

Treatment Method for Fermi Barrel Sodium Metal Residues

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June 2005



The INL is a U.S. Department of Energy National Laboratory
operated by Battelle Energy Alliance

INL/EXT-05-00421

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**Prepared for the
U.S. Department of Energy
Office of Nuclear Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517**

ABSTRACT

Fermi barrels are 55-gallon drums that once contained bulk sodium metal from the shutdown Fermi 1 breeder reactor facility, and now contain residual sodium metal and other sodium/air reaction products. This report provides a residual sodium treatment method and proposed quality assurance steps that will ensure that all residual sodium is deactivated and removed from the Fermi barrels before disposal. The treatment method is the application of humidified carbon dioxide to the residual sodium followed by a water wash. The experimental application of the treatment method to six Fermi barrels is discussed, and recommendations are provided for further testing and evaluation of the method. Though more testing would allow for a greater refinement of the treatment technique, enough data has been gathered from the tests already performed to prove that 100% compliance with stated waste criteria can be achieved.

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Treatment Method for Fermi Barrel Sodium Residues

1. INTRODUCTION

The Enrico Fermi Atomic Power Plant was a sodium metal-cooled 430 MWth reactor that operated from 1963 to 1972. After the reactor was permanently shut down in 1972, the primary sodium metal coolant was drained from the nuclear reactor into 55-gallon (208-liter) steel barrels. In total, 77,000 gallons (291,000 liters) were drained from the reactor into approximately 1400 barrels. The barrels were shipped to Argonne National Laboratory – West (ANL-W) in the early 1970's for treatment. Subsequently, during the execution of the Experimental Breeder Reactor II (EBR-II) Plant Closure Project (active between 1999 and 2002), the sodium metal was drained from the barrels and processed into 73 wt% sodium hydroxide in the ANL-W Sodium Processing Facility (SPF). After the draining process was completed, approximately 2.5 lbs (1.1 kg) of residual sodium metal remained in each of the barrels. The barrels were sealed with a nitrogen cover gas and placed into storage in cargo containers that hold approximately 80 barrels in each container. The cargo containers are now stored within the boundaries of the Materials and Fuels Complex (MFC) of the Idaho National Laboratory (INL), formerly known as ANL-W. These barrels meet the Resource Conservation and Recovery Act (RCRA) definition of an empty container and are not regulated as hazardous waste.

Although considered empty by RCRA standards, the State of Idaho has different regulations and still considers the barrels solid waste. Storage, handling, and disposal of the barrels must meet State of Idaho code for protection of human health and the environment. Additionally, the barrels are considered low level radioactive waste because of their origin and measurable radioactive content and must be disposed according to the waste acceptance criteria for the Radioactive Waste Management

Complex (RWMC) in southeastern Idaho or other equivalent facility.

Safe storage of the Fermi barrels, when full and “empty”, has been achieved for many years with no incident, but continued storage of the barrels likely cannot be achieved for an indefinite amount of time without further attention from the State of Idaho and the Laboratory. The barrels are an environmental liability and offer a small but finite safety risk. The sodium metal remaining in the barrels is chemically active and can react under the right environmental conditions (e.g, water in-leakage) to release hydrogen gas and heat.

The best way to eliminate the environmental and safety risks offered by these barrels is to treat and dispose the barrels. As a part of this process, all residual sodium metal in the barrels must be deactivated or removed because the waste disposal sites cannot accept any chemically reactive metals, including sodium, in their waste streams.

This report provides a residual sodium treatment method and proposed quality assurance steps that will ensure that all residual sodium is deactivated and removed from the Fermi barrels before disposal. The treatment method is the application of humidified carbon dioxide to the residual sodium (Sherman et al., 2002; Sherman, 2005) followed by a water wash. The experimental application of the treatment method to six Fermi barrels is discussed, and recommendations are provided for further testing and evaluation of the method. Though more testing would allow for a greater refinement of the treatment technique, enough data has been gathered from the tests already performed to prove that 100% compliance with stated waste criteria can be achieved.

2. PROPOSED TREATMENT METHOD

All of the drained Fermi barrels located at the INL's Materials and Fuels Complex (MFC) are known to contain less than 5 lbs (2.25 kg) of residual sodium metal, which is below the 10-lb threshold above which the barrels would be regulated under the Resource Conservation Recovery Act (RCRA) statutes. The exact amount of residual sodium in each barrel is unknown, however, because the barrels also contain a mixture of sodium oxides, sodium hydroxides, and sodium carbonates. Over time, air and water has leaked into the barrels to react some of the residual sodium and convert it into these other materials. Figure 1 shows a photograph of the inside of one of the drained Fermi barrels.



Figure 1: Barrel #ANL1174 before treatment

In the figure, residual sodium metal isn't visible because it is coated with other materials. The residual materials adhere to the barrel walls and the bottom with very little loose material.

Any treatment method for the Fermi barrels must be able to penetrate the layers of obstructing material to deactivate the sodium metal underneath. Also, the method must be capable of reacting the entire mass of residual sodium within each drum (10 lbs or less) in a reasonable amount of time and with an acceptable level of safety and cost. The waste

products generated by the treatment process must be compatible with the waste criteria for the chosen disposal site.

Two engineering evaluations were written to determine the best treatment method for these barrels. The first engineering evaluation (ETA EB-2001-014) recommended that the barrels be treated with steam or superheated steam and nitrogen, with the resultant caustic waste products being processed through the MFC's Sodium Processing Facility (SPF). With the steam and nitrogen process, residual sodium is reacted with steam to form liquid and solid solutions of hydrated sodium hydroxide. The nitrogen is provided to dilute the hydrogen gas generated by the water-sodium reaction and to displace any oxygen that might leak into the treatment process. After treatment, the caustic waste products would become part of the overall sodium hydroxide waste stream from the plant, and the barrels themselves would be crushed and disposed as scrap metal.

Since that evaluation was written, the SPF was placed into a stand-by condition and is no longer staffed. The SPF may be re-opened at some point if sodium metal from the Fast Flux Test Facility (FFTF) is shipped to the MFC for processing, but the certainty and time line on this activity are unknown, and it was decided not to pursue a treatment method that had an uncertain waste disposition pathway. Also, opening the SPF just to process the relatively small volume of waste materials that would be generated by the steam and nitrogen process would be cost-prohibitive.

A second engineering evaluation was written (ETA EB-2004-002) to re-examine the treatment options for the Fermi barrels, and a different treatment technique was recommended. This evaluation advocated the application of humidified carbon dioxide to deactivate the residual sodium in the Fermi barrels, the same technique that was used to treat residual sodium within the Experimental Breeder Reactor II (EBR-II) secondary sodium cooling system and is still being used to deactivate residual sodium within the EBR-II primary sodium system

(Sherman et al., 2002). Using this technique, the residual sodium metal within the barrels would be converted into sodium bicarbonate. Previous experience has shown that sodium metal up to 5-7 cm in depth can be reacted completely with this technique in a reasonable amount of time (120 days or less), and that the waste products are solid sodium carbonates, which are permissible for disposal in the chosen waste sites. The treatment process operates safely with a minimum of staffing, and has a low operating cost.

This section describes the particular application of humidified carbon dioxide to the Fermi barrels, along with adaptations made to the treatment process to ensure adequate safety and treatment effectiveness. The treatment steps are described below.

2.1 Treatment Steps

The treatment of the Fermi barrels takes place in three stages. The first stage is the exposure of the Fermi barrels to humidified carbon dioxide in order to completely convert the residual sodium metal and waste sodium oxides and sodium hydroxide into sodium carbonates. The second stage is a visual inspection, followed by a water wash in the Water Wash Vessel (WWV) at the Sodium Component Maintenance Shop (SCMS), located at the MFC. The third stage is a size reduction step, where the Fermi barrels are crushed to reduce their size, are placed into suitable waste containers or overpacks, and are disposed.

2.1.1 Stage One: Reaction of Residual Sodium

This stage is conducted in the Sodium Boiler Building (SBB), which is part of the EBR-II Facility at the MFC.

As a first step, one or more Fermi barrels are connected in series to the Carbon Dioxide Humidification cart, as shown in Figure 2. In a serial arrangement, the exhaust gases

from the first barrel in the series feed into the second barrel, and so on until the end of the chain. A serial arrangement allows for efficient use of the moisture and carbon dioxide gas. Although only 2 barrels have been tested in series, it is presumed that longer treatment trains of up to 10-20 barrels might be assembled without suffering too great a pressure drop across the barrel train, so that many barrels might be treated at one time without having to change out drums too frequently.

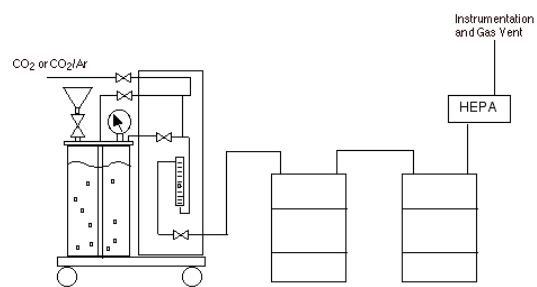


Figure 2. Carbon dioxide humidification cart and Fermi Barrels in series

In the second step, the barrel train is flushed with a mixture of argon gas and carbon dioxide. The gas mixture is initially set at a ratio of 10-to-1 argon to carbon dioxide, and then gradually increased to a 4-to-1 ratio, and then to pure carbon dioxide, in response to the measured hydrogen concentration in the off-gas and the measured temperature of the barrels. A gradual approach is needed, because the barrels contain sodium oxide in the surface layers, and sodium oxide reacts readily with carbon dioxide, resulting in the generation of heat and the release of hydrogen gas through other indirect chemical reactions.

Blending argon with carbon dioxide in the initial stages increases process safety by reducing the conversion rate of sodium oxide to sodium carbonate, which will reduce the temperature of the barrels during the initial gas flush. If pure carbon dioxide is used during this initial flush without blending it with argon,

surface temperatures on the bottom of the barrels, where the largest residual sodium deposits are located, can climb as high as 300 °C for a period of 5 minutes or more as the sodium oxide is converted into sodium carbonate. Blending argon with carbon dioxide limits the supply of carbon dioxide to the barrels and result in lower barrel surface temperatures during this initial flush. Blending argon with carbon dioxide has an added safety benefit in that the flow of carbon dioxide can be stopped altogether at any time during the initial flush without stopping the flow of inert flush gas through the barrels.

