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**Design report: An off gas trapping
system for a voloxidizer in INL of US**

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KOREA ATOMIC ENERGY RESEARCH INSTITUTE

“Design report: An off gas trapping system for a
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ABSTRACT

This reports on the “Development of Voloxidation Process for Treatment of LWR Spent Fuel”, and it is the second year since it has started from June 2004 as a tripartite cooperation project among KAERI(Korea Atomic Energy Research Institute), INL(Idaho National Laboratory) and ORNL(Oak Ridge National Laboratory).

The objective of “Development of Voloxidation Process for Treatment of LWR Spent Fuel” is to develop a voloxidation process which provides a means to recover fuel from the cladding, and to simplify downstream processes by recovering volatile fission products. This work focuses on the process development in three areas: the measurement and assessment of the release behavior for the volatile and semi-volatile fission products from the voloxidation process, the assessment of techniques to trap and recover gaseous fission products, and the development of process cycles to optimize fuel cladding separation and fuel particle size.

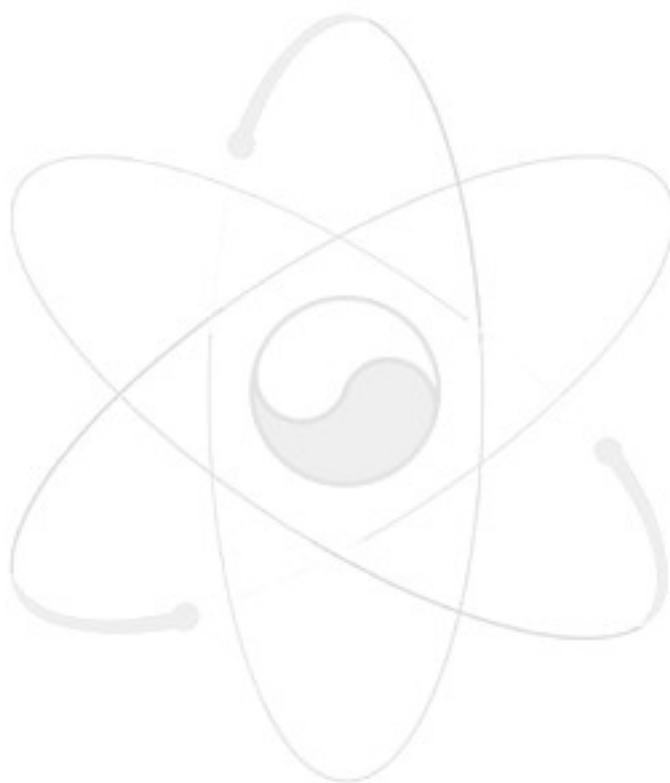
This report describes mainly the Task B2 accomplished during the first and second fiscal years. The Task B2 in proposal contains two sub-tasks. The first one is design of an off-gas treatment system for a voloxidizer to be used in HFEF of INL. For this, KAERI team developed the design of INL OTS (Off-gas Treatment System) for hot experiment in the HFEF. INL team modified and completed the design of the INL OTS. The second task is manufacturing and test operation of the INL OTS for a voloxidizer in the INL. Manufacturing of the OTS is accomplished by INL team with co-work of KAERI. KAERI provided four sets of trapping filters needed for conducting hot experiment in the INL HFEF. For this, two technical design meetings for designing the INL OTS were held among the specialists of KAERI and INL. The first technical design meeting was on September 6 to 9, 2005 at INL and the second was on February 23 to 27, 2006 at KAERI in Daejeon, Korea.

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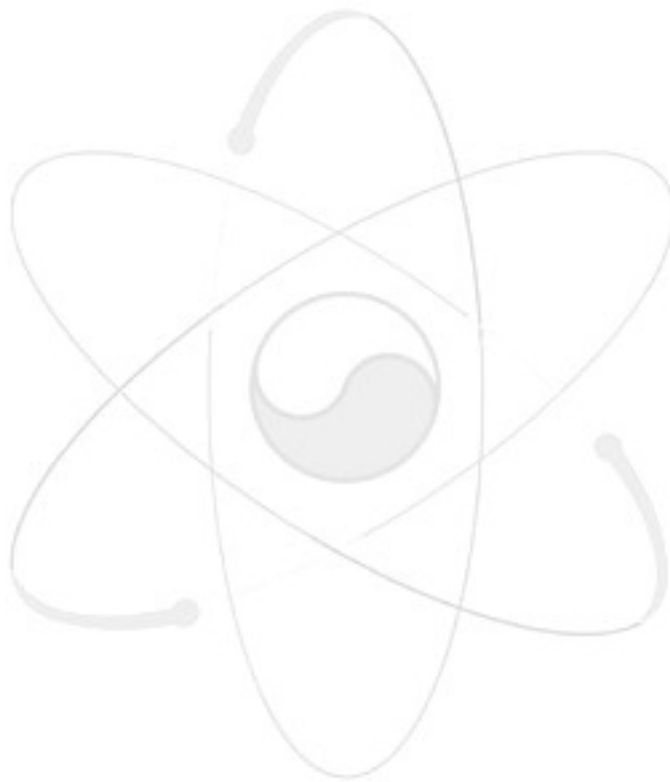
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1. INTRODUCTION

A responsible and sustainable deployment of nuclear energy should be based on a life cycle that maximizes the use and reuse of the resources and minimizes the amount of wastes, particularly those requiring geological disposition. The U.S. Advanced Fuel Cycle Initiative (AFCI) is developing an advanced spent fuel treatment process which will separate the major heat sources, volatile species, long-lived fission products, actinides, and cladding, and should be able to recover more than 95% of the spent fuel mass.

The United States Department of Energy is developing a head-end fuel treatment process, known as the voloxidation process as part of the Advanced Fuel Cycle Initiative. Voloxidation, which involves oxidizing uranium oxide fuel using either air or oxygen, provides three important advantages when used as a head-end treatment process [1, 2]. First, it may be used to separate the fuel from the cladding. A decladding step is desirable in which it may simplify process flow sheets by excluding the cladding constituents from the fuel constituents. Segregation of cladding may also result in generation of less high level waste. In addition to decladding, voloxidation may be used to decrease the particle size of the fuel, which will in turn increase the kinetics of downstream treatment operations. Voloxidation treatment may remove problematic constituents from the fuel prior to downstream treatment operations. Fission products such as ^{137}Cs , ^{129}I , ^{85}Kr , ^{133}Xe , ^{99}Tc , ^{14}C , ^3H (tritium) and etc. may be volatilized and removed, simplifying the process flow sheets and yielding more flexible waste treatment operations. Furthermore, the trapping media of various nuclides should be easy to be disposed of. Therefore, these gaseous fission products have to be trapped safely and kept from leakage to the environment. Cs is a major source of radiation and heat. Up-front removal reduces the need for process shielding. Long lived fission products are ^{99}Tc , ^{14}C , and ^{129}I . It might be desirable to trap those long lived fission products in the head-end process and to separate and keep them safely for their transmutation.

KAERI is pursuing the development of a similar technology, known as the Oxidation and REduction of Oxide fuel or OREOX process. This process is being researched in association with development of the DUPIC process for recycle of spent PWR fuel to CANDU reactors. The oxidation process is similar to the voloxidation process. KAERI has measured and analyzed the release rates of ^{85}Kr , Cs, C-14, etc. Also, various concepts for trapping these fission products

have been developed and applied to the off-gas treatment systems of the OREOX and the sintering processes in the DFDF (DUPIC Fuel Development Facility).

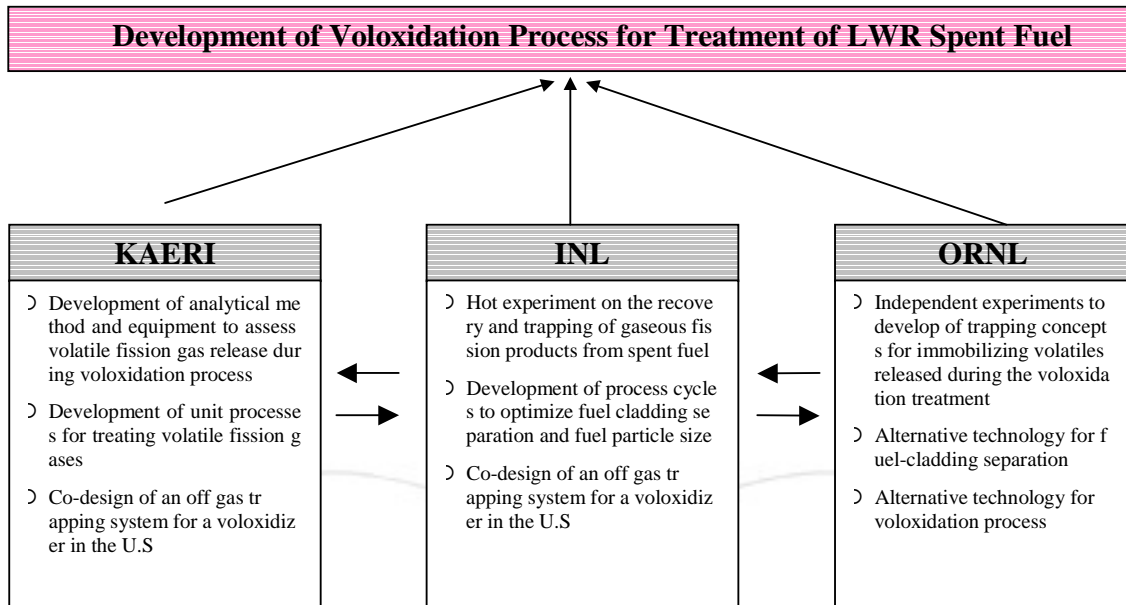
Based on literature reviews and KAERI's experimental results on the gaseous fission products trapping, appropriate trapping method for each fission product has been selected in terms of reliability, simplicity, decontamination factor, availability, disposal, and so on [3].

The report on the Task B2 in proposal, which contains two sub-tasks. The first one is the design of an off-gas treatment system for a voloxidizer to be used in HFEF of INL. For this, KAERI team developed the design of INL OTS (Off-gas Treatment System) for hot experiment in the HFEF. INL team modified and completed the design of the INL OTS. Manufacturing of the OTS is accomplished by INL team with co-work of KAERI.

The second task is manufacturing and test operation of the INL OTS for a voloxidizer in the INL. Manufacturing of the OTS is accomplished by INL team with co-work of KAERI. KAERI provided four sets of trapping filters needed for conducting hot experiment in the INL HFEF. At present, test operation is almost finished and it is waiting for hot experiment, which will be carried out by joint work between KAERI and INL. This is the main task to be done during the third project year.

Project organization, task title and responsible lead organization, and brief description of task objectives on the proposal are described in the following paragraphs.

