metals have shown some promise. In these tests the gas containing CO_2 is run through a packed bed of alkaline solid and the CO_2 reacts with the alkaline is converted to the corresponding carbonate. Another alternative technology is physical adsorption of CO_2 on molecular sieves such as or synthetic zeolites, including sieve types 4A or 13X (Goossens 1991).

1.8.4 Krypton Capture

1.8.4.1 Description of Reference Case Unit Operation

The reference unit operation for xenon/krypton capture is adsorption onto cation exchanged mordenites (e.g. hydrogen mordenite, silver mordenite). Previous work has shown that krypton adsorption properties for mordenites can be substantially increased by replacing exchangeable cations in the matrix with cations such as hydrogen or silver. Monson (1982) performed a series of isotherm tests using mordenite exchanged with hydrogen, silver, cerium, sodium, or potassium in an effort to assess their relative performance for krypton adsorption. These experiments showed hydrogen exchanged mordenite (H-mordenite) to have capacities for krypton similar to activated carbon. Silver exchanged mordenite (Ag-mordenite) adsorbed approximately ten times more Kr than H-mordenite at a given temperature and partial pressure. It will be necessary to remove xenon prior to krypton adsorption or concomitantly with krypton adsorption, since most known adsorbents preferentially adsorb xenon over krypton at a given pressure and temperature. Other gas stream constituents (e.g., NO_x, CO_2, H_2O, iodine) will also suppress or interfere with krypton adsorption. Hence, krypton capture will be the last unit operation in the off-gas treatment system, following removal of other gas constituents via the operations previously discussed. The dry gas stream containing primarily N_2, O_2, Xe and Kr flows through the fixed bed(s) of adsorbent where the krypton is retained. The reference case operation assumes Xe capture on silver mordenite at 60°C, with the effluent passing to a hydrogen mordenite bed at -80°C for retention of Kr.

The uptake of krypton onto the solid sorbent is considered to be a function of physical adsorption, where the adsorbate (krypton) is held by only weak Van der Waals forces. This weak attraction is in contrast to chemisorption phenomena often seen with more reactive gas-solid systems, in which a stronger chemical bond is formed between the gas adsorbate and solid adsorbent. Adsorption phenomena are essentially spontaneous and decrease the free energy (G) and entropy (S) of the system. The synthetic zeolites (e.g., mordenite) are thought to act as molecular sieves, where the adsorbed atom or molecule must be of a size that fits into the cage structure of the adsorbent in order to be effectively held (Monson 1982). Although it has yet to be entirely explained, this correlation between adsorbent pore size, the atomic radius of krypton, and adsorption capacity has been demonstrated in earlier work (Kitani and Takada 1965).

The adsorbent capacity for krypton is directly dependent on pressure and inversely dependent on temperature - suggesting that a krypton adsorption-desorption cycle may be accomplished by changing either pressure or temperature, known respectively as pressure or thermal swing operations. In a thermal swing scenario, krypton is adsorbed at temperatures ranging from -30°C to -80°C and removed from the bed at temperatures around 60°C (Pence 1980).

1.8.4.2 Current Research/Data Gaps

Oak Ridge is using silver mordenite in its CETE demonstration unit to capture krypton released from dissolution of actual fuel samples. The INL is conducting column tests using silver mordenite to capture krypton and from flowing gas streams that mimic the dissolver off-gas streams in terms of krypton, xenon, N_2 and O_2 concentration. The testing apparatus is designed to allow for the efficient loading and regeneration of the bed so that multiple adsorption-desorption cycles can be evaluated for a range of selected temperatures at ambient pressure. Multiple isotherms can then be generated for a range of selected temperatures to determine optimum conditions for sorption, desorption, and to evaluate adsorbent performance over many cycles. This will also generate the dynamic data necessary to estimate relevant mass transfer and heat transfer coefficients for engineering design and scale up. Researchers at Sandia and PNNL are independently developing novel adsorbents (metal organic framework, aero-gels, calco-gels, etc.) that may also be applicable to krypton capture.