In the third step, after all of the sodium oxide has been converted into sodium carbonate and the barrel temperatures have fallen to ambient temperature, the flow of humidified carbon dioxide is started in order to react the residual sodium. This step requires some physical manipulation of the barrels while the residual sodium is being reacted. During this step, the barrels are first treated in an upright position, and are then placed on their sides in drum racks, first on one side, and then the other side by rotating the barrels by 180°. When the barrels are lying on their sides, the bottom and exposed sides of the barrels are occasionally rapped with a rubber mallet in order to shake loose adhering carbonate deposits. The method is somewhat crude, but has been found to work in early experiments (see Section 3). The indication of when to flip the barrels onto their sides, and then onto the opposite sides is provided by the measured hydrogen concentration in the off-gas. When the measured hydrogen concentration decays to background levels in the upright position, the barrels are flipped to their sides. When the measured hydrogen concentration decays again to the background position, the barrels are flipped or rotated to the opposite side. Treatment with humidified carbon dioxide is terminated when the measured hydrogen concentration decays a final time to background levels.

To summarize, this stage is performed in three steps. These steps are:

- 1) Connect barrels to carbon dioxide humidification cart in a serial arrangement.
- 2) Flush barrels with argon/carbon dioxide blend with a gradual change to a pure carbon dioxide flush in order to react sodium oxide within the barrels.
- 3) React residual sodium with humidified carbon dioxide until completion.

2.1.2 Stage Two: Visual Inspection and Water Wash

This stage is performed in the Sodium Component Maintenance Shop (SCMS) at the MFC.

Inside the Water Wash Vessel tent, the barrels are individually flushed with argon gas, and are then cut in two pieces at the barrel centerline halfway between the top and the bottom of the barrels. The two barrel pieces are separated and inspected for residual sodium deposits. The bottom half of the barrels will contain loose sodium carbonate materials, which are poured or scooped out of the bottom into a suitable waste container to facilitate the visual inspection and to reduce the waste material load in the barrels. Results of the visual inspection are recorded for later evaluation.

Following the visual inspection, the barrel halves are placed into the Water Wash Vessel and are water washed using the generally accepted SCMS facility procedures for washing any sodium-containing parts or components. Water washing the barrel halves completely removes any adhering carbonate materials from the walls of the barrels, and will react any residual sodium remaining in the barrels if it is present.

Barrel halves are inspected after emerging from the Water Wash Vessel to ensure complete treatment. If any residual sodium metal remains in the drum halves after being in the Water Wash Vessel, the drum halves are set aside for further treatment, which may include another water wash.

Periodic replacement of the Water Wash Vessel liquid will need to be performed once the water wash liquid becomes saturated with sodium carbonates and sodium hydroxide materials from the barrel halves. Spent water wash liquid will be solidified by mixing it with Aquaset in waste drums and disposed as low-level radioactive waste (LLW) at RWMC or another approved waste site.

2.1.3 Stage Three: Size Reduction

The third stage is size reduction of the barrel halves. The barrel halves are to be crushed in a drum crusher installed in the SCMS. Once crushed, the scrap metal will be placed into overpacks and disposed.

2.2 Quality Assurance

The proposed treatment method described above must ensure that 100% of the treated barrels or barrel halves contain no residual sodium metal. Assurance of this fact is provided by Stage Two of the treatment process: visual inspection of the barrel halves followed by a water wash.

From the early tests tests, it was learned that residual sodium deposits, when present, are easily spotted during the visual inspection step because of their distinct physical form. The deposits are metallic gray in appearance and tend to adhere strongly to the sides or bottom of the barrels. When probed with a tool, the deposits are soft and wax-like, and retain the physical characteristics of pure sodium metal. Carbonate deposits, unlike residual sodium, do not adhere strongly to the sides or bottom of the barrels, are mechanically brittle, and are white in color. Once all of the loose material has been removed from the barrel halves during the inspection, any remaining deposits of material can be probed to determine whether the deposit is residual sodium metal or adhering carbonate.

Since there is little operating experience with this proposed treatment method, all of the barrels after the visual inspection are water washed, regardless of the visual inspection

results. Water washing has been shown to be 100% effective in removing all residual sodium metal, sodium hydroxide, and sodium carbonate materials from the inside of the barrels. After the barrel halves are water washed, the inside of the barrels are clean, and polished metal can be seen at all points.

At some point in the future, after more operating experience has been collected (perhaps after processing the first 100-200 Fermi barrels), water washing of all Fermi barrels might be eliminated in the interest of cost savings and efficiency. Visual inspection results will be recorded for all barrels, and the presence or absence of residual sodium after the humid carbon dioxide treatment will be recorded. If it is established that the visual inspection step is 100% effective in distinguishing between barrel halves that contain residual sodium and those that do not, as indicated by the generation of hydrogen in the Water Wash Vessel during the water wash step, then perhaps only those barrels failing the visual inspection might be water washed. The barrel halves not water washed can be sent directly to the drum crusher for size reduction without washing, since sodium bicarbonate and sodium carbonate are allowed for disposal at most LLW disposal sites.

3. FERMI BARREL TREATMENT EXPERIMENTS

During the development process, six Fermi barrels were treated with humidified carbon dioxide. The first four barrels were treated individually, one at a time, while the last two were treated simultaneously in a serial barrel arrangement. A summary of observations and results obtained for each barrel are presented in tabular form. After the summary of results, more in-depth explanation of the treatment process and results obtained for each barrel is given, since the total number of barrels treated during this initial development period is relatively small.

3.1 Summary of Treatment Results

Table 1 summarizes the observations and results obtained from treating six Fermi Barrels. These barrels (in order of treatment) are labeled ANL#82, 630, 1128, 1174, 1135, and 1116.

Table 1: Fermi Barrel Treatment Summary

#	Init. Temp Rise °C	Mech. Agit.?	Zero H ₂ ?	Na Pre-Wash?	Na Post-Wash?
82	Yes	No	No	Yes	No
630	120	Yes	Yes	No	No
1128	110	Yes	Yes	Yes	No
1174	40	Yes	Yes	No	No
1135	300	Yes	Yes	No	No
1116	220	Yes	Yes	No	No

In the table, the # sign indicates the barrel number. The column heading “Init. Temp. Rise

°C” shows the highest recorded temperature on the bottom of the barrel upon introduction of dry carbon dioxide to the barrel. The “Mech. Agit.?” column indicates whether the barrel was tipped and periodically agitated with a rubber mallet as described in Section 2, or whether the barrel remained in an upright position and was not agitated. The “Zero H₂?” heading shows whether the measured hydrogen concentration during treatment was allowed to fall to zero offset from background during the treatment process. The “Na Pre-Wash?” column asks whether metallic sodium was seen in the barrel prior to the water wash step. The “Na Post-Wash?” column shows whether metallic sodium remained in the barrel after the water wash step.

The most striking observation during the treatment of these drums was the large short-term temperature increase caused by the introduction of dry carbon dioxide. All of the barrels experienced a temperature increase to some degree, with three of the barrels heating to a high enough temperature (ANL#82, 1135, and 1116) to cause smoke to rise from the barrel bottoms. The paint on the barrels did not blister or change its appearance, so it is presumed that the smoke arose from grease or other contaminants on the barrel surface. The temperature rose quickly, usually within the first few minutes, stayed at or near the high temperature for several minutes, and then decayed in an exponential manner back down to ambient temperature in all cases. The initial temperature spike is presumably from the reaction of carbon dioxide with sodium oxide. The carbon dioxide-sodium oxide reaction is very energetic, and is most likely responsible for the initial high temperatures. Since the supply of carbon dioxide is essentially unlimited, the sodium oxide can react as quickly as the diffusion of carbon dioxide through the solid surface layers will allow.

The large temperature spike was accompanied by a spike in the measured hydrogen concentration. For barrels ANL#630, 1128, 1174, 1135, and 1116, hydrogen concentration in the off-gas exceeded 4 vol% for a time span nearly equivalent to the time span of

the maximum temperature. The rise in hydrogen concentration was accompanied by an increase in the measured oxygen concentration above 1 vol%. The peak height above 1 vol% was not recorded because 1 vol% was the upper threshold for the recorded signal, but in one case it was observed that the oxygen concentration did not exceed 1.6 vol%, based on a visual observation of the oxygen meter readout itself. Since hydrogen can only come from the reaction of water vapor with sodium metal, the reaction of carbon dioxide with sodium oxide must directly or indirectly cause a release of captured water from the oxide/carbonate crust within the barrels, which in turn reacts with sodium metal to create hydrogen. The hydrogen spike subsided with the subsidence of the drum temperature, and quickly fell to background levels as the barrels began to cool to ambient temperature.

In an effort to decrease the initial temperature rise, the carbon dioxide will be blended with argon gas during the initial barrel flush for subsequent barrels. Blending carbon dioxide with argon will reduce the supply of carbon dioxide within the barrel to the point where the chemical reaction is carbon dioxide limited rather than sodium oxide limited. Making the reaction carbon dioxide limited will make it more controllable, because the blend of carbon dioxide with argon can be easily adjusted to increase or decrease the reaction rate, whereas there is no control over the amount of sodium oxide within each barrel.

After the initial temperature spike and its subsidence, the treatment process operated as expected, and behaved in a manner that was consistent with the application of humidified carbon dioxide to sodium in the laboratory, and within the EBR-II secondary and primary sodium systems. The treatment process ran smoothly, and no safety problems were encountered. The bottom of the barrels tended to warm slightly to about 5°C above ambient temperature as the sodium reacted with the humidified carbon dioxide, but no smoke was generated, and the drum surfaces were safe to touch by hand.