1.1. Project Organization



1.2. Task title and responsible lead organization

| Task | Description | Institute |
|------|---|-----------|
| A | Measurement and assessment of volatile fission gas release behavior from voloxidation process | |
| A1 | Development of analytical method and equipment to assess volatile fission gas release during voloxidation process | K/O/I |
| A1.1 | Establishment of optimal analytical method to assess the release of each volatile fission product from voloxidation process | K/O/ I |
| A1.2 | Development of measuring system based upon on-line and off-line counting methods | K/O/ I |
| A2 | Hot experiment on volatile fission gases released from spent fuel during voloxidation | I/K/O |
| A2.1 | Hot experiment on release behavior of volatile fission gases from OREOX process in KAERI | K/O/ I |
| A2.2 | Hot experiment on volatile fission gases released from spent fuel during voloxidation tests in ANL hot-cell facilities | I/K/O |
| B | Assessments for the recovery and trapping of gaseous fission products | |
| B1 | Development of unit processes for treating volatile fission gases | K/O/ I |
| B1.1 | Literature survey and selection of trapping process for each fission products released during voloxidation process | K/O/ I |
| B1.2 | Non-radioactive experiments for trapping applications requiring experimental verification | K/O/ I |
| B2 | Design, manufacturing, installation and test operation of an off-gas treatment system for a voloxidizer in the U.S. | I/K/O |
| B2.1 | Design of an off-gas treatment system for a voloxidizer in the U.S | I/K/O |
| B2.2 | Manufacturing, installation and test operation of an off-gas treatment system for a voloxidizer in the U.S. | I/K/O |
| B3 | Hot experiment on the recovery and trapping of gaseous fission products from spent fuel | I/K/O |
| B3.1 | Operation of an off-gas treatment system for a voloxidizer in the U.S. | I/K/O |
| B3.2 | Measurement and evaluation of the efficiency of recovery of gaseous fission products from a voloxidation off-gas treatment system in the U.S. | I/K/O |
| B4 | Independent experiments to develop of trapping concepts for immobilizing volatiles released during the voloxidation treatment | I=K=O |
| C | Development of process cycles to optimize fuel cladding separation and fuel particle size | |
| C1.1 | Design equipment for process testing | I/K/O |
| C1.2 | Perform hot experiments to develop process parameters | I/K/O |

* I/K/O for INL/KAERI/ORNL, respectively. Lead organization is listed first.

1.3. Brief description of task objectives

TASK A:

When considering candidate voloxidation process conditions for treatment of spent LWR fuel, it is first necessary to establish the measurement system to assess the release behavior of volatile and semi-volatile fission products evolved from spent fuel. Previous studies related to the development of the voloxidation process have mainly focused on whether tritium is completely removed with varying operating parameters. However, the main frame of the Task A is classified into two areas. One is the development of analytical methods and equipment to assess the release behavior of volatile fission gases which probably depends on an applied atmosphere during the voloxidation process. The other is to obtain a source-term inventory data resulting from release of volatile and semi-volatile fission products during voloxidation and OREOX process using spent fuel in hot experiment.

TASK B:

In order to safely treat the volatile and semi-volatile nuclides released from voloxidizer in US, it is necessary to acquire information on release rates, trapping methods, design, installation and test operation of an off-gas treatment. Target nuclides to be treated are chosen based upon their radioactivity, environmental toxicity, and on the basis of release rates of volatile and semi-volatile fission products. For each chosen fission product, assessment of available treatment technology and engineering evaluation for realistic operating conditions is reviewed. The most favorable and available technology is chosen for experimental verification. To develop the most efficient trapping technology, experiments is performed to assess trapping and recovery efficiency, and safety of disposal for each gaseous fission product. The unit process for each fission product is designed based on the estimated amount of fission products arising from voloxidation process. The off-gas trapping system will be installed in the hot cell after test operation in mock-up facility. Afterwards, hot-cell experiments will be also performed to evaluate the trapping efficiency for each gaseous fission products from spent fuel.

TASK C:

A head-end decladding process will be developed through this task at INL as an alternative or supplemental activity to fuel chopping or selective separations. Testing is to be performed using irradiated fuel from the Belgium Reactor 3. Parameters that will be investigated may include fuel segment length, temperature, oxidant, oxidant flow rate, and fuel preparation processes. Tests will be undertaken in two phases. Phase I tests will include proof of principle tests and will assess the impact of reaction temperature and oxygen concentration on oxidation. Fuel will be analyzed before and after voloxidation experiments to assess the degree of fission product loss. Upon completion of characterization activities for Phase I tests, a second series of tests will be prepared and may be initiated. Issues that will be evaluated in the Phase II tests may include higher temperatures and alternative oxidants in order to optimize the process.

2. Assessments for the recovery and trapping of gaseous fission products

2.1. Design, manufacturing, installation and test operation of an off-gas treatment system for a voloxidizer in the U.S.

The Task B2 contains two sub-tasks. The first one is design of an off-gas treatment system for a voloxidizer to be used in HFEF of INL. For this, KAERI team developed the design of INL OTS (Off-gas Treatment System) for hot experiment in the HFEF. INL team modified and completed the design of the INL OTS. The second task is manufacturing and test operation of the INL OTS for a voloxidizer in the INL. Manufacturing of the OTS is accomplished by INL team with co-work of KAERI. KAERI provided four sets of trapping filters needed for conducting hot experiment in the INL HFEF. At present, test operation is almost finished and it is waiting for hot experiment, which will be carried out by joint work between KAERI and INL. This is the main task to be done during the third project year.

2.1.1. Design of an off-gas treatment system for a voloxidizer in the U.S

The joint design of an off-gas treatment system (OTS) by the KAERI and the INL has been accomplished through two design review meetings (September 2005 and February 2006) and two program review meetings (October 2005 and April 2006). The first design meeting was held at the INL in Idaho Falls, ID while the second was at the KAERI in Daejeon, Korea. Program review meetings were held at the ORNL in Oak Ridge, TN and the INL, respectively.

Given in the following sections are the final OTS design criteria, expected compositions and activities of volatiles, characteristics of the trapping agents, required tube temperatures, flow diagram, specific design requirements for the trapping units, and evolution of the filter unit design.

(A) Design criteria for OTS

- The species of interest for trapping during hot testing at the INL are seven volatiles; Cs, Rb, Cd, Ru, Tc, C-14 and I.
- The method of trapping the volatile elements is chemical adsorption at high temperature as developed at KAERI.
- The elements of Cs, Rb and Cd are to be captured by a fly ash filter. Ruthenium, Tc and C-14 are to be captured by Ca filter and I by an AgX filter. These filters are operated at their optimum trapping temperatures of 800°C, 600°C, and 150°C, respectively to effectively capture the species of interest.
- The batch size for off-gas testing is 100g of Belgium Reactor-3 spent oxide fuel. The amount of required trapping agents is determined by the assumption that 100 % of volatiles included in the spent fuel will be volatilized during the test.
- The temperatures of the connecting tubes between trapping units are heated above the boiling points of volatiles to prevent condensation inside of the tube.
- A performance test of the filters is carried out for every run.
- Filters should be sized for proper transfer in the HFEF rabbit system.
- In order to evaluating the trapping efficiency of the filters vertically, individu

al filters will comprise a filter unit.

- A filter unit is manufactured with a commercially available tube size which is capable of being disassembled in the hot cell.

(B) Expected compositions and activities of volatiles

Expected compositions and activities of the volatiles during testing are calculated by ORIGEN-ARP based on 100g of Belgium Reactor-3 (BR-3) spent oxide fuel at the condition of initial uranium enrichment of 8.26 wt.%, burn up of 42,000 MWd/tU, power rate of 37.5 MW/tHM, 25 years cooling, and three cycle. The results are represented at Table 1. Since testing is performed in air or oxygen, the chemical forms of volatiles are assumed to be oxides.

Table 1. Expected compositions and activities of the volatiles (100g BR-3 fuel basis)

| Isotopes | | Mass | | Activity | | Major isotopes |
|----------|--------------------------------|----------|--------|----------|--------|----------------|
| | | g | % | Ci | % | |
| C-14 | CO ₂ | 7.00E-06 | 0.00 | 3.12E-05 | 0.00 | 14 |
| I | I ₂ | 2.44E-02 | 2.51 | 3.41E-06 | 0.00 | 129 |
| Ru | RuO ₄ | 3.93E-01 | 40.37 | 9.47E-07 | 0.00 | 106 |
| Cs | Cs ₂ O | 3.23E-01 | 33.20 | 7.31E+00 | 99.96 | 137 |
| Tc | Tc ₂ O ₇ | 1.62E-01 | 16.65 | 1.74E-03 | 0.02 | 99 |
| Rb | Rb ₂ O | 6.08E-02 | 6.25 | 3.31E-09 | 0.00 | 87 |
| Cd | CdO | 1.00E-02 | 1.03 | 1.13E-03 | 0.02 | 133m |
| Total | | 0.973 | 100.00 | 7.31 | 100.00 | |

(C) Characteristics of the trapping agents to be used in OTS

The OTS will be equipped with a fly ash filter, a calcium-based filter and a silver impregnated zeolite filter. Characteristics of those filters are presented in Table 2.

Table 2. Characteristics of the filters to be used in OTS

| Equipment | Trapping Media | Design Base | Remarks |
|----------------------------|----------------------------|--|--|
| Cs(Rb, Cd) trapping unit | Fly ash filter | <ul style="list-style-type: none"> • Capacity : 250 mg- Cs₂O /g-bed • Velocity : < 20 cm/sec • Temperature : 800 • Decon. F. : 1,000 | <ul style="list-style-type: none"> • Specific surface area : 9.31 m²/g • Porosity : 27 % • packing density : 0.5 g/cc • Disk type |
| Ru(Tc, C-14) trapping unit | Calcium filter | <ul style="list-style-type: none"> • Capacity : 120 mg- RuO₂ /g-bed • Velocity : < 20 cm/sec • Temperature : 800 • Decon. F. : 1,000 | <ul style="list-style-type: none"> • Porosity : 30 % • Packing density : 0.3 g/cc • Disk type |
| I trapping unit | Silver impregnated zeolite | <ul style="list-style-type: none"> • Capacity : 200 mg-I₂/g-bed • Velocity : < 20 cm/sec • Temperature : ~ 150 • Decon. F. : 1,000 | <ul style="list-style-type: none"> • Ag content : 10 wt.% • Packing density : 0.65 • Granular type |

(D) Required temperature of the tubes during operation of OTS

Preventing the condensation of the volatile elements inside of the tubes before trapping on the filters, tubes connected in OTS have to be sustained above the boiling temperatures of the elements as given in Table 3.

Table 3. The minimum temperatures of the tubes during operation of the OTS

| Type of connection pipe | Pipe temp. () |
|---|----------------|
| Connection pipe between DEOX outlet and Cs(Rb, Cd) trapping unit | over 650 |
| Connection pipe between Cs(Rb, Cd) trapping unit and Ru(Tc, C-14) trapping unit | over 310 |
| Connection pipe between Ru(Tc, C-14) trapping unit and Iodine trapping unit | over 180 |

(E) Flow diagram for off-gas trapping

The flow diagram for off-gas trapping during testing at HFEF is as following

Figure 1.