As mentioned previously, the physical and chemical properties of silver mordenite will vary with manufacturers. The magnitude of this variance and how it affects krypton adsorption is an unknown that must be addressed. The mechanism leading to higher krypton adsorption on the cation exchanged mordenites has not been explained and efforts to elucidate the mechanism are also needed, since a better understanding of the governing principles behind their performance may point to an even better class of engineered sorbents.

Some information regarding krypton loading capacity and dynamic column behavior on silver mordenite is available in the open literature. This information is assumed to be adequate for developing (at least initially) a model of krypton sorption on silver mordenite. Given that the silver mordenite and operating parameters currently being assessed by the Labs (ORNL, INL and Sandia) is likely to be significantly different than that of the literature sources, refinement of the model will be required based on data generated at these labs.

1.8.4.3 Alternatives to the Reference Case Unit Operation

Cryogenic distillation is a much more mature technology for Kr and Xe recovery based on considerable operating experience. However, it is being treated as an alternative to the reference case adsorption process due to the large cost associated with this method and the large potential for improvement with an adsorption process. Nonetheless, modeling efforts are planned for both types of processes to allow for comparison.

Cryogenic methods were used to capture and recover Kr and Xe at the Idaho Chemical Processing Plant (ICPP) "Rare Gas Plant." The plant's objective was to capture and purify Kr and Xe for commercial resale – environmental concern was not the primary driver. Installation of a cryogenic distillation unit actually replaced an earlier cryogenic adsorption system that used charcoal (activated carbon) as the sorbent. The two reasons cited for replacement of the adsorption unit were: (1) the resultant noble gases were relatively impure, and (2) the required cooling was greater than the existing liquid nitrogen plant could produce on a continuous basis (Bendixsen 1969, German 1974).

The ICPP cryogenic distillation unit required that the dissolver off-gas be pre-treated to remove constituents that could freeze at cryogenic temperatures or be an explosion (flammability) hazard. In the reference case off-gas system, Kr capture occurs at the end of treatment process so most of the problematic gases will be removed prior to the Kr capture unit. The following description of the pre-treatment used at ICPP is included below for completeness of the process description.

The ICPP processing of aluminum clad fuel resulted in a DOG containing the gases listed earlier (air, water vapor, NO, NO_2) plus notable amounts of hydrogen and nitrous oxide (N_2O). At ICPP, the DOG was first compressed to 20-40 psig and then passed through a caustic scrubber/surge tank to remove NO_2. (The caustic would also have removed elemental iodine, although in the process description dated 1969, iodine-129 was not identified as being a constituent to capture. The only iodine of concern was I-131, which was dismissed by allowing the fuel to sufficiently age prior to reprocessing). The gas was then routed to rhodium catalyst beds at 1000-1200°F to reduce the N_2O to nitrogen and oxygen and convert hydrogen to water vapor. This gas was then cooled to about 90°F, which removed water, nitrogen oxides, and ammonia (formed in the rhodium catalyst bed). Make-up air was then added, if necessary, to achieve the desired flow rate of 20 scfm. A final drying stage using molecular sieves or silica gel dried the gas to the target dew point of -40°C prior to the gas entering the cryogenic process.

The cryogenic system consisted primarily of two regenerators (packed bed heat exchangers), a "primary column" (20-plate distillation column), and a batch still. The feed gas was first routed through a regenerator, which cooled the gas to about -260°F. The cooled gas was then fed to the 10th plate of the distillation column. Liquid nitrogen (at -310°F) introduced near the top of the column, flowed downward through the sieve plates, condensing and absorbing the higher boiling oxygen, xenon, and krypton. The absorbed gases (oxygen, xenon, and krypton) were concentrated in the kettle and lower sections of the distillation column. Gas discharged from the top of the column was primarily nitrogen, which was routed to the regenerators to cool them.