The best treatment results were obtained by a multi-step treatment process. First, the barrel is placed in an upright position and reacted with humidified carbon dioxide until the measured hydrogen concentration falls to background level. Then, the barrel is tipped 90° on its side and reacted again with humidified carbon dioxide. The barrel is occasionally rapped on the sides and the bottom of the barrel (i.e., “mechanical agitation”) in order to loosen adhering carbonate materials and expose fresh metallic sodium. Once the measured hydrogen concentration falls again to background levels, the barrel is rotated by 180° in the opposite direction, and exposed again to humidified carbon dioxide while the barrel is occasionally rapped with a rubber mallet. The barrel is then removed to the Sodium Component Maintenance Shop where the drum is cut in half, separating the top and bottom halves of the drum, and the loose carbonate material is removed from the barrel. The barrel is inspected, and then water washed.

Mechanical agitation and rotation of the barrels was deemed to be a very important step in the treatment process. Barrel ANL#82 was not tipped and agitated, and a large amount of sodium (1-2 lbs) remained in the barrel after it appeared that very little hydrogen (less than 0.3 vol%) was still being generated. This sodium could not be effectively treated with humidified carbon dioxide, because it had been buried under a thick layer of carbonate powder. Though the humidified carbon dioxide could still penetrate the layer of loose material, the diffusion rate was very slow and the sodium could not be reacted completely in a reasonable amount of time (1 week or less). Tipping the barrel and agitating causes the loose material to slough away from the metallic sodium underneath and more clearly exposes the sodium to the humidified carbon dioxide.

Barrel ANL#1128 was tipped and agitated, but still contained metallic sodium at the end of humidified carbon dioxide treatment. The metallic sodium was covered by a harder layer of carbonate material that did not slump when the barrel was tipped. It was believed that

this barrel is an exception, and that such exceptions in the future will be easily spotted and set aside for further treatment during the visual inspection step.

Overall, assuming the drums selected for these tests are representative of the whole, the sodium in a single barrel can be reacted in just about 1 week or less. A serial arrangement of the barrels, where the exhaust gas from one barrel flows into the next barrel, will be needed to increase the overall treatment rate.

In all cases, the visual inspection step provided clear evidence whether there still remained metallic sodium in the bottom of the barrels. When the barrels had sodium in them, the deposits tended to be large and easily distinguishable from the white, powdery carbonate material generated by the treatment process. When the barrels had no sodium in them, bottom of the barrels were clearly visible, even in the seam that joins the sides of the barrel with the bottom.

The water wash step was 100% effective in removing everything from the barrels, whether there was sodium metal in the barrels or only adhering carbonate material. After the water wash step was completed, the sides and bottom of the barrels were shiny and metallic, and no corrosion was seen inside the barrels.

The barrel crusher was not yet in operation at the time these experiments were performed, and so no Fermi barrels have yet been crushed.

3.2 Barrel ANL#82

Prior to flushing the barrel with dry carbon dioxide, the barrel was “sniffed” with a portable hydrogen detector in order to make sure that the barrel could be safely opened in air with no risk of a hydrogen combustion event. The portable detector detected an initial hydrogen reading of 1200 ppm hydrogen, which then decayed to 0 ppm hydrogen after a couple of minutes. The presence of hydrogen indicated

that water had leaked into the barrel at some point in the past and reacted with sodium metal.

Upon initial carbon dioxide introduction, the barrel experienced an increase in drum temperature after a quite period of about five minutes. The barrel was not instrumented for temperature, and the only indication of high temperature was the smell of smoke and the feeling that the drum surfaces were hot to the touch. The hydrogen and oxygen meters were not operational at the moment the carbon dioxide flush began, and no measurements of hydrogen and oxygen in the off-gas were obtained. The drum was allowed to cool before proceeding with the humidified carbon dioxide treatment.

The barrel was exposed to carbon dioxide from 9/28/2004 14:50 until 10/19/2004 9:15 at a rate of 5 scfm. During the first 15 days, the use of moisture was restricted to the day shift during the regular work days only (no weekend days). For the remaining 6 days, the barrel was allowed to react continuously. Figure 3 shows the recorded traces of the hydrogen and oxygen concentration in the barrel off-gas during this time period.

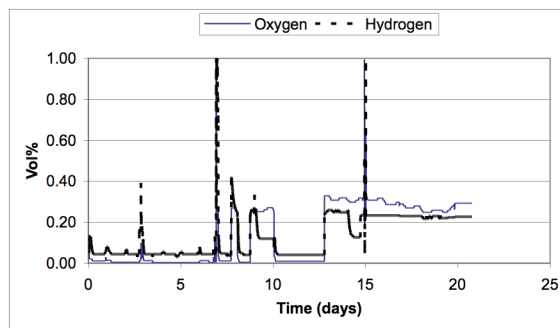


Figure 3: ANL#82 H₂ and O₂ Concentrations

In the figure, there are two large spikes in the hydrogen and oxygen concentration. These spikes were not a result of physical events within the barrel, but were related to two instrument calibrations that were performed during the test and are an artifact of those calibrations.

Due to the erratic nature of the treatment operation, the uncertainty regarding the amount of residual sodium in the barrel at the start of the process, and the lack of a defined end point in regard to the measured hydrogen concentration, it was decided to terminate the use of humidified carbon dioxide after 21 days and examine the inside of the barrel. A visual examination showed that the barrel contained more than one gallon of loose white powder and there still remained a ring of unreacted metallic sodium around the bottom rim of the barrel. In total, it was estimated that approximately 1-2 lbs of sodium was not reacted. Figure 4 shows the ring of metallic sodium at the bottom of the barrel.



Figure 4. ANL#82 with sodium remaining.

The white powder was analyzed in the analytical laboratory by X-ray diffraction and acid-base titration, and was found to be about 70% sodium bicarbonate and about 30% sodium carbonate.

Aside from the white powder and the metallic sodium, there appeared to be black flecks of material mixed in with the carbonate powder generated by the treatment process. Figure 5 shows these black flecks. These black flecks were analyzed and were found to be mostly sulfur mixed with iron. It is believed that the black flecks came from contamination that was internal to the barrel at the time the barrels were filled with bulk sodium and were not a result of the barrel treatment process.



Figure 5. Black material from ANL#82.

Physical removal of the residual sodium was attempted at SCMS by cutting the barrel sides at about 1 foot above the bottom of the barrel, so that workers could easily reach the metallic sodium and scrape it out with a tool. This proved to be somewhat hazardous because it was difficult to maintain a good argon blanket on such a short-walled vessel and the physical removal of the sodium was abandoned for chemical removal the Water Wash Vessel at SCMS. After washing, the barrel pieces emerged clean and free of any adhering sodium or carbonate materials.

3.3 Barrel ANL#630

No hydrogen was found in Barrel ANL#630 with the portable hydrogen monitor when the barrel bungs were first opened.

Before the initial carbon dioxide purge, the hydrogen and oxygen monitors on the vent line were verified to be in working order, and additional temperature probes were installed on the outer surface of the barrel.

At 11/02/2004 8:42, the barrel was flushed with dry carbon dioxide at 5 scfm and ambient temperature. When the carbon dioxide flush began, the temperature of the drum remained steady for several minutes, and then

climbed quickly to a maximum of 120 °C. The temperature remained near the maximum temperature for several more minutes, and then began an exponential decay back to ambient temperature. Full cooldown of the barrel took almost 1 hour.

The spike in the barrel temperature, especially at the bottom where the highest temperature was recorded, was correlated with increases in the measured hydrogen and oxygen concentrations in the barrel off-gas. Figure 6 shows the measured hydrogen and oxygen concentrations for a half-hour period covering the temperature spike.

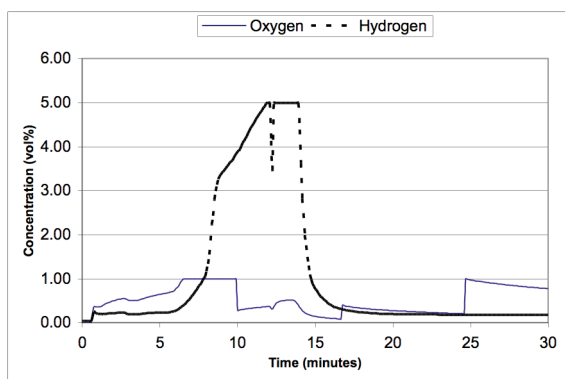


Figure 6. ANL#630 H₂ and O₂ concentrations during the initial CO₂ purge

In the figure, oxygen reaches its highest detectable level (1 vol%) first at about 6 minutes, and then hydrogen rises quickly to beyond 5 vol% for short period of time. There is also a sudden rise in the oxygen concentration at about 25 minutes, but the origin of this rise is unknown, and the high oxygen level was not sustained.

After eliminating air leaks as a cause, the most likely source for the oxygen during the purge is the reaction of water with sodium peroxide. Oxygen is generated by the reaction of sodium peroxide (Na₂O₂) with water. The formation of sodium peroxide, it is believed (Foust, 1972), requires that sodium above the temperature of 150-200 °C be exposed to air or oxygen. So, if sodium peroxide is present, then

such exposure could have only occurred when the barrels were initially filled with molten sodium, or when the barrels were drained of bulk sodium at SPF. No chemical analyses of the residual sodium oxide residues inside the barrel were performed, so it could not be verified that sodium peroxide was the cause.

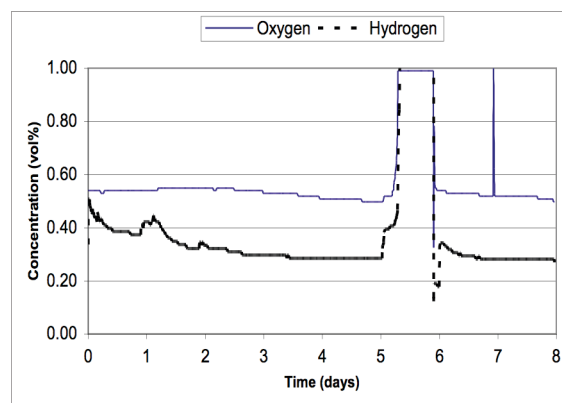


Figure 7. #ANL630 H₂ and O₂ concentrations during humidified CO₂ treatment

From 11/02/2004 9:00 through 11/11/2004 9:45, the barrel was treated with humidified carbon dioxide at a rate of 5 scfm and at ambient temperature. Figure 7 shows the measured hydrogen and oxygen concentrations during humidified carbon dioxide treatment of the barrel. Starting from the left hand side of the figure, the initial drop in hydrogen occurred when the barrel was in an upright position. The rise in the curve at Day 1 and the subsequent drop corresponds to when the drum was placed on its side and mechanically agitated with a rubber mallet. The large spike at Day 5 is artificial, and corresponds to a kinked hose in the barrel gas feed line, which stopped the flow of humidified carbon dioxide into the barrel and allowed air to infiltrate backward through the vent to the H₂ and O₂ detectors. The short rise at Day 6 and subsequent decay corresponds to a rotation of the barrel to the opposite side, and further mechanical agitation of the barrel. Although the hydrogen concentration did not decay to a true zero point, the trend in the hydrogen concentration curve seemed to indicated that there was no longer any sodium

left to react, and treatment with humidified carbon dioxide was terminated.

