

Technical Information on the Carbonation of the EBR-II Reactor

Summary Report Part 1: Laboratory
Experiments and Application to EBR-II
Secondary Sodium System

Steven R. Sherman

April 2005



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ABSTRACT

Residual sodium is defined as sodium metal that remains behind in pipes, vessels, and tanks after the bulk sodium metal has been melted and drained from such components. The residual sodium has the same chemical properties as bulk sodium, and differs from bulk sodium only in the thickness of the sodium deposit. Typically, sodium is considered residual when the thickness of the deposit is less than 5-6 cm. This residual sodium must be removed or deactivated when a pipe, vessel, system, or entire reactor is permanently taken out of service, in order to make the component or system safer and/or to comply with decommissioning and disposal regulations.

As an alternative to the established residual sodium deactivation techniques (steam-and-nitrogen, wet vapor nitrogen, etc.), a technique involving the use of moisture and carbon dioxide has been developed. With this technique, sodium metal is converted into sodium bicarbonate by reacting it with humid carbon dioxide. Hydrogen is emitted as a by-product.

This technique was first developed in the laboratory by exposing sodium samples to humidified carbon dioxide under controlled conditions, and then demonstrated on a larger scale by treating residual sodium within the Experimental Breeder Reactor II (EBR-II) secondary cooling system, followed by the primary cooling system, respectively. The EBR-II facility is located at the Idaho National Laboratory (INL) in southeastern Idaho, U.S.A.

This report is Part 1 of a two-part report. It is divided into three sections. The first section describes the chemistry of carbon dioxide-water-sodium reactions. The second section covers the laboratory experiments that were conducted in order to develop the residual sodium deactivation process. The third section discusses the application of the deactivation process to the treatment of residual sodium within the Experimental Breeder Reactor II (EBR-II) Secondary Sodium Cooling System. Part 2 of the report, under separate cover, describes the application of the technique to residual sodium treatment within the EBR-II primary sodium cooling system and related systems.

CONTENTS

ABSTRACT.....	iii
1. INTRODUCTION.....	1
2. SODIUM CHEMISTRY.....	5
2.1 Surface Layer Formation.....	5
2.2 Deactivation Process	7
3. EXPERIMENT.....	8
3.1 Materials.....	8
3.2 Equipment	8
3.3 Sample Preparation and Chamber Loading	11
3.4 Conduct of Experiment	14
3.5 Results and Analysis.....	16
3.6 Experimental Conclusions	23
4. EBR-II SECONDARY SODIUM SYSTEM.....	25
4.1 EBR-II Plant Closure Project.....	25
4.2 EBR-II Secondary Cooling System Description	26
4.3 Carbon Dioxide Humidification Cart	28
4.4 Secondary Sodium Cooling System Preparation.....	30
4.5 Deactivation of the Secondary Sodium Cooling System	30
4.5.1 Phase One Treatment.....	31
4.5.2 Phase Two Treatment.....	32
4.5.3 Visual Inspection Results	34
4.5.4 Chemical Analysis of the Carbonate Layer	34
4.6 Current State and Future Treatment Options	35

FIGURES

1. Measured sample temperature, gauge pressure, and exhaust hydrogen concentration for sodium exposed to mixture of steam and nitrogen.	3
2. Top cover of test chamber showing entry ports and thermocouple connections.	9
3. Schematic of water column, test chamber and supporting equipment.	9
4. Photograph of water column, test chamber and instrument panel. SRETF means “Sodium Reaction Experimental Test Facility.”	10
5. Kimex [®] beakers of various heights with metallic sodium. The white layer is sodium oxide.	11
6. Kimex [®] graduated cylinders filled with sodium.....	12
7. Metal Trays C3, D3, E3 from left to right.	13
8. Metal Trays F3 and B3 from left to right.....	14
9. Exposure time of Kimex [®] sodium samples in test chamber.	15
10. Measured hydrogen concentration in vol% for time interval 0 to 150 days in the test chamber.	16
11. Sample C2 after 84 days of exposure.....	17
12. Tray B3 after 29 days of exposure (shown in vertical alignment). The wire in the center is a thermocouple.....	18
13. Sample B2 after 90 days exposure.	20
14. Sample E2 after 123 days exposure.	20
15. NaHCO ₃ layer depth versus sodium depth reacted for Sample A2 at ambient conditions.....	21
16. Reaction rate versus sodium bicarbonate layer depth, based on data in Table 3.	22
17. Measured sodium reaction rate versus inverse sodium bicarbonate layer thickness.	23
18. EBR-II Secondary Sodium Cooling System, as modified for residual sodium treatment.....	27

