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SPENT FUEL TREATMENT AND MINERAL WASTE FORM DEVELOPMENT AT ARGONNE NATIONAL
LABORATORY-WEST

K. M. Goff
R. W. Benedict
K. Bateman
Argonne National Laboratory -West
P.O. Box 2528
Idaho Falls, ID 83403
(208) 533-7084

M. A. Lewis
C. Pereira
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

C. A. Musick
Lockheed Martin Idaho Technologies
P.O. Box 1625
Idaho Falls, ID 83415

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ABSTRACT

At Argonne National Laboratory-West* (ANL-West) there are several thousand kilograms of metallic spent nuclear fuel containing bond sodium. This fuel will be treated in the Fuel Conditioning Facility (FCF) at ANL-West to produce stable waste forms for storage and disposal. Both mineral and metal high-level waste forms will be produced. The mineral waste form will contain the active metal fission products and the transuranics. Cold small-scale waste form testing has been on-going at Argonne in Illinois. Large-scale testing is commencing at ANL-West.

I. INTRODUCTION

The Experimental Breeder Reactor II (EBR-II) at ANL-West in Idaho went critical in 1963. It is a sodium-cooled fast reactor with a maximum power level of 62.5 MWt while generating 20 MWe. Between 1965 and 1969, EBR-II spent fuel was processed in FCF using a melt refining operation.¹ The recovered actinides were recycled as new fuel. After 1969, FCF was modified to emphasize fuel examination services, and EBR-II fuel was treated at the Idaho Chemical Processing Plant.

In recent years, FCF underwent modifications to demonstrate the fuel cycle for the Integral Fast Reactor (IFR), an innovative liquid-metal-cooled reactor concept. The IFR was being developed to take advantage of the properties of metallic fuel and liquid-metal cooling to offer significant improvements in reactor safety, operation, fuel cycle economics, environmental protection, and safeguards.² For the IFR fuel cycle

demonstration, EBR-II spent fuel was to be refined, and the recovered actinides were to be fabricated into new fuel. During 1994, the decision was made by the Department of Energy (DOE) to terminate this program, and EBR-II was shutdown on September 30, 1994.

The EBR-II spent fuel, which is metallic fuel containing bond sodium, is unique with respect to the other fuels within the DOE complex. The sodium is fused within the fuel slug structure which swells extensively during irradiation. The presence of the sodium adds a reactive and therefore a hazardous component. Additionally, EBR-II core fuel uses highly enriched uranium. For the safe storage and eventual disposal of EBR-II spent fuel, treatment operations are required to neutralize the reactive sodium, stabilize the fission products, and place the actinides in a stable form. These operations will be performed in the Fuel Conditioning Facility and will make use of existing equipment from the terminated IFR demonstration.

II. SPENT FUEL INVENTORY

EBR-II fuel is primarily categorized as either driver or blanket fuel. Both types are metallic fuel containing bond sodium, so both require treatment. This fuel is currently stored at ANL-West in four locations: the EBR-II reactor vessel, the Hot Fuel Examination Facility (HFEF), the Radioactive Scrap Waste Facility (RSWF), and most recently, the air cell in FCF. The fuel in the reactor vessel is presently being unloaded. Additional EBR-II metallic fuel is stored at the Idaho Chemical Processing Plant and the Savannah River Site.

The driver fuel is composed primarily of four different fuel assembly types: Mark-IIC, Mark-IICS, Mark-III, and Mark-IIIA. The Mark II materials are control and safety assemblies. Most of the driver materials are Mark III type core assemblies. The bulk of the driver fuel at ANL-West is a uranium-(10 weight percent) zirconium alloy. All four fuel assembly types

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are composed of 61 fuel elements containing highly enriched uranium. The end-of-life enrichment of the Mark-II types is approximately 75 percent, and the Mark-III types are approximately 63 percent enriched. The cladding and fuel assembly hardware are made of 316, D-9, or HT-9 stainless steel.

The approximate inventory of driver fuel at ANL-West is more than 1000 kg of heavy metal. The average fuel assembly burn-up is approximately 8 atom percent, but some elements have burn-ups as high as 20 atom percent.