After completing the treatment step, the barrel bungs were removed and photos were taken of the barrel interior. Figure 8 shows one photo taken just after the treatment step. The bottom of the barrel is clearly visible with no apparent ring of sodium around the barrel seams. The white carbonate material was loose and powdery, and had a flaky consistency.



Figure 8. ANL#630 after treatment with humidified CO₂

The barrel was moved to SCMS where the top of the barrel was removed so that the white material could be removed. No sodium metal was seen during the inspection.

The barrel was washed in the Water Wash Vessel, and no hydrogen was detected during the washing.

3.4 Barrel ANL#1128

No hydrogen was found in Barrel ANL#1128 with the portable hydrogen monitor when the barrel bungs were first opened.

Before the initial carbon dioxide purge, the hydrogen and oxygen monitors on the vent line were verified to be in working order, and additional temperature probes were installed on the outer surface of the barrel.

At 11/11/2004 9:46, the barrel was first flushed with dry carbon dioxide at 5 scfm and ambient temperature. When the carbon dioxide flush began, the temperature of the barrel bottom rose immediately to 110 °C. It remained at the maximum temperature for approximately 5 minutes, and then cooled down. Figure 9 shows the measured hydrogen and oxygen concentrations during the initial purge.

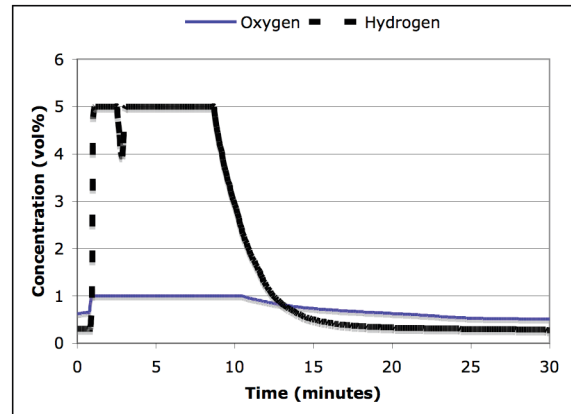


Figure 9. #ANL1128 H₂ and O₂ concentrations during initial dry CO₂ purge

As was seen with Barrel #630, the hydrogen rose quickly to above 5 vol%, and then began falling within 10 minutes. The oxygen concentration also increased during this time period to above 1 vol%, which was the maximum limit of the oxygen sensor. The increase in oxygen readings is consistent with the observed increase in oxygen concentration during the initial purge of Barrel #ANL630. The reaction of sodium peroxide with water may indeed be the cause for the increased oxygen.

Though the recorded oxygen level is limited to a maximum of 1 vol%, observations made at the time of the actual instrument read-out showed that the oxygen level reached a peak concentration of about 1.6 vol%. This is above the action level of 1 vol%, but the action was to purge with dry carbon dioxide, and so the purge was continued. This increase in oxygen is a concern when hydrogen and heat are also being generated.

Care must be taken during future drum treatment tests to avoid creating conditions that could lead to a hydrogen combustion event. The conditions encountered during this barrel purge were outside of the hydrogen flammable limit (oxygen still too low) and so there was no danger of a hydrogen fire here. However, if the flow of fresh carbon dioxide were suddenly reduced, then it may be possible to create temporary conditions inside the barrel where the hydrogen and oxygen are still being generated but are not being purged from the barrel at a fast enough rate. The carbon dioxide purge rate needed to remain as fast as possible (here 5 scfm) to dilute the hydrogen and oxygen being generated and keep the concentrations of gases below the flammable limit. In the future, such conditions might be better created by diluting the carbon dioxide with another inert gas such as argon. With less carbon dioxide present, the reaction of carbon dioxide with sodium oxide or sodium peroxide might be less vigorous, and the argon would be there to dilute the hydrogen and oxygen generated. Also, it would give operators the opportunity to stop the flow rate altogether of carbon dioxide will still maintaining an inert gas purge. In that way, if the hydrogen and oxygen concentrations approach the safety limits, the flow of carbon dioxide could be stopped while still maintaining a flow of inert purge gas.

The use of humidified carbon dioxide began at 11/11/2004 11:30 and continued until 11/22/2004 12:30. The gas flow rate was maintained at 5 scfm for the entire time span. The measured hydrogen and oxygen concentration during this treatment period is shown in Figure 10. The first peak on the hydrogen curve corresponds to the reaction of residual sodium with the barrel in the upright position, while the second and third lesser peaks in the hydrogen curve correspond to the barrel positioned on its side. Treatment was terminated when it appeared that the hydrogen concentration had leveled off at background levels.

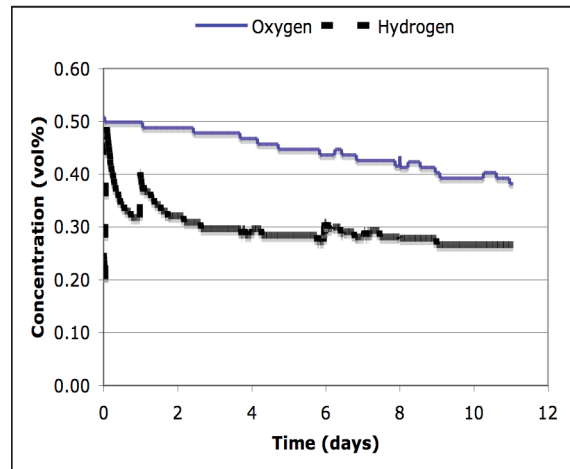


Figure 10. H₂ and O₂ concentrations during humidified CO₂ treatment of ANL #1128

The barrel was visually inspected after the humidified carbon dioxide treatment step, and it was discovered that the bottom of the barrel was covered by a large white deposit that did not slump or move when the barrel was rotated. A picture of this deposit at the bottom of the barrel is shown in Figure 11.



Figure 11. Visual inspection of ANL#1128.

Upon additional investigation of the deposit at SCMS, it was discovered that there was a significant amount of metallic sodium beneath the hard crusty layer of carbonate material.

The barrel was water washed, and no sodium or carbonate material remained after the water wash.

Although the use of humidified carbon dioxide did not fully react all of the residual sodium within the barrel, the results were encouraging in that the morphology of the deposit at the bottom of the barrel could be distinguished easily from the morphology of the deposit at the bottom of Barrel #630, the previous barrel treated. While in #630 the material at the bottom was loose and flaky, the material in #1128 was not flaky and stayed in place when the barrel was rolled side to side. This result indicated that perhaps the visual inspection step might be used in the future to distinguish between barrels that may require a water wash from those that do not.

3.5 Barrel ANL#1174

No hydrogen was found in Barrel ANL#1174 with the portable hydrogen monitor when the barrel bungs were first opened.

Before the initial carbon dioxide purge, the hydrogen and oxygen monitors on the vent line were verified to be in working order, and additional temperature probes were installed on the outer surface of the barrel.

From 11/22/2004 12:30 to 11/22/2004 14:30, the barrel was flushed with dry carbon dioxide. Figure 12 shows the measured hydrogen and oxygen curves for the first 10 minutes of this purge period. During the purge, the barrel experienced a temperature rise, but only to a maximum of 40 °C, and no smoke was generated. During this purge, the width of the oxygen peak was wider than the width of the hydrogen peak.

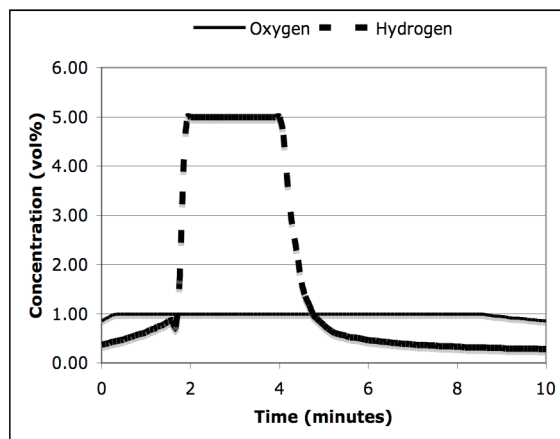


Figure 12. ANL#1174 measured H₂ and O₂ concentration during initial CO₂ purge

Treatment of ANL#1174 with humidified carbon dioxide began at 11/22/2004 14:30 and was completed at 12/1/2004 10:00. Figure 13 shows the measured hydrogen and oxygen concentrations for the first 3.5 days of treatment.

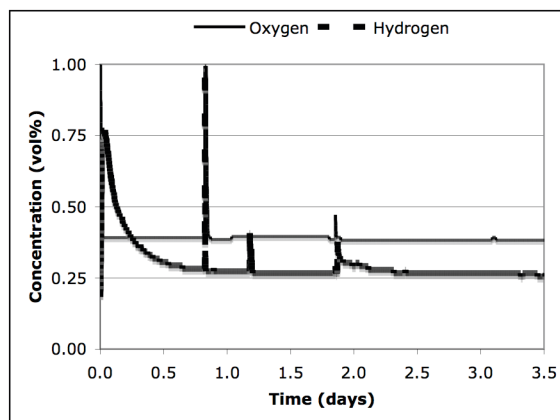


Figure 13. ANL#1174 measured H₂ and O₂ concentrations during treatment with humidified CO₂

In the figure, the barrel was reacted in a vertical position for just under 2 days, and then was placed on its side for further treatment. The first peak on the left (and the subsequent decay) correspond to the hydrogen generated while the drum was in a vertical position, and the short peak just before Day 2 corresponds to when it

was flipped on its side for the first time. There was no measured peak for the second side rotation, which occurred after Day 4 of treatment. The large spike at approximately 0.75 days occurred because the hydrogen and oxygen meters underwent calibration at that time. The measured oxygen concentration remained steady throughout treatment, and remained below 0.4 vol%.