19.	Schematic of carbon dioxide humidification cart.....	29
20.	Carbon dioxide humidification cart, from two vantage points.....	29
21.	Measured hydrogen concentration during Phase One treatment of the EBR-II Secondary Sodium Cooling System.....	31
22.	Measured hydrogen concentration during initial stage of Phase Two treatment.	32
23.	Measured hydrogen concentration during final stage of Phase Two treatment.	33

TABLES

1.	Kimex [®] Container Sodium Sample Dimensions	12
2.	Metal Tray Slit Dimensions	13
3.	Measured Sodium Reaction Depth and Sodium Bicarbonate Layer Depth.....	19
4.	EBR-II Secondary Sodium Cooling System Valve Configuration, by Pathway.....	28
5.	Phase One Treatment Times and Calculated Sodium Amounts Treated	32

Technical Information on the Carbonation of the EBR-II Reactor

Summary Report Part 1: Laboratory Experiments and Application To EBR-II Secondary Sodium System

1. INTRODUCTION

Sodium metal has been commonly used in liquid metal fast breeder reactor (LMFBR) systems as a heat transfer fluid because of its good technical characteristics (Foust 1972a), including a low melting point (97.81 °C), high boiling point (882.9 °C), a water-like viscosity (0.4519 cP at 200 °C), a high thermal conductivity (0.820 W/cm-K at 200 °C), and a high thermal heat capacity (1.34 J/g-K at 200 °C). Also, it is less chemically hazardous than other metals such as sodium-potassium alloy (NaK), and so allows for easier system maintenance activities.

Residual sodium is defined as the sodium metal remaining behind once the bulk sodium has been drained from these systems for reasons of system maintenance or decommissioning work. The residual sodium may either be in the form of a thin coating on vertical surfaces, or thicker pools in horizontal locations at the bottom of vessels, pipes, and other internal spaces. The residual sodium has the same chemical properties as bulk sodium, and differs from bulk sodium only in the thickness of the sodium deposit. Typically, sodium is considered residual when the thickness of the deposit is less than 5-6 cm. This residual sodium must be removed or deactivated when a pipe, vessel, system, or entire reactor is permanently taken out of service, in order to make the component or system safer and to comply with decommissioning and disposal regulations.

Physical removal of all accessible sodium is the best option, because it simply involves melting the sodium and allowing it to drain from the component. The sodium, once removed from the component, can be safely treated in a controlled setting. Not all residual sodium can be removed this way, however, because sodium wets metal components, and some sodium will remain. Still more can be removed by physically scraping internal surfaces where accessible, but not all locations can be reached with tools. Chemical deactivation of the residual sodium with a reactive liquid or gas is the only way to reach all exposed residual sodium within a component and convert it into a safer (and soluble) form.

The fastest way to deactivate residual sodium is to react it with an excess of liquid water. Water reacts with the residual sodium to form sodium hydroxide and hydrogen gas. The sodium hydroxide then dissolves into solution and can be easily flushed from the component being treated. This method is not recommended except under certain circumstances, because the water-sodium reaction is very rapid and exothermic, and can lead to high temperatures and pressures, uncontrolled release of caustic materials, and even hydrogen conflagrations and explosions under the right circumstances.

Water can be used to deactivate residual sodium safely, but only if the water is not available in unlimited amounts. The most commonly used methods for deactivating residual sodium are based on this principle. These methods are to expose residual sodium to steam and nitrogen, or water-saturated nitrogen at a controlled rate. The water in the treatment gas reacts with the residual sodium to form

sodium hydroxide (NaOH) and hydrogen. Less sodium reacts per unit time, and consequently less heat and hydrogen are generated, because the amount of water reacting at any one time is limited and is not available in excess. The nitrogen in the treatment gas dilutes the hydrogen generated and helps to exclude air from the system being treated. Once all of the residual sodium has been converted into sodium hydroxide and hydrogen is no longer generated, the system being treated is flushed with liquid water to dissolve the sodium hydroxide and remove it.

The technique of using steam and nitrogen to deactivate residual sodium is commonly used in the chemical industry. For instance, Safety-Kleen, Inc., an environmental services company in the United States of America, routinely uses steam and nitrogen to clean residual sodium from storage tanks and other systems, including two nearly empty 12,000-gallon sodium tanks that were once located at Argonne National Laboratory – West, in Idaho, U.S.A. Also, E.I. DuPont de Nemours, Inc., uses this technique to clean sodium rail cars once they have been drained of bulk sodium.