In addition to the standard driver fuel assemblies, there is a large quantity of experimental elements and fuel assemblies. Approximately 400 of these elements contain a uranium-plutonium-zirconium alloy.

The largest fraction (almost 23,000 kg) of heavy metal in spent fuel at ANL-West is contained in the blanket fuel assemblies. The bulk of this mass is depleted uranium; however, some plutonium was formed during irradiation in the reactor.

III. TREATMENT OPERATIONS

FCF consists of two operating hot cells. Figure 1 depicts FCF and the positioning of the equipment in the hot cells. Spent fuel will first be transferred into a rectangular-shaped, air-filled hot cell where the fuel elements will be separated from the fuel assembly hardware using the vertical assembly dismantler (VAD). Intact fuel elements will be transferred into the adjacent, annular-shaped, argon-filled hot cell.

In the argon cell, the fuel elements are first chopped into segments ranging from 0.64 cm (0.25 inch) to 1.9 cm (0.75 inch) with the element chopper. The chopped segments are then transferred to the electrorefiner in steel baskets (anode baskets).

The fuel treatment operations in the electrorefiner are based on a process employing molten salts and liquid metals in an electrochemical operation. The molten salt medium in the electrorefiner is a mixture

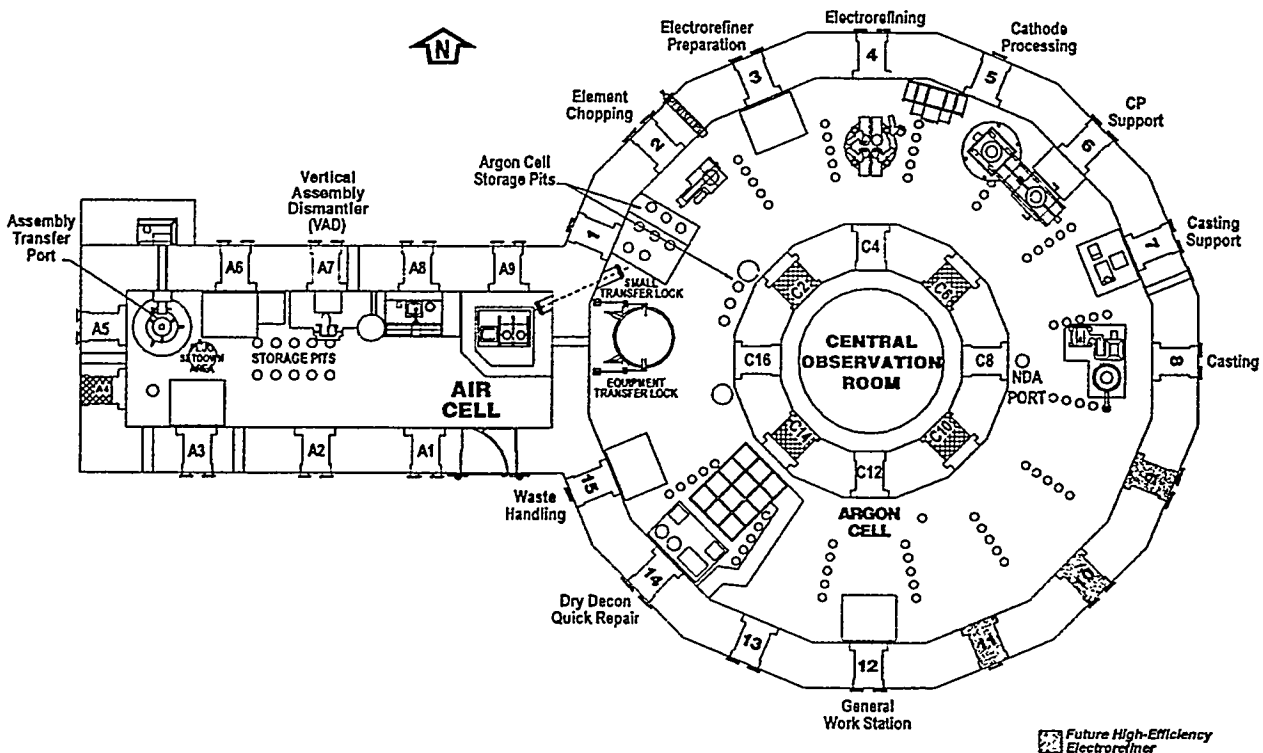


Figure 1. Fuel Conditioning Facility Hot Cells

of LiCl-KCl eutectic and actinide chlorides. Below the salt phase is a pool of molten cadmium that can serve as an anode, cathode, or just a collector for less reactive metals.