ANL#1174 was thoroughly examined before and after treatment to gain a better understanding of what changes occurred in the barrel deposits as a result of the overall treatment process. Figure 14 shows the inside of the barrel prior to treatment. The material is gray in appearance, and large chunks of material adhere to the sides and bottom of the barrel. There is very little loose material.



Figure 14. ANL#1174 prior to treatment

After treatment, the sodium and carbonate material inside the barrel underwent profound changes in appearance and morphology. The material turned white and became a loose, powdery, flaky material. This material is shown in Figure 15.



Figure 15. ANL#1174 after treatment with humidified carbon dioxide.

A thorough visual inspection of the barrel prior to the water wash step revealed that the barrel was clean of sodium metal.

Figure 16 shows the inside of the barrel after the water wash process. The water wash was very successful at removing all traces of carbonate material from inside the barrel, and the internal metal surfaces of the barrel were once again visible.



Figure 16. ANL#1174 after water wash

3.6 Barrels ANL#1135 and 1116

No hydrogen was found in Barrels ANL#1135 and 1116 with the portable hydrogen monitor when the barrel bungs were first opened.

Before the initial carbon dioxide purge, the hydrogen and oxygen monitors on the vent line were verified to be in working order, and additional temperature probes were installed on the outer surface of the barrels.

Barrels ANL#1135 and ANL#1116 were purged with dry carbon dioxide one at a time, but were treated simultaneously (in a serial arrangement) with humidified carbon dioxide. Due to the high temperatures encountered earlier during the dry carbon dioxide purge step, it was felt that it was safer to purge each barrel by itself.

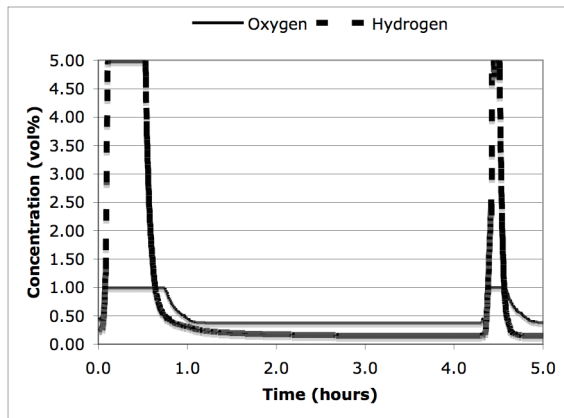


Figure 17. Barrels ANL#1135 and 1116 measured H₂ and O₂ concentrations during dry CO₂ purge

The sodium oxide/carbon dioxide reaction inside both barrels was strong, and the barrel temperatures at the bottom of the barrels peaked at 300 and 220 °C, respectively. The reaction was sustained for longer than ten minutes in Barrel ANL#1135, indicating that there was a larger amount of sodium oxide in the barrel than the other barrels treated. These strong

temperature peaks were accompanied by smoke from the outside bottom of the barrels. In spite of the smoke, the bottom of the barrels was not visibly scorched. The measured hydrogen and oxygen concentrations during the dry carbon dioxide purge of these barrels are shown in Figure 17.

The two barrels were purged simultaneously in a serial arrangement starting at 12/1/2004 15:06 and ending at 12/14/2004 15:30. Figure 18 shows the measured hydrogen and oxygen concentrations during the first three days of treatment. The figure was truncated at 3 days because no significant changes occurred in the measured hydrogen concentration after the first three days.

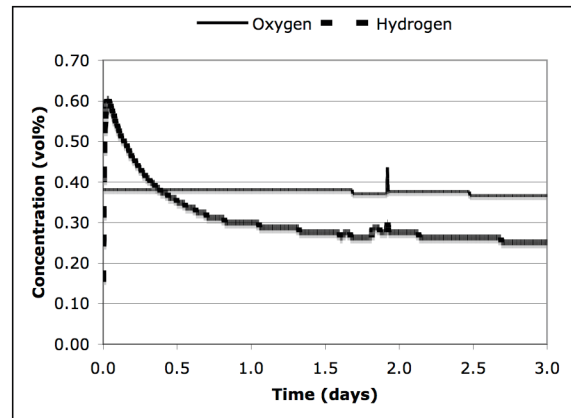


Figure 18. Barrels ANL#1135 and 1116 measured H₂ and O₂ concentration during humidified CO₂

The barrels were treated in an upright position for 1.7 days, and were then placed on their sides for further treatment. The short step increase in the measured hydrogen concentration at Day 1.7 indicates the point where the drums were rotated to their sides. The drums were rotated again to the other side after about 5 days, but no change occurred in the measured hydrogen and oxygen concentration. Presumably all of the residual sodium in the barrels had reacted at that point, and none remained to cause any increase in the hydrogen measurement.

Figure 19 shows a photo of the inside of Barrel ANL#1135 after completing the humidified carbon dioxide treatment but before it was washed in the SCMS water wash vessel. The bottom of the barrel was free of metallic sodium deposits, and contained almost a gallon of loose flaky carbonate material.



Figure 19. Barrel ANL#1135 after humidified CO₂ treatment

Barrel #1116 had a similar appearance to Barrel #1135 after treatment. Figure 20 shows the inside of the barrel. The material at the bottom of the barrel was loose and flaky. This barrel also contained black flecks of the kind seen in the bottom of ANL#82.

Both barrels emerged clean and shiny after they were washed in the SCMS water wash vessel. No sodium or carbonate residue remained in the barrels after washing, and no hydrogen reactions were observed or detected during the washing process.



Figure 20. Barrel #1116 after humidified CO₂ treatment

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- S.R. Sherman, S.P. Henslee, K.E. Rosenberg, et al., "Unique Process for Deactivation of Residual Sodium in LMFBR Systems", *Proc. Spectrum 2002* (Reno, NV: American Nuclear Society 2002)
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APPENDIX: HAZARD ANALYSIS

The contents of this appendix were originally written into Controlled Document #F0000-0213-ES-01, "HAZARD ANALYSIS: Fermi Barrel Treatment Using Humidified Carbon Dioxide", and are provided here for completeness.

Introduction

There are approximately 1400 Fermi barrels currently being stored at Argonne National Laboratory – West. Fermi barrels are 55-gallon steel drums that contain residual amounts of sodium metal, sodium oxides, and sodium carbonates. Originally, these barrels were filled with sodium metal from the Fermi-I sodium-cooled reactor in Monroe, Michigan. The bulk sodium was drained from the barrels during the EBR-II Plant Closure Project, which was active between 1999 and 2002, and the barrels were placed into storage for eventual disposal. Although the amount of sodium metal remaining in each barrel is below RCRA regulation limits, it still must be completely deactivated before the barrels can be sent for disposal, because the disposal site will not accept waste materials containing sodium metal. This hazards analysis addresses the hazards associated with the deactivation process.

The process chosen to deactivate the residual sodium inside the barrels is the humid carbon dioxide process. With this process, a flow of humidified but not saturated carbon dioxide is established through a single barrel, or a serial arrangement of barrels. The moisture in the carbon dioxide reacts with the residual sodium to form sodium hydroxide and hydrogen gas. The carbon dioxide then quickly reacts with the sodium hydroxide to form sodium bicarbonate. The hydrogen gas created by the process is diluted by excess carbon dioxide and is vented into the environment. As a dilute vapor, water reacts with the sodium metal in a controlled and steady fashion, so that any process instabilities caused by the build-up of liquid water inside the drums will be avoided.

The humid carbon dioxide process for deactivating residual sodium was developed during the EBR-II Plant Closure Project, where it was referred to as the sodium passivation process. Laboratory tests and a large-scale demonstration of the process on the EBR-II secondary sodium system showed that the process could be used safely and predictably to deactivate residual sodium within process equipment. As a result, the EBR-II Plant Closure Project adopted the process as its process of choice and was used to deactivate approximately 50 gallons (190 liters) of residual sodium within the EBR-II secondary sodium system, and approximately 60 gallons (230 liters) of residual sodium within the EBR-II primary sodium system. Since that time, treatment of residual sodium within the EBR-II primary tank was re-started in May 2004, and another 60 gallons (230 liters) of residual sodium have so far been deactivated with this process.

The principle hazards associated with the treatment process are hydrogen, sodium metal, inert gases, pressure, hot surfaces, and low levels of radioactivity. These hazards and the mitigation strategies to address them are discussed below.

Applicable Documents

The safety basis for the handling of sodium within the EBR-II facility was established by the EBR-II Hazard Summary Report (Ref. 1), a document detailing hazards and safety analyses dating back to the initial design of the reactor. Building on this document, other documents were written to analyze the process hazards associated with the deactivation of residual sodium within the EBR-II primary and secondary sodium systems using humid carbon dioxide (Ref. 2, 3, 4). These analyses concluded that the deactivation process, with its defined engineering and administrative controls, could be used safely to deactivate residual sodium within the EBR-II primary and secondary sodium systems.

Since those analyses were written, the humid carbon dioxide process has been demonstrated to work safely and effectively in the laboratory (Ref. 5), and in the EBR-II facility (Ref. 6).

The Fermi barrel treatment process has been examined in an engineering technical analysis (Ref. 7), and a non-routine procedure has been written to perform the initial testing of the deactivation process (Ref. 8). The non-routine procedure will be used to optimize operational parameters and to measure data that will be used to develop a QA/QC program for routine Fermi barrel treatment.

The hazards associated with hydrogen, sodium metal, and inert gases have already been described and mitigation procedures developed in the previous documentation. General ANL-W approved actions and protective equipment will be used to mitigate the hazards associated with these materials.