Steam and nitrogen have been used to clean nuclear systems containing residual sodium. In 1968, Atomics International, a Rockwell International company, deactivated the residual sodium in the primary heat transfer system at the Hallam Nuclear Power Facility, located south of Lincoln, Nebraska, U.S.A, using a steam-nitrogen mixture. DTE Energy Inc., at its nuclear site in Newport, Michigan, U.S.A., has used the technique in its on-going decommissioning work at the Fermi I facility, a sodium-cooled reactor that was permanently shutdown for decommissioning in 1972.

A modification of the steam and nitrogen technique was developed by Merrick Remediation Company, Inc., another environmental services firm based in the U.S. The technique, designed mainly for treating residual sodium in large vessels, uses water-saturated nitrogen to react residual sodium (Foust 1972a; Christophine, 1996, 1997). Water-saturated nitrogen is forced by pressure differential into the vessel being treated. Excess water vapor in the nitrogen stream is allowed to condense, so that small amounts of liquid water are present as well. The sodium hydroxide created by the water-sodium reaction is removed as an aqueous solution by suction, and the hydrogen gas is vented as a mixture of nitrogen and hydrogen.

Humidified nitrogen (saturated or sub-saturated) with a temperature range between ambient and 90 °C has been used at various times at the Hanford Site in Richland, Washington, U.S.A. and at Argonne National Laboratory to treat residual sodium on small parts and in simple tanks and containers. With humidified nitrogen, the sodium can remain solid or be converted to liquid sodium hydroxide while it is being treated, whereas with steam and nitrogen, the temperature of the system being treated is usually high enough to melt the sodium.

While these methods are effective at deactivating residual sodium, there are two disadvantages inherent in either technique. The first disadvantage is the instability of the reaction process. On a crude level, the deactivation reaction is controllable in that turning on the flow of steam or water-saturated nitrogen can start the reaction, and stopping the flow of steam or water-saturated nitrogen can stop the reaction. Depending upon system geometry, sometimes it is difficult to remove the sodium hydroxide as quickly as it is generated, and it can pool on top of the residual sodium. This can lead to sudden, uncontrolled water-sodium reactions that generate much heat and hydrogen at rates much faster than would be expected from the water available in the gas stream. Such uncontrolled excursions can create hazardous safety situations for workers and can damage equipment.

According to an unpublished report by the Hanford Engineering Development Laboratory at the Hanford Site, a water concentration gradient is established in the liquid layer between the surface of the residual sodium and the outer surface of the sodium hydroxide layer, with the highest concentration of water at the outer surface. If the layer is mechanically disturbed by the movement of hydrogen bubbles,

convection, mechanical agitation, etc., the sodium underneath the layer can suddenly be exposed to water-rich solution and would react violently with it. This causes sudden surges in chemical reactivity with rapid spikes in temperature, pressure, and hydrogen production. The instabilities are often preceded by an accumulation of water within the system being treated and fluctuations in the measured hydrogen concentration in the exhaust gas. An increased frequency of uncontrolled reaction excursions is correlated with increasing pool size. They discovered that the frequency of uncontrolled reactions could be reduced but not eliminated by increasing the temperature of the system being treated by 3-4 °C whenever the hydrogen concentration would begin to fluctuate, and by limiting the moisture concentration in the nitrogen to no more than 10 vol%.

Direct evidence of this unstable behavior has been measured in our laboratory. Inside an instrumented test chamber, 25 g of sodium metal were exposed to a mixture of steam and nitrogen flowing at a mass flow rate of 450 g/hour and 700 g/hour at 1 atm, respectively. The temperature of the steam-gas mixture was 83 °C. The temperature of the sodium sample was measured along with the chamber pressure and the concentration of hydrogen in the exhaust gas. Figure 1 shows that the temperature of the sodium sample varied widely between 83 and 435 °C. The temperature spikes were accompanied by surges in system pressure and hydrogen concentration. Larger surges than those measured may have occurred during the test, but the pressure instrumentation and control equipment limited the recorded pressures to no higher than +20.7 kPa-gauge.