In the electrorefiner, the spent fuel can be electrotransported out of the anode baskets and an equivalent amount of material deposited either in the cadmium pool (anodic dissolution) or directly to a solid cathode (direct transport). Material deposited in the cadmium pool can later be electrotransported to a solid cathode. The uranium will be separated from the bulk of the fission products and transuranics using a steel mandrel cathode (solid cathode). Most of the fission products and transuranics will become concentrated in the salt and cadmium phases in the electrorefiner. The transuranics and alkali, alkaline earth, rare earth, and halide fission products will be primarily in the salt phase. The sodium will be neutralized by forming non-hazardous NaCl. The more noble metal fission products and fuel alloy zirconium will be in the cadmium phase primarily as insolubles or retained in the chopped cladding segments in the anode baskets.

The cathode products from electrorefining operations will be further processed in a separate operation to distill any adhering salt or cadmium and recover the uranium which will be sampled for material control and accountability. These operations will be performed in the cathode processor and casting furnace. As part of the driver fuel processing, the solid cathode will contain highly enriched uranium. Therefore, the recovered uranium metal will be blended with depleted uranium to produce a product that is less than 20 percent enriched. The low enriched uranium products will be placed in interim storage on the ANL-West site as ingots in canisters pending a DOE decision on ultimate disposition.

As part of the treatment operations, the cadmium and salt will periodically be pumped through a metal sintered filter to remove any insolubles and most of the noble metal fission products. These materials will be combined with the stainless steel from the fuel elements and zirconium from the fuel matrix to produce a metallic waste form containing approximately 3 weight percent fission products, 15 weight percent zirconium, and stainless steel. The cadmium will be recycled throughout the treatment operations.

After filtration, the salt will be contacted with zeolite to remove the more active metal fission products (alkali, alkaline earth, halides, and lanthanides) and transuranics including plutonium. The resulting zeolite will be processed with additional zeolite and glass additives into a mineral waste form which will be qualified for disposal as high level waste. Portions of the salt will be recycled.

The electrorefining operations have been demonstrated on laboratory and engineering scales in the Chemical Technology Division at Argonne in Illinois.³ Those initial demonstrations used simulated fission products and small amounts of plutonium. The operation of the FCF equipment in the hot cells has been demonstrated using depleted uranium.^{4,5}

Limited operations with irradiated fuel will commence with approval from DOE pending an on-going environmental evaluation. During the summer of 1995, several non-government organizations questioned the adequacy of the FCF environmental assessment. Under the IFR program, an environmental assessment (EA) was prepared for the operation of FCF.⁶ During the fall of 1995, the decision was made to prepare a new environmental assessment to specifically address the spent fuel treatment operations in FCF.⁷ For the spent fuel demonstration program that the EA addresses, 100 driver and 25 blanket fuel assemblies from EBR-II will be processed to demonstrate the electrometallurgical technique. This document was issued by DOE in late January 1996. Public hearings addressing the document were held during February in Idaho Falls, Idaho and Washington, DC. The environmental evaluation is expected to be complete during spring 1996.

IV. Mineral Waste Form Development

A. Introduction

The development of the mineral waste form has been on-going at Argonne in Illinois since 1985 as part of both the IFR program and the EBR-II Spent Fuel Demonstration Program. The reference mineral waste form is a glass-bonded zeolite.

Zeolites are crystalline aluminosilicates of the group I (alkali) and group II (alkaline earth) elements. Their framework is a network of AlO_4^{4-} and SiO_4^{4-} tetrahedra linked by the sharing of oxygens. The specific zeolite being used as the base of the mineral waste form is Zeolite A, $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}]$.