Several times a day, contents from the distillation column's kettle (containing the relatively concentrated noble gases plus nitrogen and oxygen) were transferred to the batch still. After each transfer, nitrogen and some of the oxygen were allowed to boil off, thus allowing the noble gases to further concentrate. About six or seven transfers were accumulated in the still before enough product (Kr and Xe) was available to perform a fractionation run. During a fractionation run, the initial cut contained mostly oxygen and was recycled back to the feed gas compressor to prevent the loss of trace Kr and Xe. The second cut was primarily Kr, while the third was Xe. The Kr and Xe were sent to intermediate storage vessels and later bottled in conventional 191 ft^3 cylinders (Bendixsen 1969).

Fluorocarbon absorption is another alternative technology for the separation of krypton (Gombert 2007). The fluorocarbon absorption technology was developed at the Oak Ridge Gaseous Diffusion Plant and at the Kernforschungszentrum Karlsruhe (KfK) in Germany. This process uses an organic solvent (CCl_2F_2 called R-12) to selectively absorb noble gases from air or DOG streams; the noble gases are then stripped from the solvent by boiling.

The basis for this recovery process is the solubility difference that exists between the various gas compounds in the solvent chosen for the process. Process performance data have been obtained using tracer levels of 85Kr in the column described above. Krypton recoveries greater than 99% have been demonstrated with concentration factors ranging between 1000 to 10,000. Following the removal of the R-12 vapors, the typical product stream would consist of CO_2-78%, Xe-13%, N_2-5.5%, Kr-2.0%, O_2-1.4%, and Ar-0.1%.

2. PLANT LEVEL/UNIT OPERATION MODELING SPECIFIC REQUIREMENTS

The detailed feed and unit operation data presented in Section 2 provide the scope of the plant level modeling effort. Specific requirements necessary for the plant level model to effectively model the offgas processes presented in Section 2 are detailed here.

1. A plant level model will focus on the dynamic behavior of the coupled unit operations that comprise the off-gas system. Changes that occur in the feed may cause perturbations throughout the system and a model should accurately reflect these time-dependent changes through each unit operation.

2. A dynamic model involves solving the governing equations for mass and energy conservation as a function of time and bed dimension (bed depth as a minimum, but may also include radial position and/or particle depth). It is assumed the water and Xe/Kr adsorbers will be regenerated in-place, therefore, the model will be required to operate in both adsorptive and regenerative modes. The iodine adsorber is assumed to function only in adsorptive mode and when spent, the adsorption column is replaced. The CO_2 and NO_x absorbers (scrubbers) are assumed to be packed columns with liquid flowing countercurrent to the gas flow. In both scrubbers, absorption is accompanied by chemical reactions and a robust model must couple these phenomena and the resulting effect on mass transfer.

3. The plant model shall, at a minimum, include all the unit operations presented in Section 2.4 as well as necessary balance of plant unit operations such as heat exchangers and filters. In addition, the model shall be developed with the flexibility to allow for:
   - alternate sequencing of the unit operations in any desired configuration,
   - replacement of a reference unit operation with an alternate unit operation.
   - addition of unit operations to the configuration.

4. The plant model shall, as a minimum, allow a user to define or alter the following for the **feed**:
   - inlet gas composition (including H-3, C, Kr, Xe, I, H_2O, O_2, N_2, NOx, other volatiles such as Cl, Br and semi-volatiles at some point), flow rate, and temperature for the voloxidation and dissolver off-gases.

5. The plant model shall, as a minimum, be functional for **feed gas compositions** one order of magnitude higher and two orders of magnitude lower than the ranges specified in Table 3.

6. The plant model shall, as a minimum, allow a user to define or alter the following for each **adsorption unit operation**:
   - bed dimensions,
   - adsorbent properties,
   - temperature,
   - specify regeneration mode (temperature swing, pressure swing, inert gas purge).

7. The plant model shall, as a minimum, allow a user to define or alter the following for each **absorption (scrubber) unit operation**:
   - liquid to gas ratio,
   - column dimensions,
   - absorbent properties.