Program/Experiment/Test Requirements

All test procedures and requirements will be handled under the approved procedures listed in NRP-EBR-009 (Ref. 8). This non-routine procedure will cover normal and abnormal operation of the deactivation process. The procedure will cover mitigation measures for all of the hazards associated with the process, including the additional hazards not covered in previous documentation, the hazards associated with pressure and radioactive materials.

Consequences, Risk and Mitigation of Additional Hazards

There are several additional hazards that were not explicitly addressed in that documentation that will be addressed here. These hazards are pressure, hot surfaces, and the presence of radioactive materials.

Barrel pressurization is one possible hazard associated with the treatment process. Barrel pressurization may cause harm to workers either by the ejection of bungs during bung removal, or by barrel rupture due to the barrel internal pressure exceeding the burst strength of the barrel. A pressurized barrel has stored energy that can be released suddenly in the event of an uncontrolled depressurization. Ejection of a bung or the bursting of a drum may also release material from inside the barrel into the environment.

Barrel pressurization may occur from the build-up of hydrogen gas within a barrel, pressure changes due to differences between ambient pressure and static barrel pressure, or from pressurization of a barrel during the deactivation process. Injuries or near misses due to barrel pressurization and

subsequent ejection of barrel bungs or barrel rupture has been documented across the DOE laboratory complex, and so such hazards must be addressed.

The following incident is provided as an example. A near-miss occurred at Rocky Flats in August 1999, involving the ejection of a barrel top upon removal. In this incident, a worker was removing the lid from a new, empty steel barrel that had been shipped from California. The pressure difference between sea level and the air pressure at Rocky Flats was sufficient to launch the top of the barrel several feet into the air. Fortunately, the worker was not injured.

In order to address the problems posed by barrel pressurization, proper personal protective equipment (PPE) and work procedures must be adopted to provide the necessary level of protection for workers. Workers will be instructed to inspect barrels before they open the barrel bungs for signs of pressurization. Such signs would include bulging barrel tops or misshapen barrels. Barrels that appear to be pressurized will be handled on a case-by-case basis with the approval of the facility manager. Upon initial opening from drum storage, the smaller barrel bung will be opened first, and slowly, according to the procedure used to open the barrels the first time the Fermi sodium was withdrawn from the drums at the ANL-W Sodium Processing Facility (Ref. 9). Only non-sparking tools will be used to open barrel bungs. Portable hydrogen detection instrumentation will be used to monitor the opening process, and if a sufficient concentration of hydrogen is measured upon opening, the drum will be resealed and set aside for separate treatment, on a case-by-case basis.

After examining the pressure specifications of the barrels, and taking into account the pressure limits of the deactivation process, there is very little risk of barrel rupture due to overpressurization of a barrel. The Fermi barrels were used to transport sodium metal from the FERMI-I reactor facility to ANL-W. During transport, the barrels were regulated under Rule 49 CFR 178.605 (Ref. 10), which requires that drums or barrels used to transport materials falling into Packing Group I, in which sodium metal is included, must be able to handle up to 250 kPa (approximately 36 psig) overpressure without damage. Since it is presumed that the Fermi sodium was shipped lawfully to ANL-W, the Fermi barrels must conform to the rule and must be able to handle up to 36 psig without a problem. The pressure of the deactivation process is limited to a maximum pressure of 11 psig (76 kPa-g) by a pressure regulator and a relief valve (Ref. 11), and so barrel pressures during the treatment process will not approach that maximum limit. To help reduce pressure drop and the risk of a vent line blockage occurring, only ¾" tubing will be used, which provides a wider diameter flow channel than standard ¼" or ½" tubing.

Though the barrels should be able to sustain up to 36 psig without any danger of rupture or deformation, it is possible that individual barrels may be weakened in spots due to corrosion. The barrels have been in storage for many years, and it is possible that weak spots may have developed. Weak spots would reduce the pressure tolerance of the barrel and would increase the likelihood of a hole opening in the barrel upon pressurization. As a first step, barrels will be visually inspected for obvious signs of corrosion (e.g., flaked paint, large visible rust spots, etc.) before placing them in the barrel train, and set aside if the corrosion is significant. As a second step, a steel catch pan will be placed beneath each barrel during treatment to catch any material that may be ejected from the barrel if a weak spot gives way during the deactivation process. Portable carbon dioxide monitors will be in place during treatment to detect any localized increases in carbon dioxide, so that any gas leaks occurring from process piping or from a breached barrel can be quickly detected and handled.

During the course of treatment, it could be speculated that there would be a sudden pressurization of a barrel due to a runaway water/sodium reaction within a barrel, but past operating experience with the deactivation process indicates that no such reactions will occur. All operating experience to date shows that the process behaves in a steady manner with no uncontrolled excursions in pressure and temperature.

Therefore, there is no credible risk of drum rupture due to a sudden runaway sodium reaction under normal operating conditions. The operating performance of the humid carbon dioxide treatment is in contrast with the performance of the steam-nitrogen process as applied to the S1G sodium tank. In that situation, the S1G sodium tank was subject to occasional pressure and temperature spikes that, if experienced in the Fermi barrels, may lead to barrel damage.

Similarly, no problems should be encountered from rupture of the Tygon[®] tubing used to connect various pieces of equipment in the drum chain. Tygon[®] tubing has a burst pressure limit of 110 psig (760 kPa-g). With a maximum system pressure of less than 11 psig, there will be no credible risk of bursting the Tygon[®] tubes.

Another hazard associated with Fermi barrel treatment is the presence of hot surfaces. The chemical reactions involved in the deactivation process are exothermic, and it is very likely that the barrel surfaces near sodium deposits will become hot from the heat of reaction. Workers will be required to wear gloves when touching the barrels during the deactivation process to protect against burns.

The other possible hazard associated with deactivation of the Fermi barrels is the radioactivity of the residual sodium, mainly due to ²²Na, ⁹⁰Sr, and ¹³⁷Cs. In 1985, the measured levels of radioactivity of these components in the Fermi sodium were 0.82, 0.36, and 0.73 nCi/g (30, 13, 27 Bq/g), respectively (Ref. 12). At the time of Fermi drum deactivation, the activity levels will have decayed to below 0.0052 nCi/g, 0.23 nCi/g, and 0.47 nCi/g (0.19, 8.5, 17 Bq/g). These activity levels are very low, but precautions still must be taken when there is risk of contacting the material, or when there is a possibility of releasing the material into the environment.

The total amount of radioactivity that can be released to the environment is limited by the amount of sodium in each barrel. All of the Fermi barrels have already been drained of bulk sodium and contain less than 5 lbs of sodium per barrel. Therefore, the total amount of radioactivity that could potentially be released at any one time is less than 1.6 μCi (5.9 x 10⁴ Bq) per barrel.

To protect against any releases of radioactive material through the vent line, the vent line will be equipped with a HEPA filter. The HEPA filter will be DOP tested or replaced on an annual basis in order to comply with existing rules and regulations.

Proper personal protective equipment will be used by workers whenever handling or inspecting barrels, and proper procedures used to handle barrels will be described in the operating procedure documentation. Specialized procedures will be written to handle barrel inspection for the purposes of verifying that all of the residual sodium has been reacted, so that the risk of worker exposure to the radioactive material is minimized.

Conclusions

The hazards presented by the presence of hydrogen, sodium metal, pressure, hot surfaces, and radioactivity do not present any additional hazards to workers or to the facility, and do not affect our ability to maintain a safe and acceptable risk posture. The risks due to these hazards are minimized through engineering and behavioral controls, and the deactivation process can be performed safely.

**ADDENDUM:
Hazard Analysis of Fermi Barrel
Pre-Treatment With Dry Carbon Dioxide**

Introduction

Prior to treatment, the Fermi barrels contain a mixture of residual sodium metal, sodium oxide, sodium hydroxide, and sodium carbonate species. The components are not uniformly mixed, and the materials are believed to be divided in layers, with sodium at the deepest parts, and hydroxides, oxides and carbonate layers covering it.



Figure 1: Inside of Fermi Barrel #ANL1174 prior to treatment

As seen in Figure 1, the material inside the Fermi barrel is lumpy and adheres to the walls and the bottom. The residual sodium in the barrel is not visible due to the presence of oxide, hydroxide, and carbonate layers. Such materials are believed to originate from years of air and water vapor in-leakage into the barrels. Such findings may also suggest that there is little chance of pressure build-up in the Fermi barrels prior to treatment, since there seems to be an open pathway for air and water vapor to leak into the barrels, and for hydrogen to leak out of the barrels as it is created.

At the start of the residual sodium treatment process, the Fermi barrels are purged with dry carbon dioxide. During the past application of this treatment technique to clean residual sodium (metal visible or covered with a very thin oxide coating), the dry carbon dioxide was inert and showed no evidence of reacting in any way with the residual sodium.

Unlike clean residual sodium, the material in the Fermi barrels has proved to behave very differently in regard to its reactivity with dry carbon dioxide. Upon introduction of carbon dioxide into the Fermi barrels (as observed in Fermi Barrels #ANL630, ANL1128, ANL1174, ANL1135, and ANL1116), chemical reactions are occurring that generate heat, hydrogen, and perhaps a small amount of

oxygen. The chemical reactions occur quickly, with little induction time, and then subside, usually within 15 minutes after the introduction of carbon dioxide.

The temperature of each barrel was measured at 6 different spatial points during the carbon dioxide purge, and the highest readings were observed on the bottom of the barrel. The measured temperatures varied from barrel to barrel, and peak temperatures reached between 40 and 300 °C. The temperature of the barrels at the top, where the Tygon tubing attaches to the outlet, was observed to climb as high as 50 °C. For several of the barrels purged, the high temperatures caused the bottom of the barrels to smoke. In one barrel, the smoke was accompanied by a discoloration of the barrel bottom.

During peak reaction times, the measured hydrogen concentration rose to about 5-6 vol% (with a CO₂ input rate of 5 scfm or 134 slm). Oxygen may also have been generated. Due to the way the exhaust manifold is plumbed and the relatively slow response time of the oxygen meter, it was difficult to get an accurate reading of the oxygen concentration in the exhaust gas. The exhaust manifold suffers from air in-leakage when the system is not actively being purged and the oxygen meter reads high until gas flow is established through the barrel(s). Even so, the measured oxygen concentration tends to remain around 1 vol% until the chemical reactions subside, and then it drops down to baseline levels (less than 0.4 vol% at the exhaust manifold).