The networks of tetrahedra in the zeolite form cages in which molecules are occluded. The sodium ions in this structure are subject to ion exchange. Both of these properties are taken advantage of with the mineral waste form.

When treating EBR-II spent fuel in the FCF electrorefiner, the active metal fission will be allowed to build up in the salt. The transuranics, including plutonium, will also remain in the electrorefiner. After the demonstration quantity of fuel is processed through the electrorefiner, the salt will be passed through a column containing zeolite pellets.

The zeolite column material is 1.6 mm (0.0625 inch) diameter pellets of Zeolite A held together with a clay binder. Prior to use in the column, the pellets will be dried and contacted with LiCl-KCl to preclude the zeolite with clean salt and convert the sodium based zeolite to a lithium-potassium based zeolite. The lithium and potassium will chemically exchange with the sodium ion in the zeolite.

When the electrorefiner salt is passed through the zeolite column, the fission products are removed from the salt by ion exchange with the lithium and potassium in the zeolite. The salt can be recycled back to the electrorefiner for reuse. Once concentrated with fission products, the zeolite pellets will be removed from the column, ground to reduce their size to approximately 10 microns, and combined with additional powder zeolite A to occlude any surface salt remaining on the column material. This material will then be combined with glass frit (approximately 10 microns) and loaded into a steel can which will be processed into a solid monolith in a hot isostatic press (HIP).

When there is no longer a programmatic need for the salt, it can be cleaned of fission products by passing it through a zeolite column and then combined with zeolite material that has not been precluded with salt. In this operation the salt, which will only have trace contaminants, will be occluded in the zeolite and converted to non-high-level waste form.

B. Status of Work at Argonne in Illinois

Since the early stages of development of the IFR program and the electrometallurgical technique for treating spent nuclear fuel, waste form development work has been on-going in the Chemical Technology Division (CMT) of Argonne in Illinois. This work was performed in conjunction with the development of the electrometallurgical technique.⁸ In the mineral waste area, the focus was primarily concentrated on a glass-bonded zeolite waste form and a sodalite waste form.

The process materials employed with the sodalite waste form are the same as used with the glass-bonded zeolite. To produce sodalite, the zeolite is processed in the HIP for a longer time, at higher temperatures, and/or at higher pressures so that zeolite is converted to sodalite. The chemical formula for sodalite is $\text{Na}_6[(\text{AlO}_2)_4(\text{SiO}_2)_4] \cdot 2\text{NaCl}$. Zeolite has a large α cage (11.4 angstroms in diameter) and a smaller β cage (6.6 angstroms in diameter) in which to occlude salt. Sodalite only has β cages and can therefore occlude less salt per unit volume. The use of glass frit is not required to the same extent in the sodalite waste form.

In CMT, small-scale samples with surrogate materials were prepared of both mineral waste forms

using a hot uniaxial press (HUP).⁹ After initial scoping tests, the decision was made to concentrate more on the glass-bonded zeolite, with sodalite as a back-up. A hot isostatic press was acquired and placed into operation during the fall of 1995, and numerous samples were prepared in the months following. Samples sizes tested were 2.5 cm (1 inch) in diameter by either 2.5 cm (1 inch) or 7.5 cm (3 inches) in height. Straight-walled HIP cans were used. The purpose of these continuing tests is to determine the appropriate waste form composition and processing parameters. The waste form compositions developed at CMT will be employed on large-scale cold and hot samples at Argonne-West, and the processing parameters will be scaled for the increased waste form size.

C. Status of Work at Argonne-West

The work at Argonne-West is focused on producing large-scale waste forms and on studying the effects of fission products and transuranics in the mineral waste. Presently issues associated with scaling up from the Illinois experience and qualifying equipment for operations with irradiated materials in hot cells are being stressed. To accomplish these tasks, the equipment for producing large-scale samples is first being used out-of-cell in gloveboxes or with enclosed atmospheres to produce cold samples. The process for preparing these cold waste form samples is depicted in Figure 2. This cold work is presently focused on the mineral waste form preparation equipment and pressing operations. Work with zeolite columns will follow.

