

# Options Study for the Neutralization of Elemental Sodium During the Pyroprocessing of Used Nuclear Fuel

Brian Westphal<sup>1</sup>, David Tolman<sup>2</sup>, Kevin Tolman<sup>2</sup>, Steven Frank<sup>2</sup>, Steve Herrmann<sup>2</sup>, Stephen Warmann<sup>2,\*</sup>, Kenneth Marsden<sup>2</sup>, and Michael Patterson<sup>2</sup>

<sup>1</sup>Walsh Engineering Services, 330 Shoup Ave., Suite 300, Idaho Falls, ID 83402, USA

<sup>2</sup>Idaho National Laboratory, 775 MK Simpson Blvd, Idaho Falls, ID 83402, USA

(Received November 26, 2019 / Revised March 12, 2020 / Approved June 16, 2020)

An options study was performed for the treatment of residual elemental sodium in driver plenums following the chopping operation during the pyroprocessing of used nuclear fuel. Given the pending availability of a multi-function furnace for distillation and consolidation operations in the Fuel Conditioning Facility, the furnace was considered for the processing of driver plenums. Although two options (oxidation and distillation) could be performed in the multi-function furnace, neither option has been developed sufficiently to date to warrant the use of the furnace for treatment operations. Thus, it was decided to defer the treatment of elemental sodium from driver plenums in the multi-function furnace until more developed technologies and/or furnaces become available. In the interim, storage of the plenums and characterization efforts are recommended.

**Keywords:** EBR-II, Sodium, Pyroprocessing

\*Corresponding Author.

Stephen Warmann, Idaho National Laboratory, E-mail: [stephen.warmann@inl.gov](mailto:stephen.warmann@inl.gov), Tel: +1-208-524-2286

## ORCID

Brian Westphal

<http://orcid.org/0000-0002-3631-0348>

David Tolman

<http://orcid.org/0000-0001-9263-1421>

Kevin Tolman

<http://orcid.org/0000-0001-6041-5011>

Steven Frank

<http://orcid.org/0000-0001-8259-6722>

Steve Herrmann

<http://orcid.org/0000-0002-9373-4913>

Stephen Warmann

<http://orcid.org/0000-0002-5385-8794>

Kenneth Marsden

<http://orcid.org/0000-0002-5366-7568>

Michael Patterson

<http://orcid.org/0000-0002-8698-3284>

This is an Open-Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited

## 1. Introduction

For fast breeder reactors like the Experimental Breeder Reactor-II (EBR-II) and the Fast Flux Test Reactor (FFTF), elemental sodium was utilized as a thermally-conductive bond between the fuel and cladding in fuel elements so that heat could be efficiently transferred to the reactor coolant. The sodium-bonded fuel when coupled with sodium reactor coolant in fast breeders provided numerous advantages over water-cooled reactor systems. Since elemental sodium is highly reactive, treatment of the used nuclear fuel from these reactors is necessary and has been on-going at the Idaho National Laboratory (INL) since 1996 on the EBR-II and FFTF inventory [1]. The treatment of the sodium-bonded fuel by pyroprocessing includes neutralizing the sodium in a chloride media such that sodium chloride results. Chopped fuel elements are loaded into steel baskets and electrorefined to separate uranium from the bond sodium, fission products, and transuranics [2]. Once reacted, the sodium chloride can be dispositioned with the other chloride species in the electrorefiner salt as a high level or transuranic waste [3].

Over the course of operations at the EBR-II and FFTF reactors, used nuclear fuel was removed from the reactors and stored either on-site or transferred to the INL for treatment of the sodium via pyroprocessing in the Fuel Conditioning Facility (FCF). Treatment of the used driver and blanket fuel occurs in two similar electrorefiners; the Mk-IV and Mk-V, respectively. Driver fuel was located centrally in the reactors and contained the fissile components necessary for sustained nuclear reactions while the blanket fuel surrounded the driver and enabled breeding of additional fissile materials. Associated with both driver and blanket fuel elements is the fueled and plenum sections with elemental sodium residing around the fuel slug, see Fig. 1. The plenum region allows for the accumulation of fission gases such that element breaches are minimized. Prior to electrorefining, the fueled sections of both driver and blanket elements are pneumatically-chopped into approximately

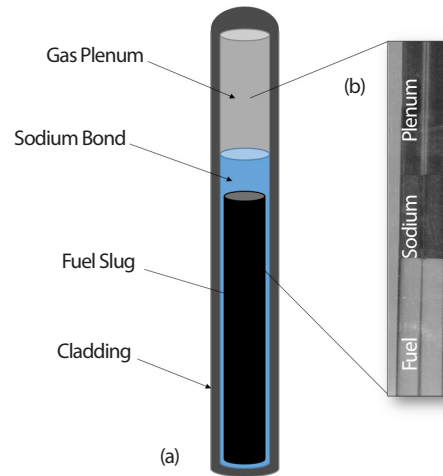


Fig. 1. The gas plenum is at the top of the fuel element (a) and the sodium bond extends beyond the fuel into the plenum region (b).