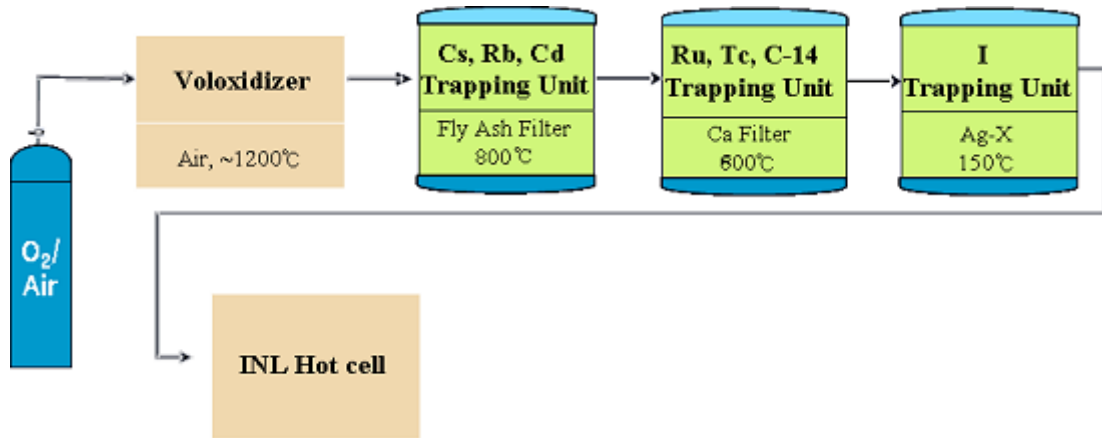


Figure 1. Flow diagram for off-gas trapping system.

(F) Specific design requirements of the off-gas trapping units

Design requirements such as trapping media, fission products to be trapped, design temperatures of the trapping units, optimum operation temperatures and specifications of the filters for the OTS are summarized in Table 4.

Table 4. Specific design requirements of the off-gas trapping units

| Trapping unit | Trapping media | FPs to be trapped | Design temp., | Operating temp., | Design spec. |
|-----------------------------|----------------|-------------------|---------------|------------------|---|
| Cs (Rb, Cd) trapping unit | Fly ash filter | Cs, Rb, Cd | ~ 1,000 | 800 | D = 2.0cm BH = 3.6cm SV = 10.0cm/sec CT= 0.36sec |
| Ru (Tc, C-14) trapping unit | Calcium filter | Ru, Tc, C-14 | ~1,000 | 600 | D=2.0cm BH= 8.0cm SV= 10.0cm/sec CT= 0.8sec |
| I trapping unit | AgX | I | ~500 | 150 | D = 2.0cm BH = 5.0cm SV = 3.8cm/sec CT = 1.3sec |

* D: diameter, BH: bed height, SV: superficial gas velocity, CT: contact time

(G) Evolution of the OTS filter unit design

The OTS filter design has evolved significantly from the first design review meeting held at the INL where the proto-type filter units shown in Figure 2 were presented by the KAERI. Following this meeting, it was decided by the INL and the KAERI to manufacture an entirely new furnace and OTS assembly in order to meet the heating and sealing requirements associated with the filters. The second filter units manufactured by KAERI for this new furnace and OTS are shown in Figure 3. Following final design changes to the filter units, the approved drawings given in Figures 4-8 have been produced for the mesh and disk type filter cartridges. Shown in Figure 9 are the final designed filter units delivered to the INL from the KAERI.



Figure 2. First filter units manufactured by KAERI.



Figure 3. Second filter units manufactured by KAERI.

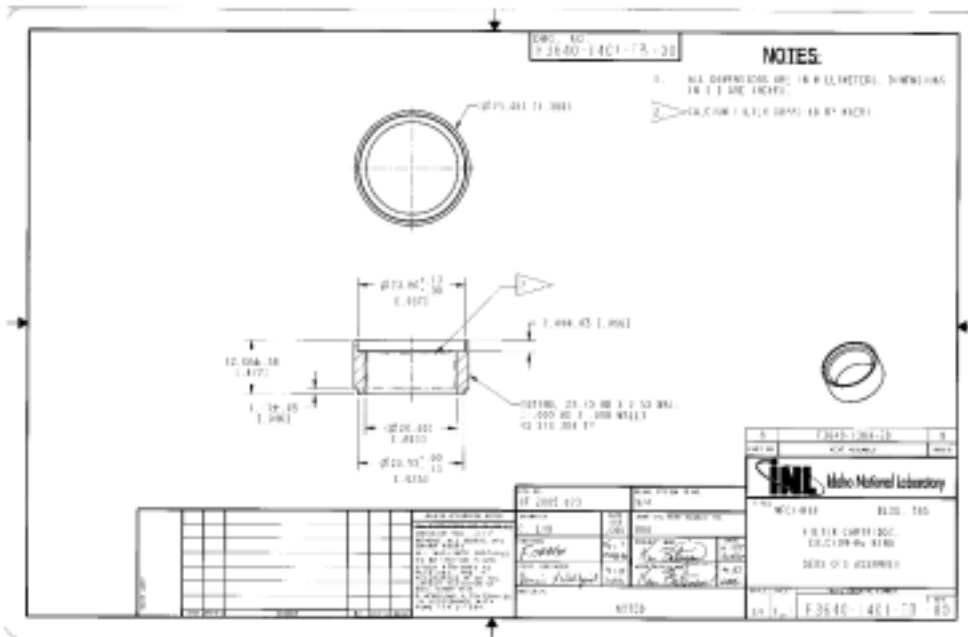


Figure 8. Disk Filter Cartridge – Calcium (INL Drawing No. F3640-1401-EB-00).



Figure 9. Filters delivered to INL by the KAERI (INL Photo No. MFC-060727-1182 & MFC-060727-1183).

2.1.2. Manufacturing, installation and test operation of an off-gas treatment system for a voloxidizer in the U.S.

Following the decision to utilize a new furnace as part of the OTS, vendor contact was initiated to discuss possible designs. The new design consists of a vertical split tube furnace with four separate heating zones (Figures 10 and 11). The lower zone is used to volatilize the spent nuclear fuel up to 1200°C. The next three zones are for trapping volatile off-gases and are heated to 800°C, 600°C, and 150°C, respectively.

Some of the advantages of this new design are:

- Furnace heater elements are remotely replaceable.
- A leak check can be performed out-of-cell on most of the OTS assembly.
- The off-gas will remain hot between the zones without additional heating.
- Filter cartridges can be transferred directly to the laboratory without additional preparation.
- Filter design is simplified.

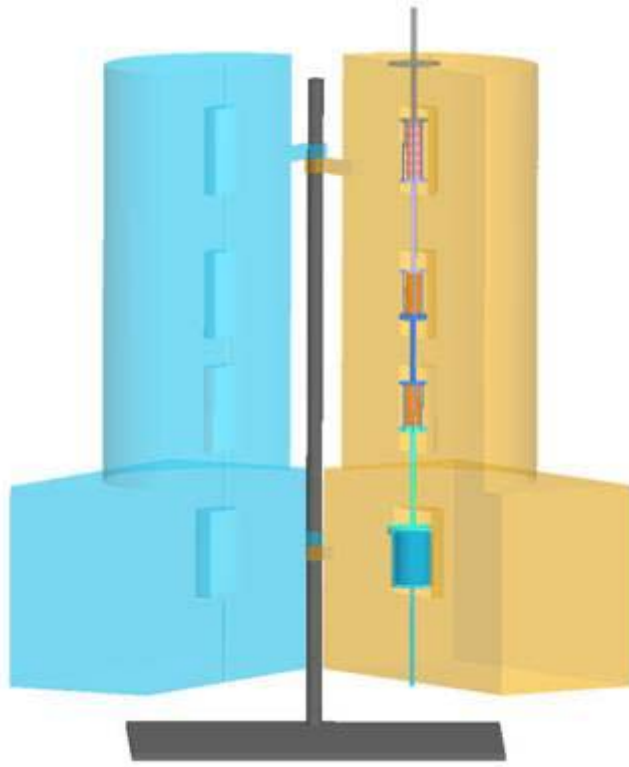
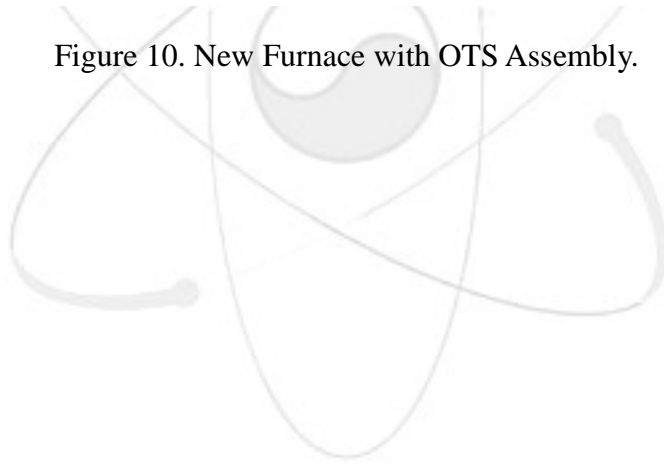


Figure 10. New Furnace with OTS Assembly.



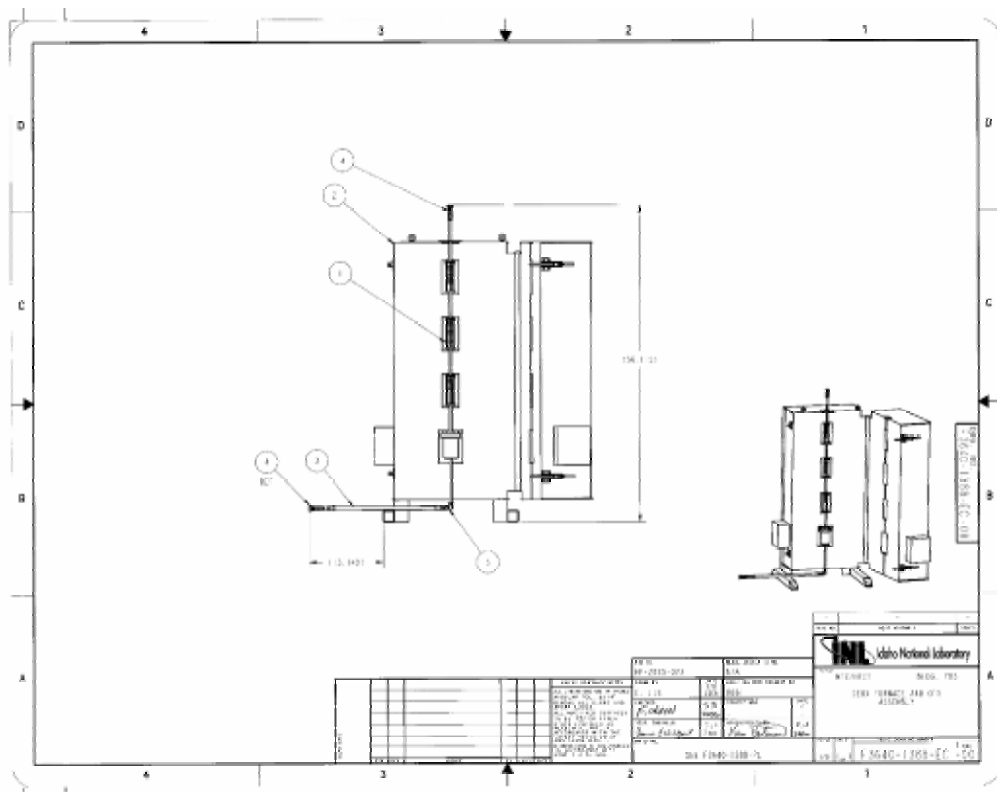


Figure 11. New Furnace with OTS Drawing (INL Drawing No. F3640-1388-EC-00).