The first piece of equipment encountered in this flowsheet is the heated mixer which serves multiple roles. It first dries the zeolite. Zeolite A occludes more than 20 weight percent water. This water is removed before the zeolite is contacted with salt. The mixer is also used to contact ground salt with zeolite powder to occlude the salt. Both of these operations are performed at temperatures between 400°C and 600°C. It is finally used as a cold mixer to combine the salt-loaded zeolite with glass frit.

The heated mixer was designed and fabricated at ANL-West. It is capable of batch sizes between 15 and 20 kg. Because of its size, this device is not housed in a glovebox, but instead has an argon purge system to limit the exposure of salt and zeolite to moisture. The purge system also serves to remove moisture during drying operations. It is essentially a large tube furnace through which argon flows, with a mixer that can be raised and rotated at any vertical position in the furnace. Loading and unloading will take place in a small argon purge box. This device is presently being set up in the Fuel Assembly Storage Building (FASB) at ANL-West. It will be operational during April 1996.

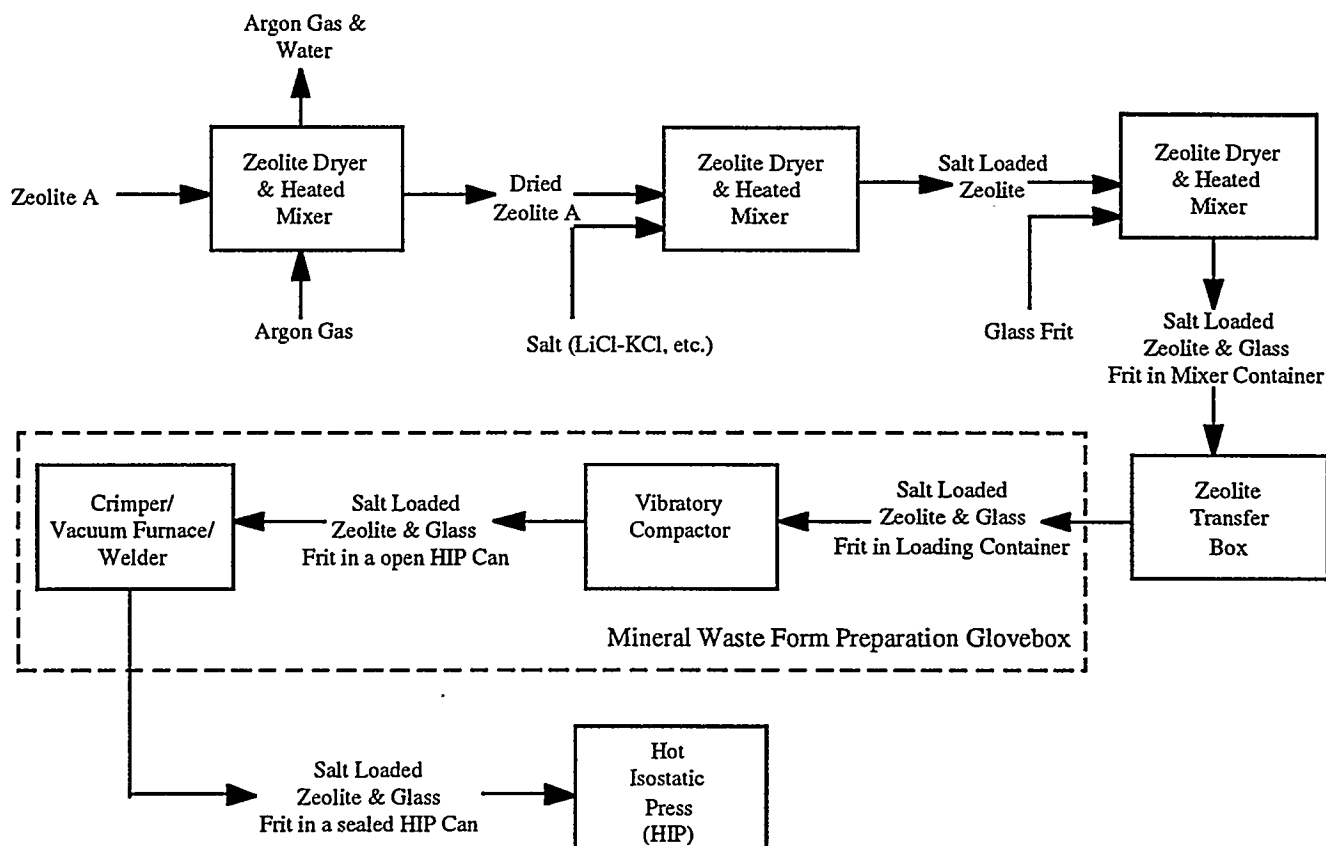


Figure 2. Flowsheet for Cold Mineral Waste Form Testing at ANL-West

Material from the heated mixer is transferred via a loading can to the Mineral Waste Form Preparation Glovebox, also in FASB. This glovebox has an argon atmosphere and a gas purification system. The loading can is placed in an inverted position on top of a vibratory packer/loader, which is used to load material into a HIP can.

Two HIP can designs are presently available for testing at ANL-West. Both designs are 11.4 cm (4.5 inches) in diameter and 22.9 cm (9 inches) in height. The two designs differ in that one is a straight wall can, and the other has bellows. A bellows can is pictured in Figure 3 next to one of the 2.5 cm (1 inch) cans that has been used in Illinois.

When small-scale sample cans are prepared at Argonne in Illinois, the glass and zeolite are loaded into the can gradually and compacted using a uniaxial press. The top of the can is then welded into place, and it is heated and evacuated through a small tube in the can top prior to crimping and sealing. At ANL-West, the can top will be welded onto the large cans prior to loading, which will occur through a 2.5 cm (1 inch) tube in the