1 cm lengths and loaded into steel anode baskets for electrorefining. The plenum sections with varying amounts of elemental sodium are currently being stored in FCF following chopping awaiting a final disposition. Although similar in design, the blanket plenums contain significantly more sodium which may be better suited for a different disposition path. Additionally, the processing of blanket fuel has been given a lower priority than the driver fuel while alternatives to electrorefining are being investigated for which the blanket plenums may also be better suited.

The intent of this paper is to present an options study for the treatment of elemental sodium in the driver plenum sections using a new induction furnace, called the Multi-Function Furnace (MFF), scheduled to be operational by 2021.

## 2. BACKGROUND

The MFF is being designed and built for multiple functions in the FCF including salt distillation from electrorefiner cathodic materials with subsequent melting of uranium, salt distillation and consolidation of cladding hulls, resizing uranium products for fuel fabrication, and potentially plenum processing. The baseline for plenum processing

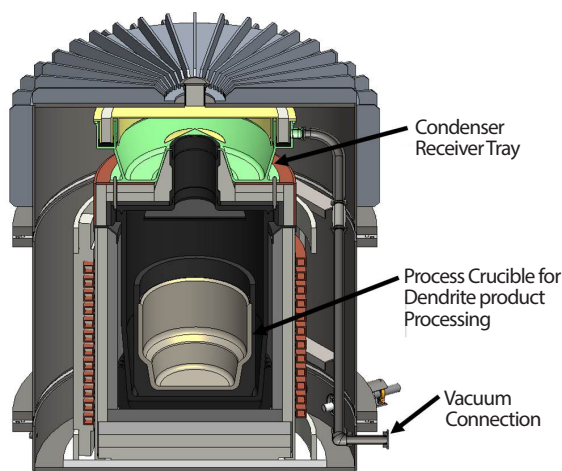


Fig. 2. Schematic of the MFF capable of distillation and consolidation operations.

has been to include the plenums with the claddings hulls into the metal waste processing scheme in the Hot Fuel Examination Facility (HFEF). Exploratory research with iron dichloride as an oxidant for the elemental sodium showed promise although the materials tested were surrogates and not actual plenums from used fuel. Since irradiated metal waste operations have not been fully initiated in HFEF other than several test ingots [4], plenum processing has not yet been implemented.

The MFF is a high temperature (1700°C maximum) induction furnace with an atmosphere controlled (argon gas) vacuum chamber. The top portion of the furnace is designed with heat shedding features for the condensation portion of the distillation process. The furnace also has the capability for liquid sampling via injection of a quartz tube through a top port and linear drive mechanism. Condensable materials, i.e. salt and possibly minor amounts of cadmium, are funneled through the lower region of the crucible assembly via a graphite cylinder to the condenser region. Salt ingots can then be removed from the condenser for further processing or waste packaging. Consolidated metallic products (either cladding or uranium) are collected in the lower graphite crucible assembly and dispositioned as waste or products.

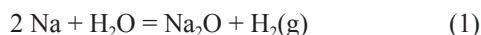
Supplementary to the furnace is a vacuum and argon supply skid that provides atmospheric control for the furnace chamber and inner distillation processes. Argon supply, induction power electrical leads, vacuum pump motor electrical leads, and instrumentation and control leads, are brought into the FCF argon cell via four floor feedthroughs. Out-of-cell equipment includes, the induction power supply, the induction power supply cooling water skid, a PLC cabinet, an operator control station (OCS), the argon supply and electrical panels.

As stated, driver plenums with elemental sodium are under consideration for processing in the MFF. Sampling (19 total) of EBR-II Mk-III driver plenums has been performed historically for elemental sodium and the results indicate approximately 3.5% of the total sodium loaded into the element during fabrication remains in the plenum region post-chopping. As a matter of comparison, sampling (12 total) of EBR-II blanket plenums indicated significantly more elemental sodium; approximately 33% of that loaded initially and hence may be more suited for alternative treatment processes. For both driver and blanket elements, chopping occurs slightly above the fuel slugs to ensure that no residual fuel is left in the plenum sections.