Since the OTS assembly (Figures 12 through 14) is not part of the furnace, most of it can be assembled and leak checked outside of the HFEF hot cell. The crucible holder and hose fitting will be the only connections made in the hot cell. This reduces multiple leakage paths that existed in the original design. An inconel C-ring with a nickel coating was chosen as the sealing material to be used between the ring type filter cartridges. A standard viton O-ring will be used between the mesh type filter cartridges, because the temperature in the top zone will be below 200 °C. The seal material for the crucible holder (1200 °C) is still under investigation. One potential solution is to use a nickel coated titanium V-ring, however, they are quite costly. Grafoil sheeting is a possibility but it tends to break down in an elevated

temperature oxygen environment. Grafoil may be acceptable for single-use testing purposes.

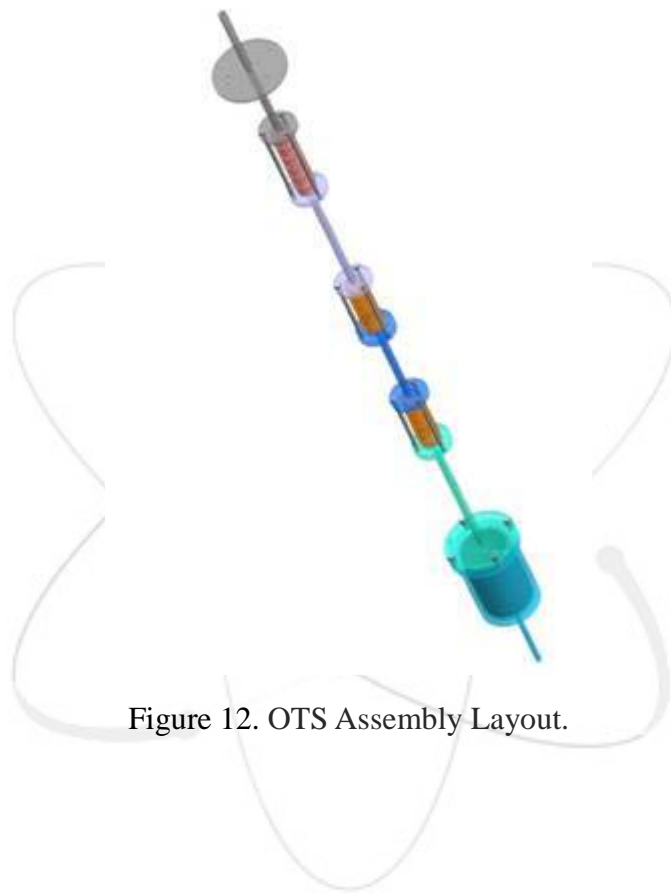


Figure 12. OTS Assembly Layout.

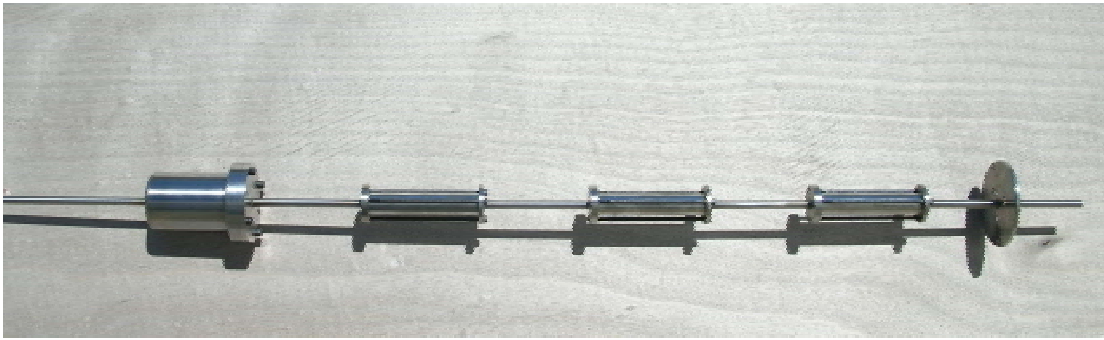


Figure 13. Fabricated OTS Assembly.

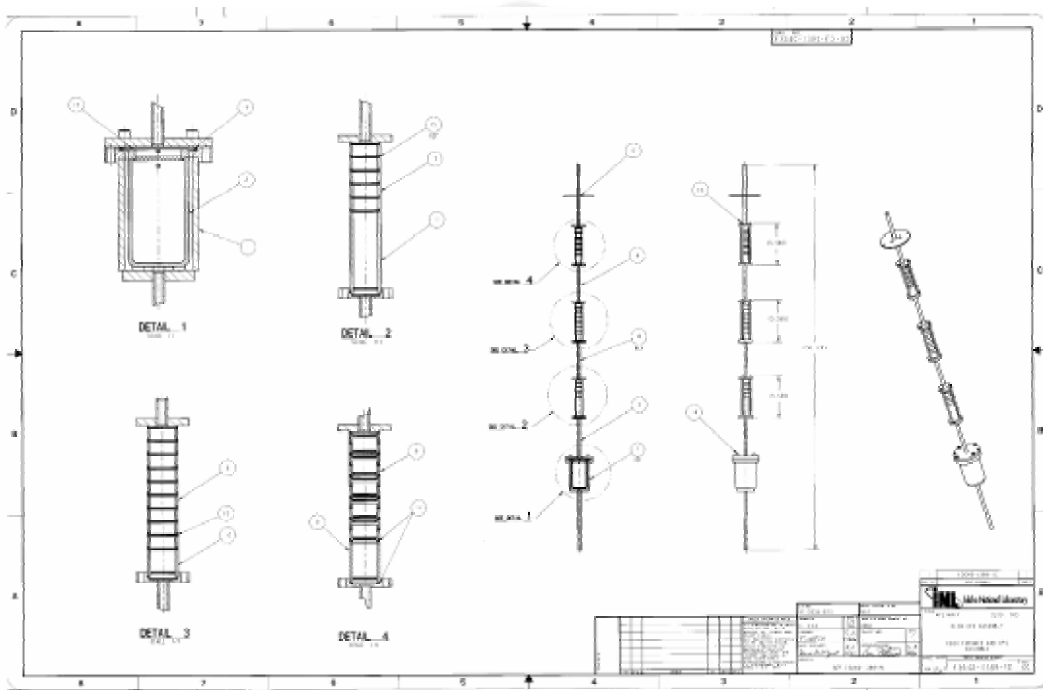
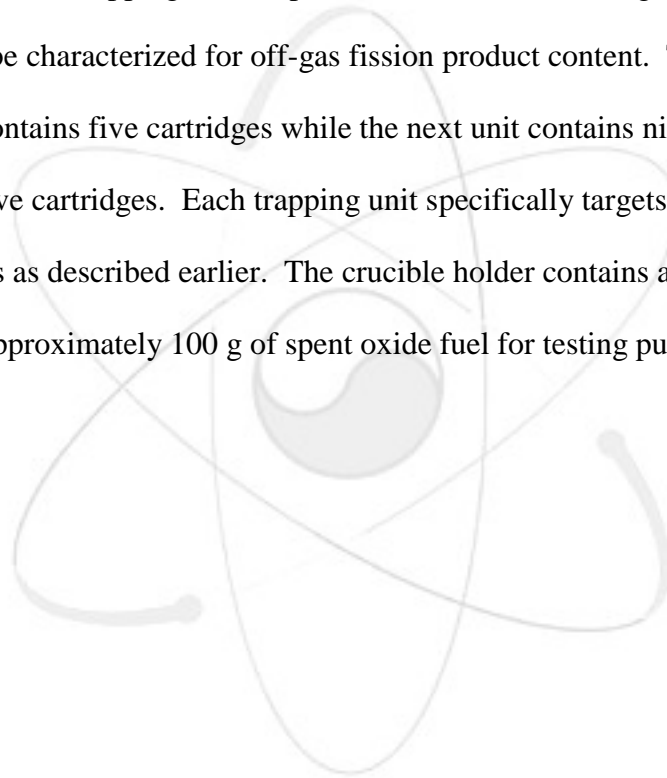


Figure 14. OTS Assembly Drawing (INL Drawing No. F3640-1389-ED-00).

A new feed-through will be required in HFEF as part of the furnace operation. Station 10M has been identified as the location for the furnace. All the power and thermocouple requirements will be incorporated into the feed-through design. In

addition, a new table at 10M is planned as part of another project and will be utilized for furnace operation.

Following an oxidation and trapping test, disassembly of the OTS will be necessary in order to sample the filter media. A conceptual model of the OTS disassembly fixture has been completed and is shown in Figure 15. The fixture allows disassembly of the three filter trapping units as well as the crucible holder. Disassembly of each trapping units exposes the individual cartridges so that the cartridges can be characterized for off-gas fission product content. The lowest trapping unit contains five cartridges while the next unit contains nine and the upper unit contains five cartridges. Each trapping unit specifically targets different off-gas fission products as described earlier. The crucible holder contains an alumina crucible with approximately 100 g of spent oxide fuel for testing purposes.