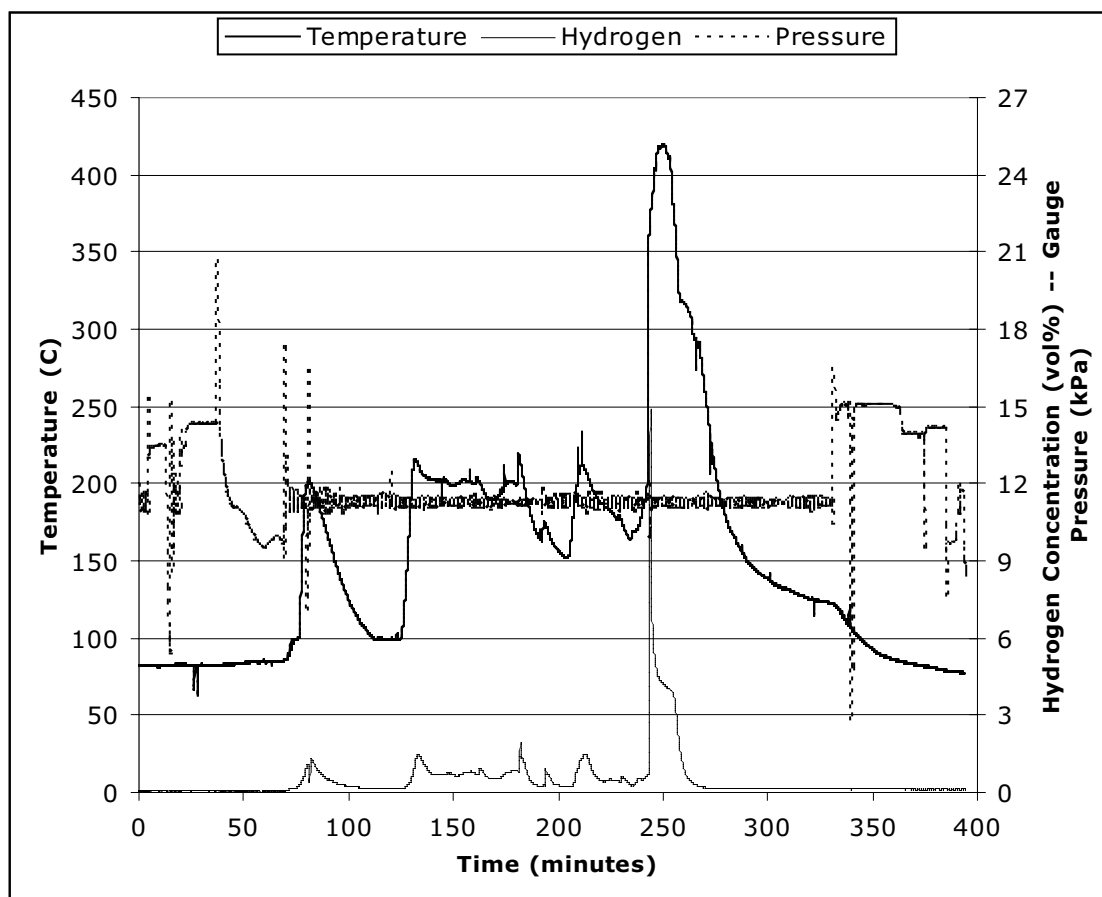


Figure 1. Measured sample temperature, gauge pressure, and exhaust hydrogen concentration for sodium exposed to mixture of steam and nitrogen.

The second disadvantage of using steam and nitrogen or humidified nitrogen to treat sodium is the creation of concentrated solutions of sodium hydroxide. Concentrated sodium hydroxide solutions are corrosive to equipment and hazardous to workers. Often sodium hydroxide solutions must be neutralized before disposal, which adds to the expense of the deactivation process and creates a larger volume of waste.

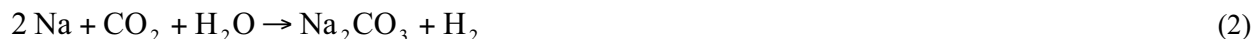
As an alternative to the established residual sodium deactivation techniques, there is another deactivation process that does not suffer from pressure and temperature instabilities and does not produce waste that normally requires neutralization. This process is the reaction of residual sodium with humidified carbon dioxide. In this process, humidified carbon dioxide is used to convert residual sodium into sodium bicarbonate and sodium carbonate in a two-step reaction process. The water vapor in the carbon dioxide first reacts with the residual sodium to form sodium hydroxide, and then the carbon dioxide reacts with the sodium hydroxide to convert it into sodium bicarbonate. Sodium carbonate may subsequently form from the degradation of sodium bicarbonate at higher temperatures, or by reacting with sodium hydroxide. The reaction products are solid, and pools of aqueous sodium hydroxide cannot form because of the rapid reaction of sodium hydroxide with carbon dioxide. The reaction products formed are porous, brittle, and are much less corrosive and toxic than sodium hydroxide.