Because elemental sodium has a high solubility for cesium, the driver plenums also contain fission product cesium in minor quantities (approximately 1-2% of the elemental sodium in the plenums) causing the sodium to be radioactive. The source of cesium is as decay products ( $^{133}\text{Cs}$ ,  $^{135}\text{Cs}$ , and  $^{137}\text{Cs}$ ) from gaseous xenon isotopes ( $^{133}\text{Xe}$ ,  $^{135}\text{Xe}$ , and  $^{137}\text{Xe}$ ). Approximately 80% of the total volatile xenon isotopes reside in the plenum region of a fuel element following reactor operations [5]. The decayed cesium isotopes are soluble in the sodium as a liquid or deposited in the plenums as a gas due to its high vapor pressure relative to reactor temperatures. As a matter of reference, driver plenums have been investigated for cesium and it was found to be distributed throughout the plenum. Another observation from plenum sampling has been that sodium can be distributed well above the expected gravimetric meniscus

level due to either splattering or wetting phenomena during reactor operations.

Due to their storage in the argon atmosphere of FCF, the driver plenum sodium may have reacted with water and oxygen impurities in the cell given the levels of the impurities (typically around 100 ppm) and the storage time. The following equations represent the oxidation reactions for elemental sodium and are all thermodynamically favorable to the right:



The delta G of free energies at 298 K for the preceding three equations are -148 kJ, -302 kJ, and -753 kJ, respectively.

In all cases, the products for these reactions are stable compounds of sodium which would remove the reactivity characteristic of the elemental sodium.

The three options considered for this study to neutralize elemental sodium in driver plenums in the MFF are oxidation, distillation, and completely excluding the process from MFF operations. The following sections will describe these three options with their advantages and disadvantages concluding with a recommendation for a path forward.

### 3. DESCRIPTION OF OPTIONS

Oxidation processes for the treatment of elemental sodium can include both hydration as well as chlorination reactions according to equations (1-2) and the following equation:



where  $\text{MCl}_x$  represents a metal chloride that will oxidize sodium. The hydration reactions are typically performed

using steam, although alcohol has also been used, and a carrier gas such as nitrogen or carbon dioxide. Numerous problems have been encountered with these methods including: passivation layers causing reaction instabilities, exothermic excursions, and material design issues related to the caustic sodium hydroxide product [6]. For the MFF located in the argon cell of the FCF, water/steam is not desirable due to the atmosphere and specialized equipment necessary to control both water and hydrogen.

The chlorination of elemental sodium in the MFF is considerably more desirable than hydration since the other functions of the furnace are to handle chloride species via distillation operations. Typical oxidants for elemental sodium include uranium trichloride and iron dichloride according to the following equations:



As mentioned, iron dichloride experiments have been performed with non-irradiated materials featuring non-plenum geometries, i.e. simulant chopped cladding. Another advantage of chlorination is the incorporation of both sodium and cesium chloride species into the current electro-refiner salt waste stream since both species already exist in the salt. If elemental sodium in the driver plenums has been oxidized by the cell atmosphere, it is expected that an oxidant such as uranium trichloride or iron dichloride will ultimately chlorinate sodium oxide and sodium hydroxide.

The primary disadvantage to chlorination is assuring complete reaction of the oxidant with elemental sodium such that unreacted elemental sodium would then be transported with the salt species throughout the MFF. The incompatibilities of sodium with graphite are well known and design features would have to be included into the MFF graphite components to either prevent this interaction or additional equipment would need to be available so as not to impact other operations in the furnace. Since it is anticipated that stoichiometric excess oxidant, such

Table 1. Advantages and disadvantages of each neutralization option

Option	Advantages	Disadvantages
Oxidation	Chlorination results in species that can be handled by current equipment Chlorination results in species that can be dispositioned in current waste streams	Damage to equipment by incomplete oxidation reaction Hydration not acceptable in argon hot cell environment Hydration has technical processing issues Insufficient operating data available for chlorination implementation
Distillation	Well-developed processes and equipment for blanket materials	Elemental sodium still requires additional oxidation for waste disposition Additional hardware necessary to prevent equipment damage Failure to remove elemental sodium if previously oxidized
Deferment	Simplifies design of multi-function furnace Allows alternative technologies/furnaces to be further developed	Delays a solution to a pending storage problem

as iron dichloride, would be necessary to chlorinate elemental sodium according to equation (6), the effect of iron dichloride on the salt should also be considered for the subsequent processing of the salt during either waste operations or disposition. Lastly, additional chlorination experiments are necessary with irradiated plenums to discern the most effective operating parameters, the amount of excess oxidant, the degree of sodium chlorination, and the layout required to sufficiently expose elemental sodium to the chlorinating agent.