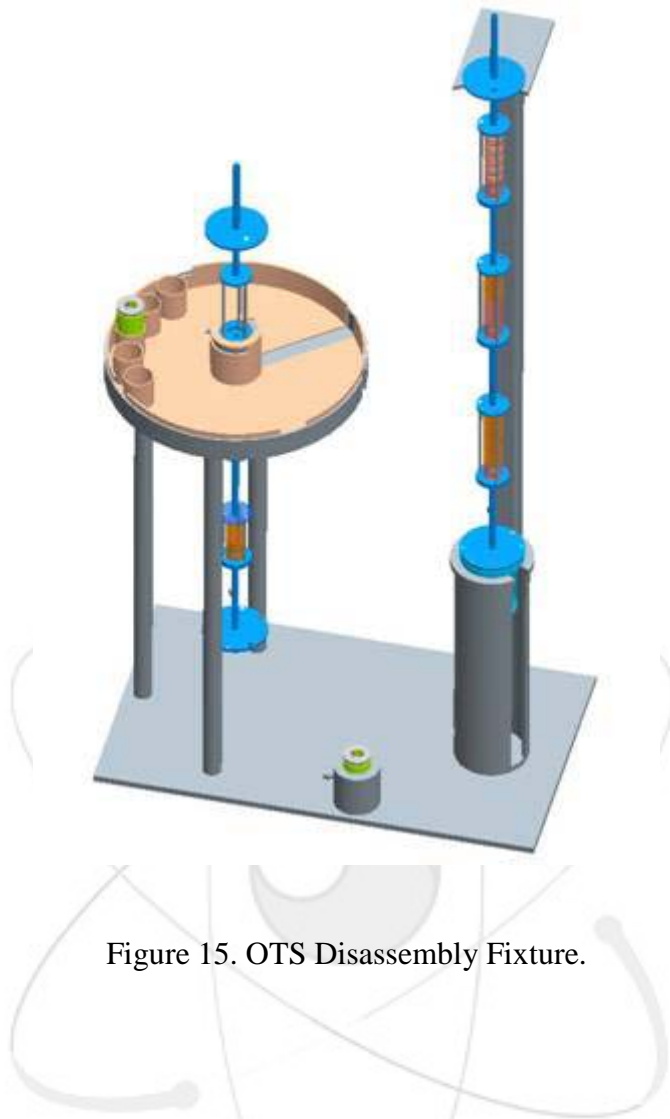


Figure 15. OTS Disassembly Fixture.

The new furnace associated with the OTS was received from the vendor (Thermcraft, Inc.) in June 2006. A qualification plan for equipment assembly checkout and the out-of-cell acceptance testing was initiated as well as associated safety and environmental evaluations. The filter cartridges were shipped to the INL from KAERI in July 2006. Following completion of the safety and environmental evaluations, the equipment qualification for the OTS and furnace was performed in the mock-up area of the Fuel Conditioning Facility in August 2006 (Figures 16 through 20).



Figure 16. Furnace with OTS during Qualification (INL Photo No. MFC-060727-1192).



Figure 17. Control Cabinet for Furnace (INL Photo No. MFC-060822-1196 & MFC-060822-1197).

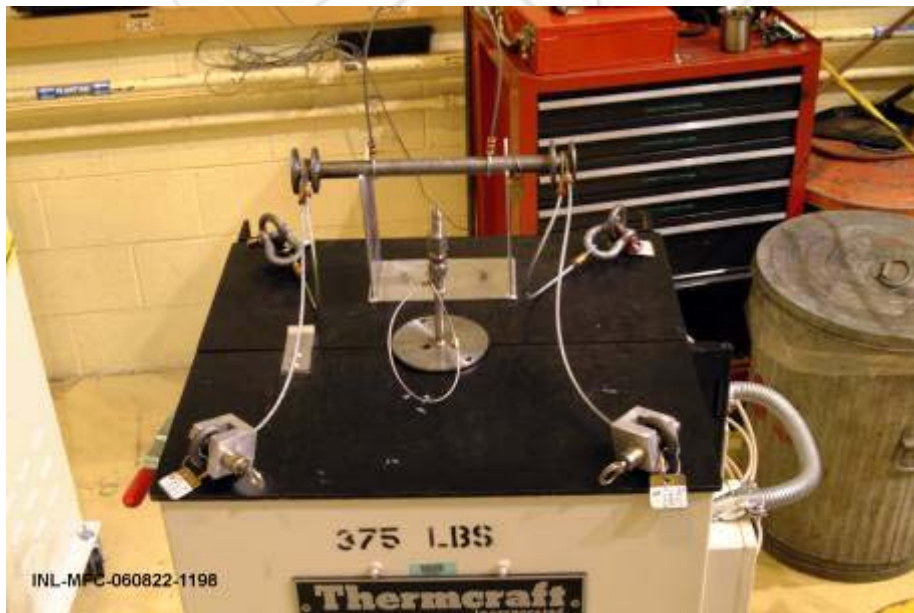


Figure 18. Top of Furnace with OTS installed (INL Photo No. MFC-060822-1198).



Figure 19. Left and Right Side of Furnace (INL Photos No. MFC-060822-1202 & MFC-060822-1200).

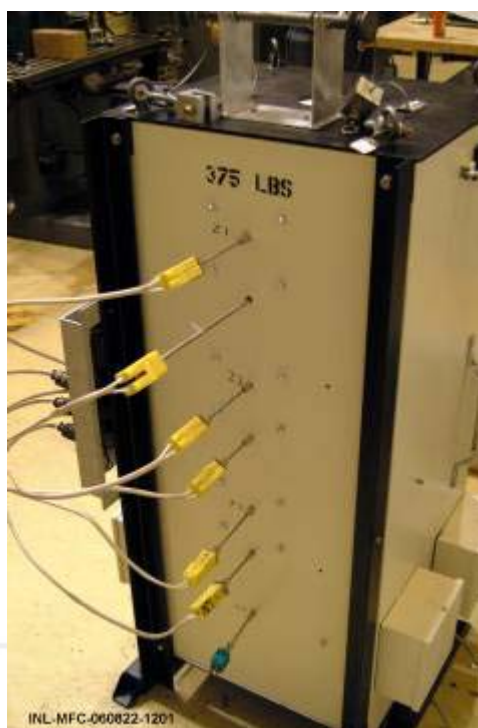


Figure 20. Back Side of Furnace (INL Photo No. MFC-060822-1201).

The qualification for remote operations of the OTS and furnace was completed in August 2006. Installation encompassed the completion of qualification and included the equipment assembly, functional checkout, remote modifications, and out of cell acceptance testing of the equipment as it will be configured in the HFEF.

Additionally, the following test operations were performed during qualification: oxidant flow and vacuum conditions, leak checking, and determination of axial temperature profiles. Temperature data for the different zones of the furnace are given in Figure 21.

Figure 22 is a photograph of the furnace and OTS after completion of the qualification testing. The furnace and OTS are ready to be transferred to HFEEF pending completion of the in-cell qualification for the work table at 10M. The table has been placed at 10M but still requires final approvals. Following the qualification of the 10M table, the furnace and associated feed-through will be transferred to HFEEF for its in-cell qualification. Testing with irradiated materials will commence following the in-cell qualifications.

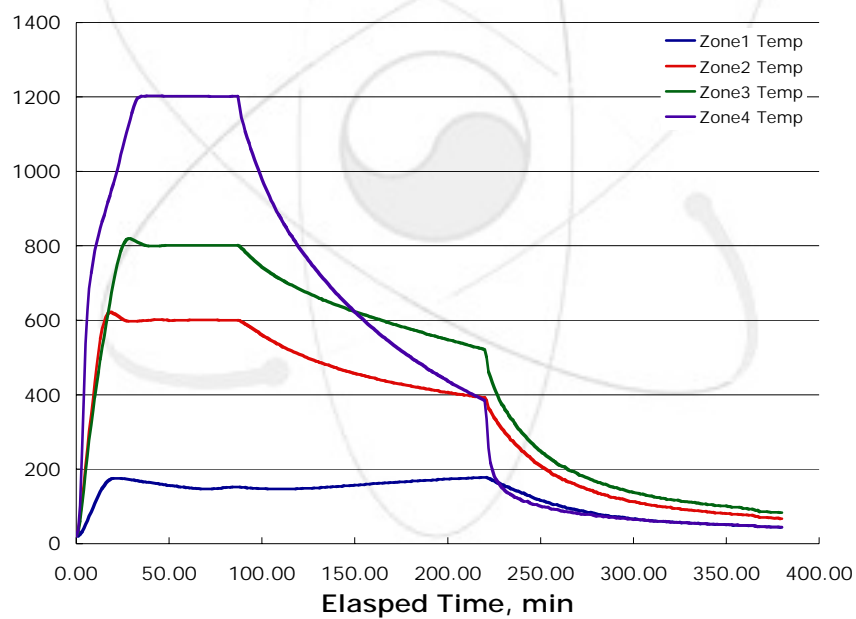


Figure 21. Furnace Temperature Profile with OTS.



Figure 22. Furnace and OTS After Qualification (INL Photo No. MFC-060822-1205).

2.2. Independent experiments to develop of trapping concepts for immobilizing volatiles released during the voloxidation treatment

The most promising trapping method for each fission product has been proposed for the development of the INL off-gas trapping system. A calcium filter is proposed as a trapping media for ruthenium, technetium, and ^{14}C trapping unit. In-active tests using reagent were carried out to evaluate performance of trapping material in a bench scale. These experimental data can be used in comparing with hot data to be carried out in the HFEF. Also, these can be helpful for predicting hot experimental data.

(A) Ruthenium trapping technology

A certain amount of ruthenium is known to be in spent nuclear fuel as a fission product. It generally exists in the form of metallic precipitate and is easily oxidized to RuO_2 when heated in oxidation atmosphere. When RuO_2 is exposed to such high temperature and oxidation atmosphere as in the dissolution and separation processes of wet reprocessing treatment, it is oxidized and volatilized to sublimate RuO_4 whose boiling point is 25.4 °C.

Ruthenium is present in spent LWR fuel as RuO_2 , which is very stable in a reducing or inert atmosphere. Even in air at temperatures below 500 °C, it is stable. However, in air or under oxidizing conditions at elevated temperatures (> 500 °C), the ruthenium dioxide oxidizes to the tetra oxide (RuO_4), which is very volatile. Both the oxidation and vaporization rates increase considerably with increased temperature. At 1200 °C the rate of vaporization is about 4000 times faster than at 700 °C. Gaseous RuO_4 decomposes back to the dioxide as it cools to temperatures below 500 °C. Once RuO_4 vapor transports from the hot zones of processing equipment, it would be

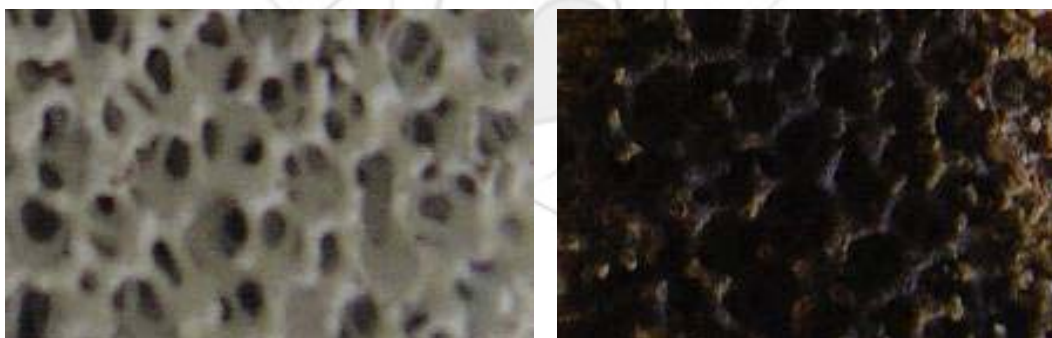
expected to transport primarily as fine particulates of RuO₂ associated with aerosol. In this form the ruthenium can be captured by filtration.