Figure 3. Argonne-West Large-Scale HIP Can vs. Argonne-Illinois Can

top of the can. This loading scheme is designed to eliminate complicated welding operations in the hot cells. Therefore, an uniaxial press will not be employed on the large cans to increase the initial packing densities as was used with small cans. A uniaxial press with more than 20 times the force used for the small cans would have been required for the larger diameter cans.

A vibratory compactor will instead be used to increase by more than 30 percent the density over that which can be achieved by merely dumping material into the can. Densities over 50 percent of theoretical are expected. The compactor, produced by Labworks, is presently operational and installed in the glovebox.

Because of the lower packing densities obtained on the large cans compared to the small ones, initial testing at ANL-West will use the bellows cans. They will tend to allow more can deformation in the axial direction instead of radially; therefore less stress will be applied to the welds at the top of the can.

Prior to processing in the HIP, the loaded cans are heated and evacuated, the loading tubes are crimped shut, and the crimped tube is welded closed. The crimper-welder is installed and operational in the Mineral Waste Form Preparation Glovebox. It is a resistance welder from Roman Manufacturing.

The ANL-West hot isostatic press, pictured in Figure 4, is manufactured by ABB Autoclave, Inc. It has a maximum operating temperature of 1450°C and a maximum pressure of 30,000 psi. The operating gas is argon. The HIP chamber size is 15.2 cm (6 inches) in diameter and 30.5 cm (12 inches) in height. The device is set up and operational in the Engineering Laboratories on site.

V. SCHEDULE

The HIP and all the preparation equipment associated with the mineral waste form will first be operated with nonirradiated materials. There are four phases of cold operations. During the already completed first phase, small-scale cold samples prepared at Argonne in Illinois were processed in the HIP using a cycle that was employed on similarly processed materials in Illinois. The purpose of these tests was to demonstrate that the small-scale Illinois work could be duplicated using the HIP in Idaho. Three small-scale samples were processed; one is presented in Figure 5. The HIP cycle employed is given in Figure 6. The maximum temperature and pressure were 750°C and 25,000 psi,