This report is Part 1 of a two-part report. It is divided into three sections. The first section describes the chemistry of carbon dioxide-water-sodium reactions. The second section covers the laboratory experiments that were conducted in order to develop the deactivation process. The third section discusses the application of the deactivation process to the treatment of residual sodium within the Experimental Breeder Reactor II (EBR-II) secondary sodium system.

Part 2 of the report, under separate cover, will focus on the application of the humid carbon dioxide deactivation technique to the EBR-II primary sodium cooling system, including the EBR-II primary tank, the intermediate heat exchanger (IHX), and other ancillary EBR-II components. It will also include the application of the treatment technique to a new application, the deactivation of residual sodium within sodium waste barrels, in order to illustrate new safety findings and to contrast that experience with the deactivation of residual sodium in the laboratory and within the EBR-II secondary sodium system.

2. SODIUM CHEMISTRY

Sodium metal reacts with carbon dioxide and water to form sodium bicarbonate and/or sodium carbonate, depending upon the temperature and the availability of water and carbon dioxide. These chemical reactions are generally stated by Equations (1) and (2).

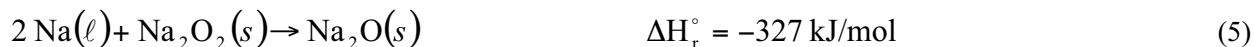


In Equation (1), sodium metal reacts with gaseous carbon dioxide and water to form sodium bicarbonate and hydrogen gas. In Equation (2), sodium metal reacts with carbon dioxide to form sodium carbonate and hydrogen gas. Though the reactions above are thermodynamically favorable, they do not proceed as written and follow multiple steps to reach their conclusion.

2.1 Surface Layer Formation

Depending upon the history of the sodium being treated, the sodium may be clean, or it may be coated with a surface layer. Inside well-maintained systems, clean sodium surfaces with little or no surface contamination of oxides, hydroxides, and carbonates can be expected. Such surfaces will appear silver-colored and metallic. For systems exposed to air under uncontrolled conditions, a substantial surface layer containing oxides, hydroxides, and carbonates can be expected. The surface layers form by a number of chemical mechanisms.

Sodium oxides can form on exposed sodium surfaces when the sodium is exposed to air or oxygen. Sodium oxide formation is shown in Equations (3)-(5).



In Equation (3), sodium metal reacts with oxygen to form sodium oxide. In Equation (4), sodium metal reacts with oxygen to form sodium peroxide. In Equation (5), sodium metal reacts with sodium peroxide to form sodium oxide. All three reactions are exothermic and spontaneous, but only Equation (3) will go forward to any great extent below 200 °C. Equation (4) will not occur in the presence of oxygen until temperatures rise to above 200-300 °C, and Equation (5) generally requires the sodium to be a liquid before it will go forward to a measurable extent (Addison 1984; Foust 1972b)

Sodium hydroxides on the surface of the sodium form by exposing the sodium or the surface layer of oxides to water. These reactions are shown in Equations (6)-(8).



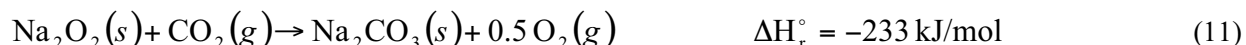


In Equation (6), sodium reacts with water to form sodium hydroxide and hydrogen gas. In Equation (7), sodium oxide reacts with water to form sodium hydroxide with no gas evolution. Equation (8) shows a reaction of sodium peroxide with water to form sodium hydroxide and oxygen. All are exothermic and will occur spontaneously.

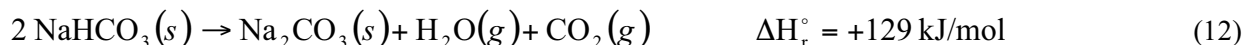
Sodium carbonates can also form on the surface of the sodium, but only if the sodium has been exposed to humid air containing carbon dioxide. Sodium hydroxide must first be present. The carbon dioxide can then react with it to form sodium bicarbonate, as shown in Equation (9).



Sodium carbonate will form if there are quantities of sodium oxide present, as shown in Equations (10) and (11).