To apply calcium oxide for off-gas treatment system of gaseous ruthenium, it should be manufactured as a disk form. Also, it is necessary to obtain the information on the operating conditions of ruthenium trapping unit using the calcium-based filters. Calcium oxide and aluminosilicate material were used. To manufacture a ceramic foam filter, Calcium oxide, aluminosilicate material, polyvinyl alcohol as a binding material were mixed together to make a uniform slip solution. This slip solution was impregnated with a polyurethane sponge and surplus slip was removed from the sponge. And then it was dried at 95°C and sintered at 1250°C. The heating rate was constantly maintained at 5°C/min and sintering time was 6 hours.

Two-zone furnace of alumina tube is shown in Figure 23. In the first hot zone, ruthenium (99.9%, Aldrich Co.) was used to generate a controlled source of gaseous cesium, which was scheduled to pass through the calcium based filters mounted in the second hot zone. Filters were tightly packed in an alumina tube of furnace by using an alumina sheet. The experiments were conducted under the air condition because gaseous ruthenium was considered to be released during the voloxidation process. The trapping efficiency of volatile ruthenium by the calcium based filters was over 99% in the case of ruthenium generation quantity of 0.06g-Ru/h, reaction temperature of 600 °C, reaction time of 6 hours and filter depth of 0.021 to 0.035m in air condition. Figure 24 shows photographs before and after trapping gaseous ruthenium by using calcium-based filter. According to the XRD analysis for the ruthenium compound reacted with calcium based filter, CaRuO₄ of perovskites structure was formed.



Figure 23. Photograph of two-zone furnace.



(before trapping)

(after trapping)

Figure 24. Ca-based filters before and after trapping gaseous ruthenium.

(B) C-14 trapping technology

In this study, we examined the thermal behaviors of CaO with CO₂ at temperatures from 400 to 800 °C in CO₂/air mixture. High purity calcium oxide (Shinyo Pure Chemicals Co.) was used. This was sintered at 900 °C for 6 hours in a box furnace and stored in a desiccator before use. CO₂ of 1% in an air balance gas was used. A weighted sample of CaO was placed in an aluminum oxide crucible and positioned in the heating zone of TGA apparatus inside quartz tube. The sample of CaO was heated from room temperature to 400 °C and held at 400 °C for 3 hours. The heating and holding temperatures were changed to 500 °C, 600 °C, 700 °C and 800 °C in the each run. The sample weight was monitored throughout the experiments. TGA analyzer was used to investigate the thermal behaviors between CaO and CO₂ at different temperatures. The reaction products were identified by XRD (X-ray Diffraction)

Figure 25 shows the TGA patterns of the CaO as a function of trapping temperature curves in the temperature range of 400 to 800 °C. TGA showed a little weight gain when CaO was heated to 400 °C and 500 °C, respectively. The trapping capacity for CaO with CO₂ at 600 °C enhanced greatly. However, TGA showed considerable weight loss of the CaO when it was heated above 700 °C. The amounts of weight loss at 700 °C and 800 °C were unobserved in significant difference.

XRD analysis of the adsorbent surfaces reacted at 600°C of trapping temperature showed that CaO and CaCO₃ was identified as shown in Figure 26. However, no CaCO₃ peak was detected under a high temperature above 700 °C. From the above results, it could be concluded that the suitable temperature of CaO for trapping CO₂

is 600 . In the case of high temperature above 700 , there is no trapping for CO₂ on calcium oxide.

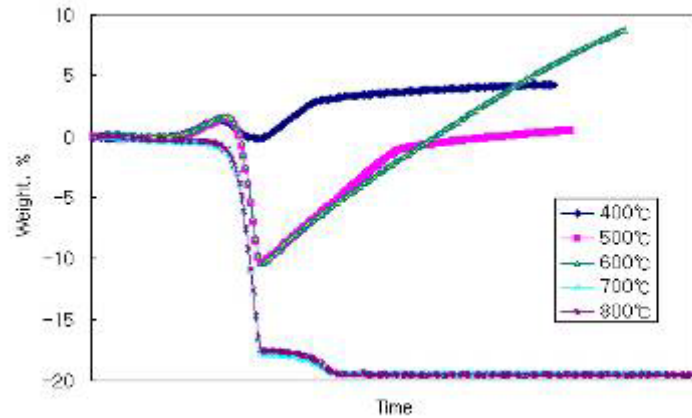


Figure 25. TGA patterns of the CaO as a function of trapping temperature.

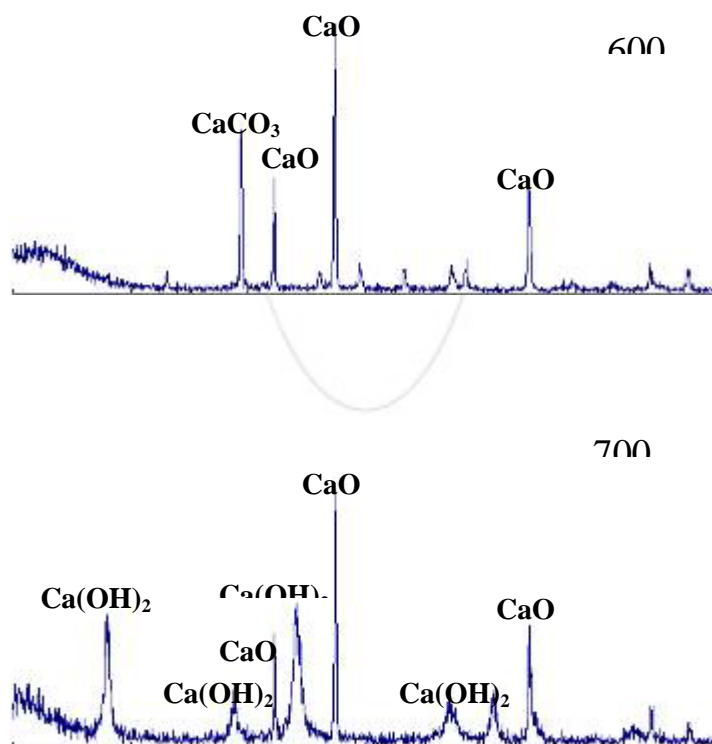


Figure 26. XRD patterns of the CaO as a function of trapping temperature.

The trapping efficiency of CO₂ by the calcium based filters was over 99% in case of CO₂ concentration of 1%, reaction time of 10 min and filter depth of 0.035 to 0.070 m in the air atmosphere.

(C) Technetium trapping technology

Technetium is fission product forming metallic precipitate. The radioactive technetium produced as uranium fission by-products would be subjected to this oxidation step resulting in the generation of Tc₂O₇. In high temperature processes, it is possible to volatilize Tc oxides. The most stable oxide, Tc₂O₇, has a melting point of 119.5 °C and a boiling point of 311 °C. Technetium dioxide sublimates above 900 °C and decomposes into Tc and Tc₂O₇ at temperatures above 1100 °C. Technetium is an artificially produced element. In its chemical behavior resembles Rhenium. Rhenium has a very high melting point (over 3180 °C), thermally cycles well, and is stable in reducing atmospheres. However, it readily reacts with oxygen and forms a series of thermodynamically rhenium oxides. There are three principle oxides such as Re₂O₇ (g), ReO₃ (g), and Re₂O₆ (g).

Rhenium (99.9%, Aldrich Co.) was used as a surrogate of technetium in this study. Trapping experiment was performed to investigate the trapping characteristics of Re with calcium oxide at 900 °C for 3 hours under air condition by using TGA (Setaram, TG-DTA 92) analyzer. The samples made to have 1:1 mole ratio of Ca to Re in the mixture of Re and CaO. After trapping experiment, the reaction products were identified by XRD(X-ray Diffraction).

Figure 27 shows the TGA curve for the mixture of CaO and Re. As shown in Figure 27, it is indicated that Re was started to react with CaO at the temperature of 600 °C. There is no evidence on the change of TGA curve up to 900 °C. This shows that thermally stable compounds are formed.

Two-zone furnace of 5.0 cm I.D. alumina tube as shown in Figure 23 was used to trap gaseous rhenium. In the first hot zone, rhenium was used to generate a controlled source of gaseous cesium, which was scheduled to pass through the calcium based filters mounted in the second hot zone. Filters were tightly packed in an alumina tube of furnace by using an alumina sheet. The trapping efficiency of volatile ruthenium by the calcium based filters was over 99% in the case of cesium generation quantity of 0.14g-Re/h, reaction temperature of 600 °C, reaction time of 6 hours and filter depth of 0.021 to 0.035m in air condition. Figure 28 shows photographs before and after trapping gaseous rhenium by using calcium-based filter. According to the XRD analysis for the rhenium compound reacted with calcium based filter were mainly formed $\text{Ca}(\text{ReO}_4)_2$ as shown in Figure 29.

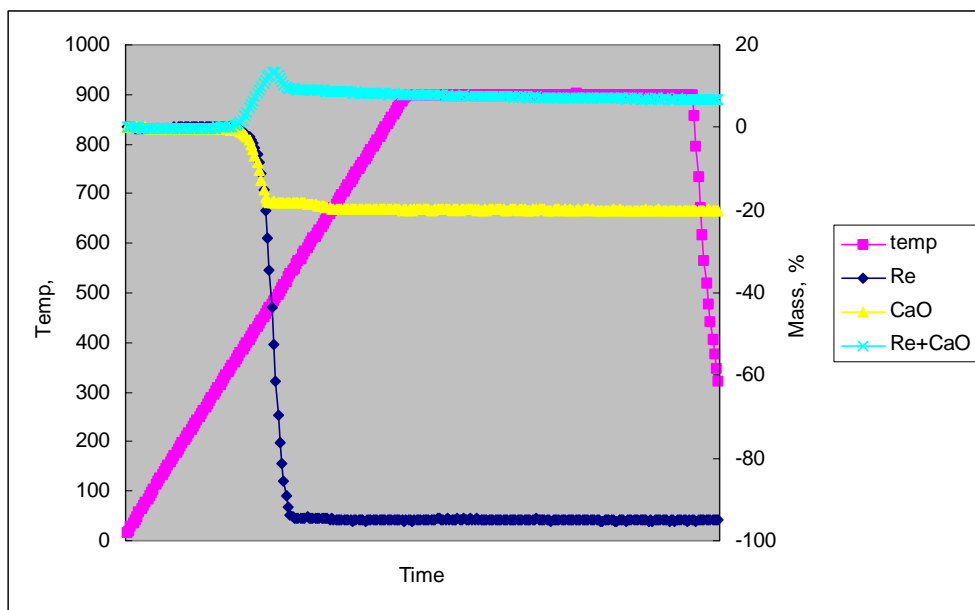
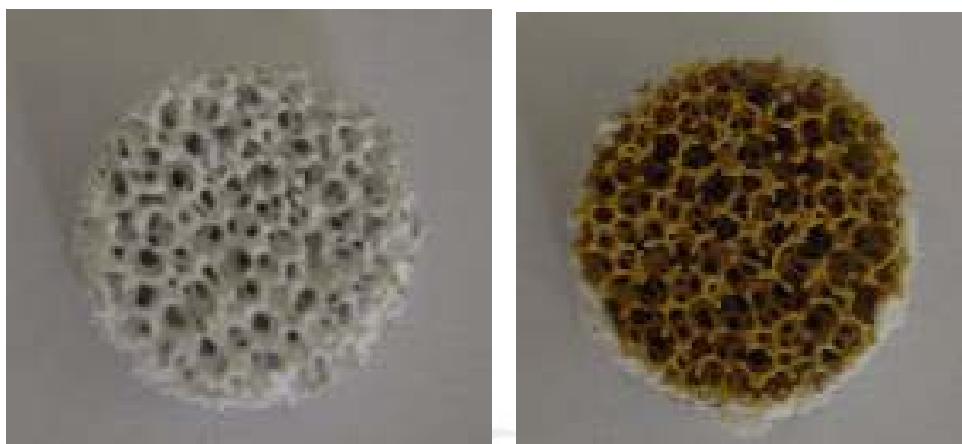


Figure 27. TGA curve for the mixture of CaO and Re.