8. The plant model **output information** shall, as a minimum, include the following:
   - outlet gas composition, temperature, and pressure as a function of time,
   - constituent concentration profile in the sorption columns as a function of time,
   - temperature profile in the sorption columns as a function of time,
   - the information above presented in tables,
   - visual display of the above information

9. The plant level model will ultimately be used to perform comparative evaluations for different operating modes and feed conditions; therefore, a means of comparing alternatives shall be developed.

10. The plant model shall be developed so that it can be integrated with other models developed for a separations facility including front end operations (e.g., chopping, voloxidation, dissolution), the separation processes, and waste/product immobilization operations. Additionally, the off-gas plant model shall be able to function as a standalone model.

11. Individual unit operation models utilized for the plant model shall also be functional as standalone models that can be used by the Off-Gas Sigma Team and other users.

12. It is envisioned that after the initial stages of model development, additional functionality will be added to the model and will likely include, as examples, the following:
    - integration with the separations model to allow feed characteristics to be directly linked to the output from the separation model,
    - integration with the ORIGEN code or spreadsheet containing fuel radionuclide data thereby allowing a used to specify fuel type and fuel throughput rate.

3. FUNDAMENTAL MODELING

The plant level model should also allow for fundamental, first principle type models that are developed to be incorporated, if desired, as described in the Section 1.2 Plant Level Toolkit. These fundamental models are key to understanding the mechanisms and fundamental chemistry occurring in the systems. Gaining this understanding of what is occurring in the capture systems will enable design of more effective and efficient processes. Some of these fundamental modeling efforts may be pursued through the Fundamental Methods and Models element of the NEAMS Program described in Section 1.1.2.

The following areas for fundamental modeling were identified by the Off-Gas Sigma Team (Nenoff 2010):

- Code development for proper force fields for use in simulating specific known metal organic frameworks (MOFs), based on the metal centers, oxidation states, and metal configurations, plus framework geometry. Understanding of how existing MOF frameworks preferentially sorb gases can be applied to predicting new frameworks, and the design and experimental building of optimized frameworks.

- Grand Cononical Molecular Dynamics (GCMD) code studies of mixed gas systems (eg., Xe/Kr in MOFs); also to be extended to mixed gas simulant streams through MOFs, Zeolites, aerogels, etc. and resultant preferential sorption due to mixtures.

- Kinetic mechanism modeling of Iodine sorption onto Ag-MOR; correlate with existing static structural studies (d-pair distribution function, d-PDF) and on-going in-situ structural studies (PDF) of loading I2 onto Ag-MOR.

4. PATH FORWARD

The SafeSep IPSC modeling team will develop models for individual unit operations presented in this document. Priority of the modeling efforts is based on input from the Off-Gas Sigma Team and will begin in FY-2011. The primary initial focus will be on development of unit operation models to support efforts towards the separations plant level model. Fundamental modeling efforts will also be initially pursued at a lower level of priority. The modeling platform and software will be evaluated in FY-2010 by the SafeSep IPSC team to determine the best approach for achieving the requirements outlined in this document. Specific plans for modeling include:

- Development of dynamic adsorption and absorption unit operation models.
  - Adsorption models - iodine, krypton, xenon and tritium capture
  - Absorption models – carbon-14 and NO_x
  - Initial modeling will focus on iodine and krypton capture since these are the two areas with significant ongoing R&D. Experimental data from this research will be used to support development of these models.
  - As completed, these unit operation models will be made available for use by the Off-Gas Sigma Team and other customers.
  - Alternative unit operation models, such as cryogenic distillation for Kr capture, will also be developed to allow comparison of technologies.
- Development of the off-gas portion of the separations plant level model.
  - The unit operation models will also be integrated into the plant level tool kit architecture to support development of the plant level model.
- Working with the Off-Gas Sigma Team and the Fundamental Methods and Models element of the NEAMS Program to perform the fundamental modeling efforts identified by the Sigma Team, including those in Section 4.

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