There are several safety questions that must be addressed in response to this chemical reaction that haven't been dealt with already in previous safety or hazard analyses. These are:

- Why is dry carbon dioxide reacting with the residual content in the Fermi barrels, and, with the small amount of hydrogen generated, does this present an immediate fire hazard within the barrels during the dry carbon dioxide purge?
- Is there a potential hazard associated with the approximate 1400 barrels in storage in regard to these chemical reactions?
- The chemical reactions generate a substantial amount of heat, which sometimes causes the bottom of the barrels to smoke. Does this heat present any external safety hazards?
- What mitigation strategies might be employed to lessen the hazards associated with the above activities?

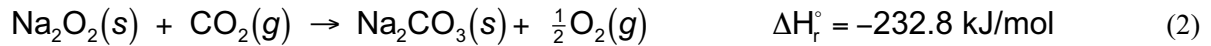
This addendum will address these questions, and will propose methods for mitigating or reducing the hazards associated with the use of dry carbon dioxide during the purge of the Fermi barrels.

Carbon Dioxide Reactions and Analysis of Immediate Internal Hazards

There are multiple chemical reactions that are occurring in the barrels upon CO₂ exposure. Almost all of the chemical reactions are exothermic (generating thermal energy), but only certain reactions are giving rise to the generation of hydrogen and perhaps oxygen. For this analysis, these chemical reactions are divided into three categories: initiating reactions, hydrogen generation steps, and side reactions. All thermodynamic data provided below was obtained from Ref. 13.

Initiating Reactions

The initiating reactions that occur in Fermi barrels in regard to carbon dioxide that do not appear to occur with any significant impact with "clean" sodium are the reactions of carbon dioxide with sodium oxide and sodium peroxide. These reactions are shown in Equations 1 and 2.



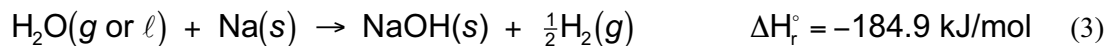
In Equation 1, carbon dioxide reacts with sodium oxide to produce sodium carbonate. In Equation 2, carbon dioxide reacts with sodium peroxide to produce sodium carbonate and oxygen. Both reactions are strongly exothermic.

Sodium oxide and perhaps a small amount of sodium peroxide are believed to be in the barrels prior to the start of the treatment process by reason of logical and chemical arguments. Air in-leakage has certainly occurred over the lifetime of the Fermi barrels, resulting in the exposure of the residual sodium to oxygen. Oxygen reacts readily with sodium metal to form sodium oxide, with sodium oxide being the most stable oxide species at room temperature. Sodium peroxide can be formed by heating sodium oxide in the presence of oxygen to temperatures in the range of 200-300 °C (Ref. 14). The Fermi barrels are stored at ambient temperature, but the past history of the barrels is uncertain, and it is possible that such conditions could have been experienced some time in the past. Unlike potassium, sodium does not form super oxides at ambient conditions and at normal atmospheric pressures (Ref. 15).

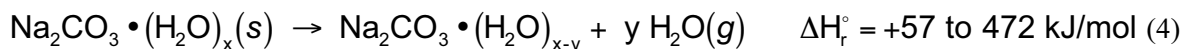
Chemical samples taken after full treatment of Barrel #ANL630 were analyzed, and were determined to have a composition of approximately 30 wt% sodium carbonate, with the balance being sodium bicarbonate. If sodium oxide were not present in the drums prior to starting treatment, then the composition of the post-treatment powder would have contained less than 5 wt% sodium carbonate, as was seen in samples taken from laboratory experiments and the EBR-II Secondary Sodium System after treatment with humid carbon dioxide (Ref. 16). No samples have yet been taken from the Fermi barrels prior to treatment, and so no definite confirmation of this hypothesis can yet be provided.

Hydrogen Generation Steps

Equations 1 and 2 above provide an explanation for the large amount of heat and the suspected amounts of oxygen generated by exposing the residual Fermi material to carbon dioxide, but they do not explain the development of a significant amount of hydrogen during the reaction. Hydrogen can only be generated by exposing sodium metal to water, as shown in Equation 3.



Since there is no water vapor in the dry carbon dioxide that was introduced into the Fermi barrels, the water must already be present in the barrel, but in a form that was not available until the initiating reactions occurred. It is speculated that the water is being held inside the barrels in the form of sodium carbonate hydrates. Sodium carbonate has a high capacity for storing water under the right humidity conditions, and has the capacity to release it upon modest temperature increases. Equation 4 shows the prototypical reaction associated with the decomposition of sodium carbonate hydrate.



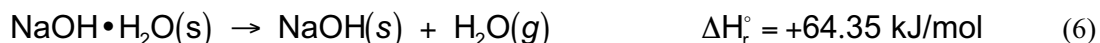
In Equation 4, x may have a value of 10, 7, or 1. And the decomposition reactions occur at 25, 32, and 100 °C, respectively. Though these reactions are endothermic, the initial reactions of carbon dioxide with

sodium oxide and sodium peroxide would liberate more than enough thermal energy to provide heat to these endothermic decomposition reactions.

Water may also be liberated from the decomposition of another sodium carbonate hydrate form, sodium sesquicarbonate, as shown in Equation 5. This reaction occurs above 70 °C.



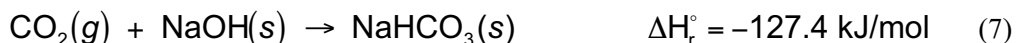
Lastly, water may also be released from sodium hydroxide species. Since the material in the barrels is dry, it is not likely that there are sodium hydroxide hydrate species beyond sodium hydroxide monohydrate, which begins to lose water above 60 °C. This reaction is shown in Equation 6.



Given the uncertain history of the barrels (long-term storage in an uncontrolled environment), it is very likely that the water source for the sodium-water reaction that is responsible for the hydrogen is sodium carbonate hydrates and perhaps sodium hydroxide monohydrate. Without taking samples of the starting materials, it is difficult to know the specific species involved. From a safety standpoint, knowing which specific species are involved will have little effect on how the drums are treated, and it is enough to know that they are very likely present in the barrels and that the treatment procedures must be adjusted in response.

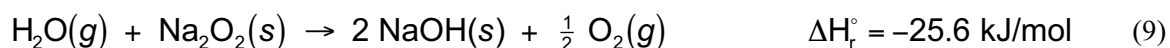
Side Reactions

There are other chemical reactions that release heat and may contribute to the high temperatures measured in the barrels. One reaction is the combination of carbon dioxide with sodium hydroxide, as shown in Equation 7.



The sodium hydroxide may already be present in layers close to the sodium surfaces, or may have been created by the water/sodium reaction shown in Equation 3.

Water vapor may also react with sodium oxide or sodium peroxide to liberate some thermal energy, though the reactions are less energetic than water-sodium metal reactions. These reactions are shown in Equations 8 and 9.



Analysis of Immediate Internal Hazards

The immediate hazard present due to these reactions is the evolution of heat. While the heat itself does not present any internal hazard, it may have an effect on the Tygon[®] tubing used to carry the exhaust gas to the vent, and may serve as a trigger for a hydrogen/oxygen reaction, if other reaction conditions are favorable (e.g., sufficiently high oxygen levels).

The measured hydrogen levels emerging from the Fermi barrels have been in the range of 5-6 vol%. If oxygen were present at concentrations above 5 vol%, then this hydrogen concentration would be in the flammable range. The measured oxygen concentrations were no higher than about 1.2 vol%, and so there is no immediate danger of hydrogen combustion within the barrel(s) during the purge.

The highest measured temperature at the tops of the barrels adjacent to the gas outlet during the dry carbon dioxide purge was about 50 °C. The recommended temperature limit of Tygon[®] tubing is 74 °C, above which it loses its strength and can sag, stretch, or otherwise lose its shape. Even at 50 °C, the tubing becomes somewhat more flexible and can sag and pinch. Care must be taken to avoid kinking or collapsing the tubing so that the barrel does not become pressurized or un-vented during the purge. The tubing should be positioned properly or supported during the purging period to avoid closing off the exhaust line. As an added precaution, it is suggested that a short section of metal-braided tubing be attached to the drum bung, to which the Tygon[®] tubing can be attached. The metal-braided tubing would help vent some of the heat from the exhaust gases prior to flowing through the Tygon[®] tubing. Metal-braided tubing would not kink. Alternatively, if available in larger diameters, the Tygon[®] tubing could be replaced with Teflon[®] tubing, which has a higher temperature tolerance.

Also, with the high exhaust temperature, it is recommended that a serial arrangement of barrels be avoided if more than one barrel is being with purged pure carbon dioxide at the same time. In a serial arrangement, the gas exhausted from one barrel becomes the inlet gas for the following barrel. With the high heat generated in the leading barrel, the second barrel in series would experience still higher temperatures, and so on down the line until the exhaust temperatures exceed the temperature limit of the Tygon[®] tubing and it collapses. In addition, the hydrogen concentration in the gas stream would be amplified in each successive barrel, so that a more hazardous condition is created further down the serial chain than would have been present with just one barrel.

A parallel arrangement is perhaps the better way to approach the problem of purging more than one barrel at a time under the current purging conditions. Exhaust gas temperatures would stay below the temperature limit of the Tygon[®] tubing, and hydrogen and oxygen concentrations would not be amplified. The overall flow rate of carbon dioxide would need to be increased, however, to keep the gas flow rates through each barrel similar to the flow rate used to purge just one barrel at a time.