(before trapping)

(after trapping)

Figure 28. Ca-based filters before and after trapping gaseous rhenium.

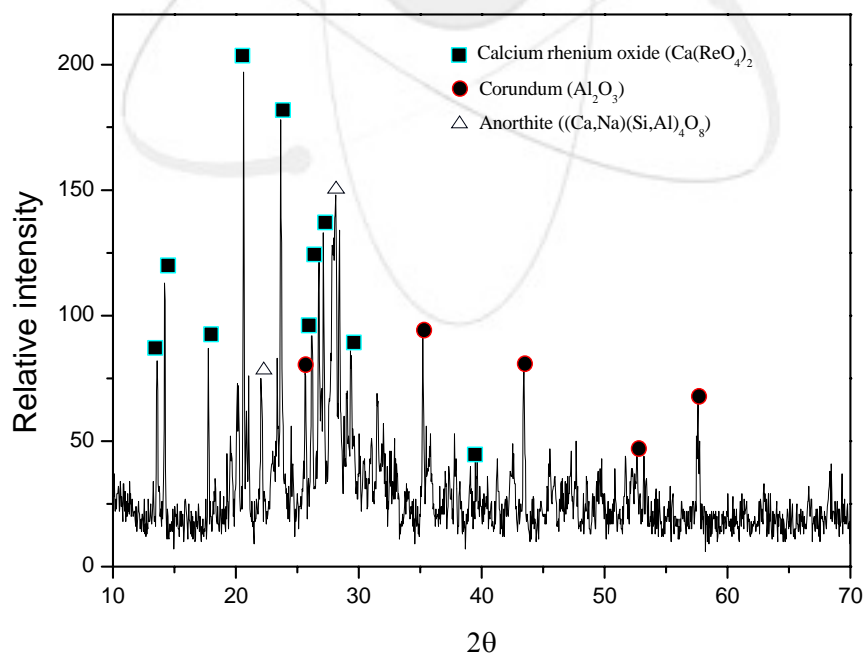


Figure 29. XRD pattern of reaction product formed by the reaction of calcium based filter and Re.

3. Planned next year activities

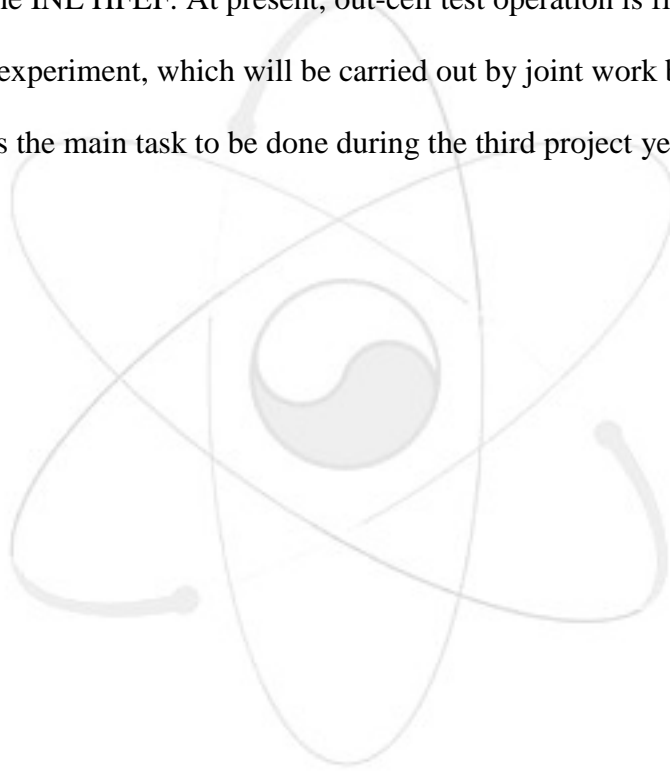
The planned next year activities from June 2006 to May 2007 in KAERI on the hot experiment on the recovery and trapping of gaseous fission products from spent fuel is as following Table 5.

Table 5. Planned next year activities

| Activities | Schedule (2006) | | | | | | | | | | | |
|--|-----------------|---|---|---|---|---|---|---|---|----|----|----|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| <ul style="list-style-type: none"> • Hot experiment on the recovery and trapping of gaseous fission products from spent fuel - Manufacturing and offering the filter sets for INL hot experiments - Operation of an off-gas treatment system for a voloxidizer in the U.S. - Measurement and evaluation of the efficiency of recovery of gaseous fission products from a voloxidation off-gas treatment system in the U.S. - Independent experiments to develop of trapping concepts for immobilizing volatiles released during the voloxidation treatment | | | | | | | | | | | | |
| | | | | | | | | | | | | |

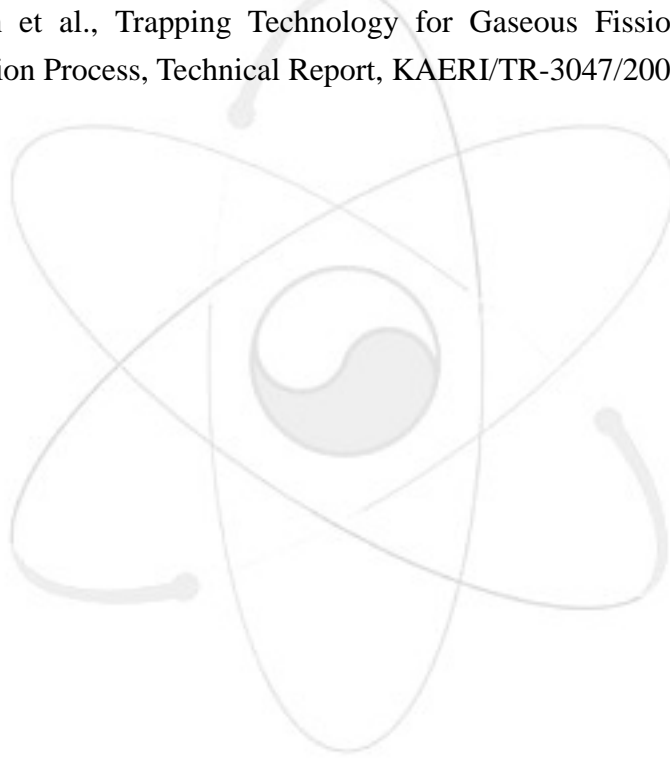
4. Conclusion

KAERI developed the design of INL OTS (Off-gas Treatment System) for hot experiment in the HFEF. INL team modified and completed the design of the INL OTS. Manufacturing of the OTS is accomplished by INL team with co-work of KAERI. Manufacturing of the OTS is accomplished by INL team with co-work of KAERI. KAERI provided four sets of trapping filters needed for conducting hot experiment in the INL HFEF. At present, out-cell test operation is finished, and it is waiting for hot experiment, which will be carried out by joint work between KAERI and INL. This is the main task to be done during the third project year.



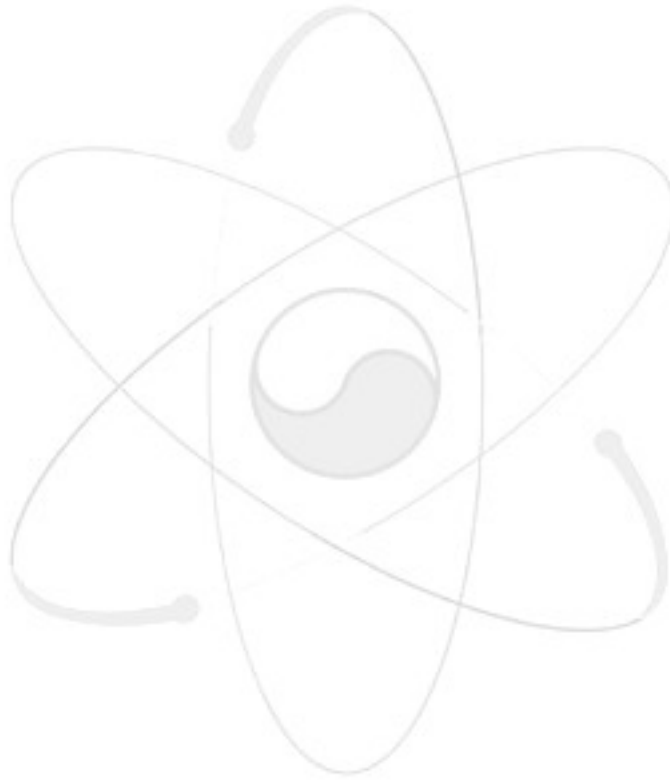
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2. D.S. Cox et al., “Fission product release from UO_2 in air and inert conditions at 1,700 ~ 2,350K : Analysis of the MCE-1 experiment”, AECL-10438, Chalk River National Lab., Canada (1991).
3. J.M. Shin et al., Trapping Technology for Gaseous Fission Products from Voloxidation Process, Technical Report, KAERI/TR-3047/2005 (2005)



APPENDIX

1. Attachment I : 1st Technical Design Meeting Minutes (September 6-9, 2005)
2. Attachment II : 2nd Technical Design Meeting Minutes (February 23-27, 2006)



Attachment I:

September 7, 2005

CCN 202449

Distribution

CONTRACT NO. DE-AC07-05ID14517 – MEETING MINUTES FROM KAERI VISIT (SEPTEMBER 6-9, 2005) TO DISCUSS DESIGN OF OFF-GAS TREATMENT SYSTEM (OTS) FOR JOINT I-NERI PROGRAM