Figure 4. Hot Isostatic Press Used at Argonne-West

Figure 5. Processed Small-Scale HIP Can

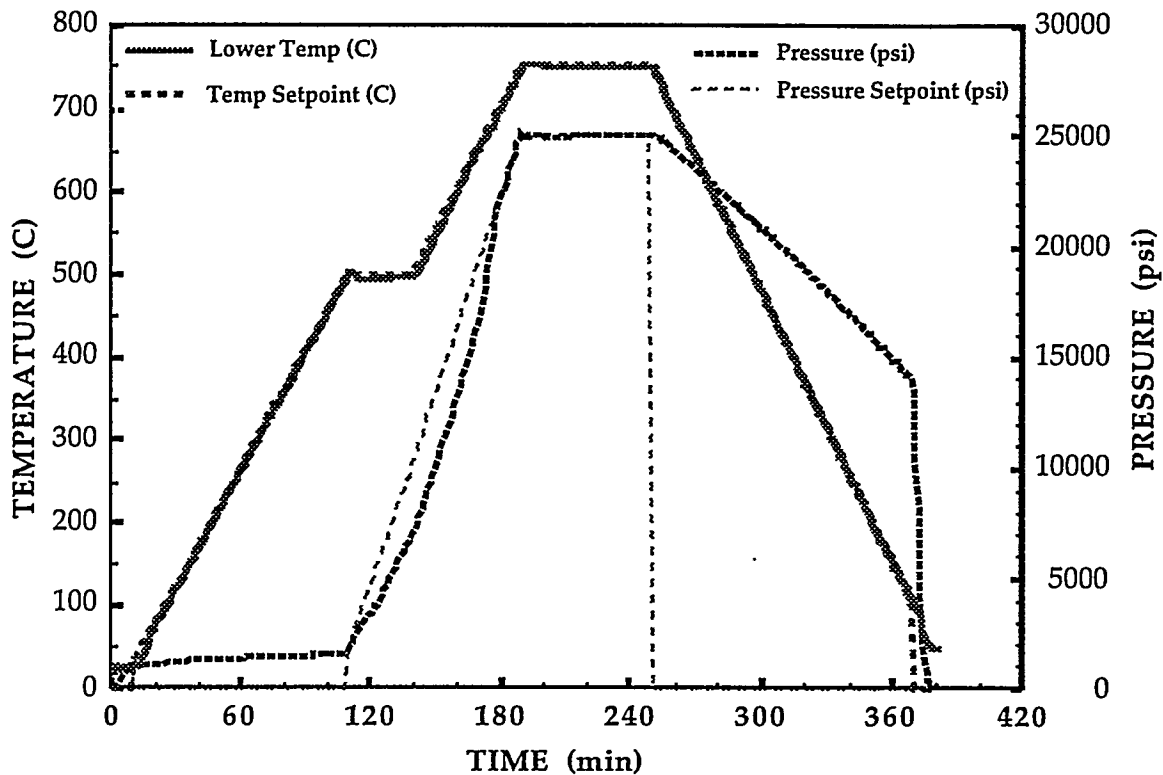


Figure 6. HIP Operating Cycle for Initial Cold Tests

respectively. There was an hour hold time under these conditions. According to X-ray diffraction results, all three of the samples were the same as the one processed in Illinois.

During the next phase of cold operations, samples with glass frit and/or dried zeolite (without loaded salt) will be processed. Tests with these items will help develop parameters for processing the large-scale samples given a HIP cycle for a small-scale sample. This phase of operation is now starting as the preparation equipment is coming on-line. Zeolite and glass frit will be processed once the dryer qualification is completed in April 1996.

The third phase of cold operations will include processing glass frit with salt-loaded zeolite. Only the base salt, LiCl-KCl eutectic, will be used in these tests. During the fourth phase, surrogate fission product chlorides will be added to the salt. These phases of operations will commence after initial testing of the heated mixer during April and May 1996.

Operations with irradiated materials will begin after qualifying the equipment and moving it to the hot cells in the Hot Fuel Examination Facility (HFEF) at Argonne-West. Hot operations are also dependent on approval from DOE to start treating irradiated fuel in FCF.

VI. CONCLUSIONS

Production of the mineral waste form at Argonne-West as part of the EBR-II Spent Fuel Treatment Program is on-going. This task is an extension of the waste form development work in the Chemical Technology Division at Argonne in Illinois. The present focus at Argonne-West is on producing large-scale cold samples to address scale-up issues and on qualifying the process equipment for operations in hot cells. Work with irradiated materials will follow. This work is aimed at producing a mineral waste form that will be qualified for disposal as a high-level waste.

ACKNOWLEDGMENTS

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