During the purge period, carbon dioxide is supplied to the barrel in excess, so that the consumption of carbon dioxide within the barrel is much less than the flow rate of carbon dioxide through the barrel. This excess flow serves to dilute the hydrogen and oxygen generated during the purge process, and helps to remove excess heat energy. If the flow of carbon dioxide were stopped to the barrel during the purge, it is speculated that the carbon dioxide already within the barrel could be quickly used up, resulting in a negative pressure in the barrel and a relative increase in the concentrations of hydrogen and oxygen. A negative pressure may also cause the backflow of gas from the vent line or air in-leakage through the bung threads. Such conditions may lead to an increased fire hazard. Also, the negative pressure may buckle the barrel and make further treatment more difficult. As the barrel treatment process stands now, operators will have to resist the temptation to reduce the flow of carbon dioxide to the barrel when the purge operation is underway in response to high barrel temperatures, and will have to maintain maximum carbon dioxide flow rates during the purge to minimize the risk of a hydrogen ignition.

Fermi Barrel Storage Hazards

The question has been asked whether there is a potential hazard in the way the Fermi barrels are stored on-site. Currently, the Fermi barrels are stored in unheated storage containers. Could the high temperatures and hydrogen evolution witnessed during the carbon dioxide purge step occur in any of the stored Fermi barrels as a result of changing environmental conditions, especially on hot summer days? Under such circumstances, the principle hazards would be the generation of hydrogen and the development of excess barrel pressure, which could potentially lead to hydrogen leaks and the development of a potentially hazardous atmosphere inside a barrel storage unit.

For hydrogen to evolve, the water stored in the form of hydrates would need to be released, and then react with residual sodium metal. For a significant hazard to exist, oxygen and heat would also need to be present in sufficient amounts to push the hydrogen into the flammable zone and then initiate a hydrogen/oxygen reaction. The initiating chemical reactions in these circumstances would be the direct decomposition of the hydrate species in response to increased environmental temperatures, as opposed to the triggering conditions caused by the reaction of carbon dioxide with sodium oxide and sodium peroxide. Hydrogen and heat could also be evolved from the direct in-leakage of liquid water, but such an event is extremely unlikely as long as the barrels are stored in closed storage containers, the storage containers are kept on dry ground, and the barrel bungs are on tight.

There are several factors that make the creation of hazardous conditions inside a barrel very unlikely during storage, even on hot summer days. First, air in-leakage past the barrel bungs is unlikely to lead to the creation of an oxygen-rich environment. As evidenced by the build-up of oxides and carbonate materials in **Figure 1**, sodium metal is a very good getter of oxygen. As air leaks into the barrels, the oxygen is consumed to form sodium oxide and sodium peroxide, leaving the nitrogen. Even with a continuous leak, oxygen will continue to become consumed until the oxide layers are so thick that oxygen cannot reach the sodium metal underneath. At that point, an air atmosphere may develop in the barrel, but the sodium metal is not readily available for further chemical reactions and is protected against reactions with water vapor.

Second, the sodium carbonate species that presumably exist in the surface layers decompose endothermically. That is, thermal energy must be supplied to power the decomposition reactions. As a result, the decomposition reactions will tend to suppress the temperature of the material as they decompose, helping to lower the temperature and slow down the decomposition reactions. With up to ten moles of water released for every mole of sodium carbonate hydrate decomposed, this effect, however, may be a small one.

Third, due to the presence of deep layers of sodium oxide (and perhaps sodium hydroxide) coating the residual sodium, it is relatively unlikely that the water released by the decomposition of the hydrates will come into contact with residual sodium. The oxide layers are not just a resistive barrier, but also a reactive one, and will consume water before it reaches the sodium surfaces (see Equations 8 and 9). Such chemical reactions will release heat but will not generate hydrogen.

So, given these factors, it is very unlikely that a hydrogen combustion event will occur in the Fermi barrels as a result of environmental changes during storage.

If all of these factors work against the generation of hydrogen while the barrels are in storage, how is it that hydrogen is so readily generated during the dry carbon dioxide purge step? There is much more sodium oxide and sodium peroxide present than sodium carbonate, and so much more heat is generated during the purge step than can be generated by the release of water from the hydrates and its

subsequent reaction with other chemical species in the barrel. According to the measured hydrogen readings from the treatment of the first six barrels, only about 18 to 36 grams of water reacted with residual sodium in each barrel to form hydrogen during the purge step, or about 1 to 2 moles of water. Such small amounts of water reacting with sodium would not be enough to raise the temperature of the barrels up to the high temperatures witnessed during the purge step. The conversion of sodium oxide to sodium carbonate is very energetic (almost twice as energetic as the sodium/water reaction), and given the unlimited supply of carbon dioxide in the barrel atmosphere, would provide enough heat energy to release all of the stored water very quickly.

The conversion of sodium oxide to sodium carbonate also causes large volume changes in the surface layers, such that the protective surface covering the residual sodium would be disrupted. The molar volumes of sodium oxide, sodium hydroxide, and sodium carbonate are 27.3, 18.7, and 41.9 cm³/mole, respectively. While the reaction of a small amount of water with a large amount of sodium oxide is not likely to significantly disrupt the surface layers covering all of the residual sodium in the case of stored barrels, the protective surface layers are significantly more disrupted by the complete conversion of all sodium oxide into sodium carbonate, which has a volume expansion factor of at least 1.53 (see Equations 1 and 2). It is believed that this surface layer disruption, coupled with the rapid release of stored water, is giving rise to the measured hydrogen readings, by allowing the released water vapor to react directly with unprotected residual sodium. Figure 2 shows an example of how much the larger clumps and particles inside a Fermi barrel can be disrupted by changes in molar volume.

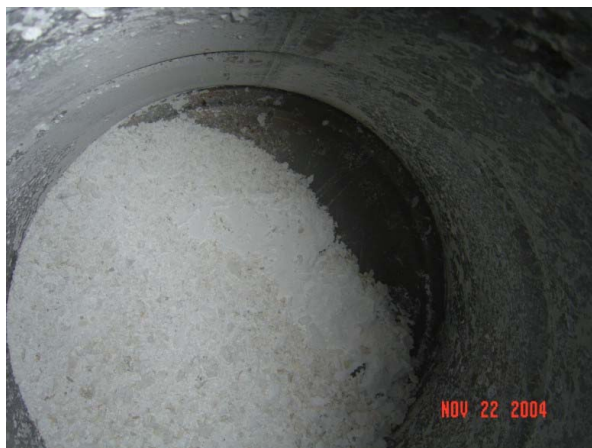


Figure 2: Inside of Fermi Barrel #ANL1174 after treatment

The material shown in Figure 2 is approximately 70 wt% sodium bicarbonate, with the balance being sodium carbonate. It is not the same transformation that is discussed above, but it does show that the material in the drum eventually disintegrated into a powder, largely due to molar volume changes in the material and an increase in material porosity.

Without a significant source of carbon dioxide, the initiating reactions that occur rapidly during the dry carbon dioxide purge would not happen, and the response of the drums to environmental temperature changes would be moot. Therefore, there is no perceived risk in the way the Fermi barrels are currently stored.

Analysis of External Hazards

The Fermi barrel surfaces can get quite hot and are a hazard to workers. Workers should use gloves whenever handling the hot barrels, and should refrain from contacting the barrels during the peak reaction period.

Of the six barrels treated so far with dry carbon dioxide, four got hot enough on the bottom of the barrels to smoke. In one case, the smoke was thick enough to cause a haze to build up in the upper levels of the Sodium Boiler Building. No flames were observed. Scorching was evident on the bottom of barrel #ANL11116, but the other barrels showed no sign of scorching or changes in the barrel paint.

As a precaution, all combustible materials should be kept away from the barrel surfaces during the purge step. A fire watch should be designated for the duration of the purge step, and an all-purpose fire extinguisher made available to the fire watch.

Hazard Mitigation Strategies

The real sources of the hazards associated with the dry carbon dioxide purge are the chemical reactions of carbon dioxide with sodium oxide and presumably sodium peroxide. These hazards occur because the supply of carbon dioxide is unlimited, and the reactions, once started, cannot be safely stopped without creating additional hazards. The only thing limiting the reaction rate at the sodium oxide surfaces is the diffusion rate of carbon dioxide through the sodium carbonate surface layers. As a result, operators must wait for the chemical reactions to finish before terminating the dry carbon dioxide purge.

The dry carbon dioxide purge can be made safer by making the supply of carbon dioxide the limiting factor, rather than allowing the reaction rates to be controlled at the oxide layer surfaces. This can be accomplished by down-blending the carbon dioxide with an inert gas such as nitrogen or argon. With carbon dioxide as the limiting reactant, the reaction rate can be slowed down and controlled by adjusting the concentration of carbon dioxide in the inlet gas. Slowing down the reaction rate will reduce the temperature of the barrels during the purge and will allow more time for the evolved thermal energy to dissipate.

With independent controls on the flow of inert gas and carbon dioxide, the chemical reactions may be started and stopped at will. To increase the reaction rate, increase the flow of carbon dioxide, and to decrease or stop the chemical reactions, slow or stop the flow of carbon dioxide while maintaining the flow of the inert gas. This adds an element of control that is not present in the current purge process, and would allow the operator to stop the purge altogether at any time, if safety or operational conditions dictate.

Under a carbon dioxide-limited condition, the barrels being purged could be arranged in a serial fashion, just as the barrels are arranged for the humid carbon dioxide treatment step. The problems of increasing heat load and amplification of hydrogen and oxygen concentrations are not present under carbon dioxide-limited conditions, because the supply of carbon dioxide limits the amount of heat generated throughout the serial chain, and indirectly limits the evolution of hydrogen by limiting the temperature increases. The presence of the inert gas also dilutes any hydrogen or oxygen generated and thus significantly reduces the chances of creating a combustible atmosphere inside the barrels.

As an added precaution, to help prevent the backflow of air into the barrels during the dry carbon dioxide purge, the use of a check valve or back-pressure regulating device should be investigated for use

on the exhaust line. Although a negative effect of preventing backflow may be the partial collapse of a barrel, such a collapse is more of a treatment risk than a safety risk. Given the choice between a partial collapse of a barrel due to a negative pressure, and the backflow of air into a hot drum, the partial collapse of a drum is preferred. Under negative pressure conditions, the check valve or back-pressure regulating device would close, and limit the flow of gas from the vent line back into the barrels being treated. Installation of such a device should be considered if the pressure drop created by the fitting does not significantly impact the treatment operation.

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