The second option for neutralization of the sodium in driver plenums is distillation since the MFF is capable of the temperatures and pressures necessary to remove elemental sodium from the plenums. The temperatures required for salt distillation are higher than for sodium distillation. When compared to the oxidation of elemental sodium, the development of sodium distillation at the INL has progressed significantly and has resulted in complete removal of the sodium from blanket elements [7]. Of the disadvantages to distillation, the most significant is the fact that distilled elemental sodium would still need to be oxidized prior to its final disposition in an additional process step. Also, additions to the MFF for sodium distillation would be necessary to

prevent sodium vapor and graphite reactions, i.e. contained system within the MFF for sodium distillation operations. And finally, if elemental sodium has been compromised by the cell atmosphere, distillation of sodium oxide and sodium hydroxide would not occur at the conditions (650°C and 1 Torr) targeted for sodium distillation.

The third option considered for processing of the driver plenums in the MFF is to exclude the operation from the initial list of functions to be performed by the furnace. Although this option still requires that the elemental sodium in the plenums be addressed sometime in the future, it allows for the alternative technologies to be developed further. For example, several direct oxidation tests have been performed with a ternary salt (LiCl/KCl/UCI<sub>3</sub>) and irradiated blanket segments at 500°C that show promise to completely oxidize the elemental sodium into the salt. For this method to be utilized for driver plenums, it is expected that the plenums would need to be sized or shredded to ensure interaction of the salt with the entire interior of the plenum. As mentioned, the distillation of blanket elements has progressed to the point where furnaces are being designed to address Fermi blanket elements initially and EBR-II blanket elements ultimately. The availability of these furnaces

would allow further distillation testing with irradiated driver plenums. The greatest disadvantage to excluding processing of driver plenums in the MFF is the uncertainty of future distillation furnaces and available space within the FCF argon hotcell for said furnaces; however, as long as the MFF design does not preclude it, the MFF could be fitted with a future designed sodium distillation containment system internal to the MFF. The primary reason to exclude processing the driver plenums in the MFF is simplification to the current design, increased throughput to the facility with one less set of operations, and reduced risk for equipment damage from sodium vapors.

## 4. CONCLUSIONS

Based on the aforementioned arguments, it is recommended that the initial MFF design not include the neutralization of driver plenum sodium. Given the lack of knowledge pertaining to the chlorination and distillation options in terms of process efficiencies and required additional processes, respectively, the choice to forgo these options at this time is advisable and allows for further development of these technologies as well as others that may be more applicable. Storage of the driver plenums in FCF should be continued and characterization of the elemental sodium in those plenums, both quantitatively and for the degree of oxidation, should be an on-going priority. Table 1 summarizes the advantages and disadvantages of each option.

## ACKNOWLEDGEMENTS

The authors would like to acknowledge the Hot Fuel Examination Facility and Fuel Conditioning Facility operations personnel for their recent contributions. This work was supported by the U.S. Department of Energy, Office of Nuclear Energy, Science, and Technology, under DOE-NE Idaho Operations Office Contract DE-AC07-05ID14517.

## REFERENCES

- [1] DOE Record of Decision for the Treatment and Management of Sodium-Bonded Spent Nuclear Fuel, Federal Register, 65, 182 (2000).
- [2] C.E. Till and Y.I. Chang, *Plentiful Energy: The Story of the Integral Fast Reactor*, Createspace (2011).
- [3] M.F. Simpson and P. Bagri, “Basis for a Minimalistic Salt Treatment Approach for Pyroprocessing Commercial Nuclear Fuel,” *J. Nucl. Fuel Cycle Waste Technol.*, 16(1), 1-10 (2018).
- [4] B.R. Westphal, S.M. Frank, W.M. McCartin, D.G. Cummings, J.J. Giglio, T.P. O’Holleran, P.A. Hahn, T.S. Yoo, K.C. Marsden, K.J. Bateman, and M.N. Patterson, “Characterization of Irradiated Metal Waste from the Pyrometallurgical Treatment of Used EBR-II Fuel”, *Met. Trans. A*, 46, 83-92 (2015).
- [5] R.G. Pahl, D.L. Porter, D.C. Crawford, and L.C. Walters, “Irradiation Behavior of Metallic Fast Reactor Fuels”, *J. Nucl. Mat.*, 188, 3-9 (1992).
- [6] D. Vaden, *Sodium Removal and Disposal Handbook*, Argonne National Laboratory Report ANL-87-30 (1987).
- [7] S. Herrmann et al., “Removal of Bond Sodium from an Irradiated Full-Length EBR-II Blanket Element via Melt-Drain-Evaporate Process”, *Proc. Global 2019, ANS*, Seattle, WA (2019).