Concerns/Agreements

- 1) Detection of Ru-106 will be difficult with gamma-scan considering the age of the BR-3 fuel, thus ICP-OES is the preferred detection method for elemental ruthenium.
- 2) The most important examinations of the filter packs are, in order: gamma-scanning, chemical (ICP), XRD, SEM, and EPMA/XRF. Depending on the activity of the samples, XRD and SEM may not be possible due to sample size/handling restrictions in INL facilities.
- 3) The original plan to remove filters every 5 runs was changed to remove filters every run. The filter size can be reduced to approximately 1 inch size for ease of handling in the analytical laboratory and for shipping in transfer (rabbit) system.
- 4) Since the filters will be removed after every run, using 304 SS at 1000°C should not cause material problems for the filter design.
- 5) The use of a bubbler in HFEF is not necessary and was eliminated from the design. A flow meter was suggested as an alternative.
- 6) For easy procurement of Inconel in Korea, INL may be able to assist in its procurement. Initially, it appears that 2 inch diameter piping is easily available, will continue pursuing smaller diameter.
- 7) After meeting with Cal Morgan and Mark Huntley, the proposed methods for analyses of C-14 and I-129 are acceptable. In fact, the method for I-129 is very interesting in that it would be new technology for the INL. Also discussed with Mark was the detection of Cs-137 and geometric requirements for optimal analyses.
- 8) It was agreed upon to split the division of work between KAERI and INL as such: KAERI is in charge of design of three filter packs including the disk, grip, housing, and OTS. INL is in charge of design of furnace system which includes the redesign of current DEOX furnace. The redesign would better accommodate planned batch sizes and

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relocation of equipment in HFEF. Included in the furnace system is the piping between filter packs and temperature controls as proposed by KAERI.

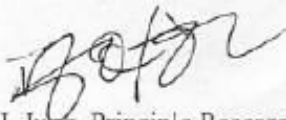
- 9) The proposed schedule by KAERI is being evaluated to determine if we can meet the June 2006 deadline to "Complete Hot Cell Installation".

Actions Items:

- 1) INL will evaluate proposed schedule.
- 2) INL will determine ability to perform XRD and SEM examinations
- 3) KAERI will discuss redesign of current DEOX furnace.
- 4) KAERI and INL will initiate design of OTS including new DEOX furnace section.
- 5) KAERI will provide procedure for I-129 analyses.



B. R. Westphal, Engineer
Nuclear Programs / Pyroprocessing Technology Department



I. Jung, Principle Researcher
Korean Atomic Energy Research Institute (KAERI)

BRW:mlh

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Attachment II:

Date: Feb. 23-27, 2006

To: Distribution

From: Jang Jin Park, Korea Atomic Energy Research Institute
Kenneth J Bateman, Idaho National Laboratory

Subject: Meeting Minutes for the Off-gas Trapping System (OTS) Design for International Nuclear Energy Research Initiative (I-NERI) Program on “Development of Voloxidation Process for Treatment of LWR Spent Fuel”

The second OTS design review meeting for the INERI Project associated with the development of a head-end voloxidation process was held Thursday, February 23 - Monday February 27, at Korea Atomic Energy Research Institute in Daejeon, Korea. The meeting was attended by representatives from each of the cooperating organizations - Korea Atomic Energy Research Institute (KAERI) and Idaho National Laboratory (INL). The purpose of this meeting - followed the first OTS meeting at INL during Sep. 5, 2005 – Sep. 11, 2005 - was to discuss the design of the OTS being installed at HFEF (Hot Fuel Examination Facility) of INL. The meeting included presentations of detail drawings of each side, tour of DUPIC Fuel Development Facility (DFDF), Irradiated Material Examination Facility (IMEF) and Advanced Conditioning Process Facility (ACPF) at KAERI site.



The meeting began with self-introduction of each attendant, followed by agenda review by Jang Jin Park and presentation from each party. After the presentation, a technical discussion was made to review and adjust further action items for the project. The action items, general comments, and suggestions drawn from the meeting are listed in the following.

Concerns and agreements

- INL presented outline of DEOX experiment, background, OTS Criteria, Proposed OTS Design, Design Considerations, responsibilities between INL and KAERI, OTS design of INL and design considerations.
 - INL will lead the OTS and furnace design and fabrication.
 - KAERI will lead the OTS filter design and fabrication.
- Installation of OTS at HFEF will be completed in July 2006.
- INL provided to KAERI one “Prototype” OTS for reference.
- KAERI presented plan action schedule of Task B (OTS), activities summary on OTS, and design of KAERI OTS.
- KAERI showed prototype OTS fabricated for independent experiments.
- KAERI noticed that the operation temperature of Ru trapping unit is lowered from 800 to 600 as results of investigation in KAERI.
- According to the proper administration procedures of KAERI, KAERI will supply sets of filters – Cs, Ru, and I – required for the i-NERI project (Voloxidation). In order to meet the proper administration procedures, KAERI needs official request letter from INL.
- INL and KAERI agreed on the design of some part of OTS as follows;
 - INL will use the spacer at the bottom of each trapping unit to have more exact temperature zone and improve gas flow pattern. And mesh screen or other proper material will be installed at the bottom of spacers of every trapping unit to prevent particulate inflow.
 - INL will provide the spacers. The maximum distance of the furnace zones is 152mm; therefore, the filter assemblies can not exceed 146mm per zone.
 - The number of filters has been modified to the following: five Cs, nine Ru, and five I.
 - The dimension of ring type container of Cs and Ru will be changed to 25.4mm in OD, 20.4mm in ID, 12mm in height, and tolerance +/-0.05mm. Others will follow NL design.
 - Bottom of mesh type filter will be changed to 25.4mm in OD, 20.4mm in ID, 12.7mm in height, and tolerance +/-0.05mm for using the Korean commercially produced tube.
 - Inconel gaskets will be installed between ring type containers for sealing system so that all the off-gas flows through the filter media. Viton O-ring will be used for mesh type container for the same purpose. KAERI will not provide inconel gaskets and viton O-rings.

Action Items

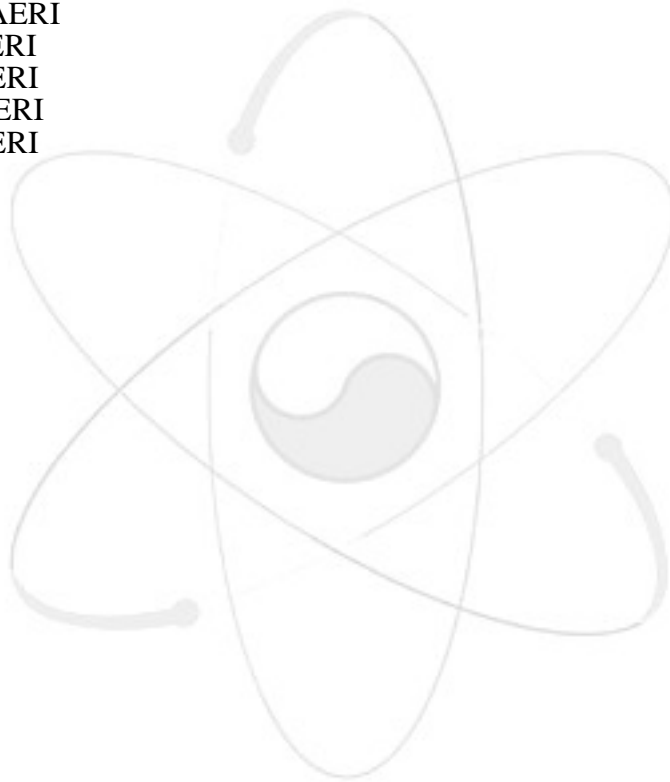
1. INL will send revised drawings of ring type and mesh type containers to KAERI by e-mail as soon as possible.
2. INL will request the quantity of filters for experiments to KAERI at least 8 weeks before.

Kenneth J. Bateman, Task Manager
Idaho National Laboratory (INL)

Jang Jin Park, Project Manager
Korea Atomic Energy Research Institute (KAERI)

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G. I. Park, KAERI
I. H. Jung, KAERI
J. M. Shin, KAERI
H. H. Lee, KAERI



| BIBLIOGRAPHIC INFORMATION SHEET | | | | | |
|--------------------------------------|--|---|------------------|---------------------|---------|
| Performing Org. Report No. | | Sponsoring Org. Report No. | | Standard Report No. | |
| KAERI/TR-3245/2006 | | | | | |
| Title / Subtitle | | Design report: An off gas trapping system for a voloxidizer in INL of US | | | |
| Main Author and Department | | In Ha Jung (Dry Process Fuel Technology Development Division) | | | |
| Researcher and Department | | J.M. Shin, G.I. Park, H.H. Lee J.J. Park (Dry Process Fuel Technology Development Division), Ken Batman, Wahlquist Dennis, Brian Westphal (Idaho National Laboratory) | | | |
| Publication Place | Taejon | Publisher | KAERI | Publication Date | 2006. 9 |
| Page | 55 p. | Ill. & Tab. | Yes(V), No () | Size | A4. |
| Note | | | | | |
| Classified | Open(V), Restricted(), -___ Class Document | | Report Type | Technical Report | |
| Sponsoring Org. | | Contract No. | | | |
| Abstract(15-20 Lines) | | <p>This reports on the “Development of Voloxidation Process for Treatment of LWR Spent Fuel”, and it is the second year since it has started from June 2004 as a tripartite cooperation project among KAERI(Korea Atomic Energy Research Institute), INL(Idaho National Laboratory) and ORNL(Oak Ridge National Laboratory).</p> <p>This report is described mainly for the Task B2 accomplished during the second project year. The Task B2 in proposal contains two sub-tasks. The first one is design of an off-gas treatment system for a voloxidizer to be used in HFEF of INL. For this, KAERI team developed the design of INL OTS (Off-gas Treatment System) for hot experiment in the HFEF. INL team modified and completed the design of the INL OTS. The second task is manufacturing and test operation of the INL OTS for a voloxidizer in the INL. Manufacturing of the OTS is accomplished by INL team with co-work of KAERI. KAERI provided four sets of trapping filters needed for conducting hot experiment in the INL HFEF.</p> | | | |
| Subject Keywords (About 10 words) | | Voloxidation process, Gaseous fission products, Off-gas treatment, Off-gas trapping system design, Head-end process | | | |

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| / | Design report: An off gas trapping system for a voloxidizer in INL of US | | |
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| | Ken Batman, Wahlquist Dennis, Brian Westphal (Idaho National Laboratory) | | |
| | | | 2006. 9 |
| | 55 p. | (V), () | A4 |
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| <p>2004 6 KAERI(Korea Atomic Energy Research Institute), INL(Idaho National Laboratory) and ORNL(Oak Ridge National Laboratory) 3</p> <p>Task B2</p> <p>4 set KAERI INL INL INL</p> | | | |
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