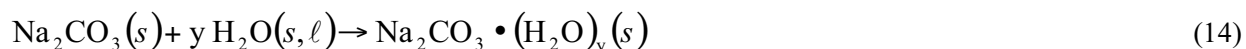
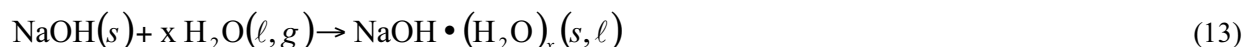


In Equation (10), sodium oxide reacts with carbon dioxide to form sodium carbonate. In Equation (11), sodium peroxide reacts with carbon dioxide to form sodium carbonate and oxygen. If the temperature of the system rises above 50-60 °C when there is sodium bicarbonate present, then sodium carbonate can form by the degradation of sodium bicarbonate, as shown in Equation (12).

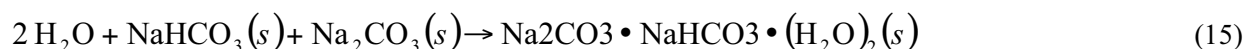


In Equation (12), sodium bicarbonate decomposes to form sodium carbonate, water, and carbon dioxide. This is the chemical reaction that occurs during baking when sodium bicarbonate (baking soda) is used as a food ingredient.

If the humidity in the air is high enough, then the surface layer may also store water in the form of sodium hydroxide hydrates or sodium carbonate hydrates. Sodium hydroxide monohydrate is a solid at ambient conditions, but sodium hydroxide dihydrate and higher hydrates are liquid at room temperature. Sodium carbonate can form a monohydrate, a heptahydrate, or a decahydrate, all of which are solid at room temperature. Unlike with sodium hydroxide hydrates, the water molecules are not so strongly held by the higher carbonate hydrate species, and the sodium carbonate hydrates decompose at 25, 32, and 100 °C, with no sodium carbonate hydrate present above 100 °C. These hydration reactions are shown in Equations (13) and (14).



In Equation (13), x can vary between 1 and infinity, whereas in Equation (14), y can have a value of 1, 7, or 10, depending upon the humidity and moisture conditions. Another sodium carbonate hydrate may also form, depending upon the initiating conditions. This hydrate is sodium sesquicarbonate (trona). The formation reaction is shown in Equation (15). This sodium carbonate hydrate decomposes at 77 °C.



2.2 Deactivation Process

Regardless of whether the sodium is clean or has a substantial surface layer, the deactivation process proceeds in the same manner. The residual sodium is exposed to a flowing stream of humidified carbon dioxide. The water vapor in the carbon dioxide reacts with sodium metal to form sodium hydroxide, as seen in Equation (6). The carbon dioxide, available in excess, reacts with the sodium hydroxide to form sodium bicarbonate, as shown in Equation (9). The carbon dioxide is then used as a carrier gas to dilute the hydrogen generated and to remove the heat of reaction as it flows out of the system being treated.

If there is a significant amount of sodium oxide on the sodium surface, then sodium carbonate may also form by the reaction of the carbon dioxide with sodium oxide, as seen in Equations (10) and (11). If the surface layer completely obscures the residual sodium underneath, then this side reaction of carbon dioxide with sodium hydroxide will predominate until the surface layer of sodium oxide is converted into sodium carbonate, and the integrity of the surface layer is disturbed by the large increase in molar volume, due to the transformation of sodium oxide into sodium carbonate. At that point, water vapor can reach the sodium underneath the layer and begin to convert it into sodium hydroxide. The sodium bicarbonate layer that is formed is porous and allows for the penetration of humid carbon dioxide through the layer.

3. EXPERIMENT

Laboratory experiments were performed in order to study the effects of humidified carbon dioxide on samples of sodium metal. The goals of the experiments were to determine the stability of the deactivation process in regard to sudden temperature and pressure changes and changes in the hydrogen generation rate, confirm the chemical composition of the sodium bicarbonate layer, observe the morphology and measure the density of the sodium bicarbonate layer, and determine the deactivation rate as a function of sodium bicarbonate layer thickness and moisture input rates.

In these experiments, samples of sodium metal were placed into a test chamber and exposed to a continuous flow of humidified carbon dioxide. The concentration of hydrogen and oxygen in the exhaust gas were measured and recorded. The growth of the sodium bicarbonate layer on the samples was observed over time and measurements were taken on the growth rate of the layer versus the consumption rates of the sodium samples. Observations were recorded concerning the morphology of the sodium bicarbonate layer and samples were taken of the layer for chemical analysis. This section presents a summary of the experimental equipment, procedures, and experimental results and analyses.

3.1 Materials

The sodium metal used for the samples was obtained in 0.454 kg cans from Fischer Scientific International, Inc., and contained less than 0.002 wt% chlorides and 0.001 wt% iron. The 99.99% pure carbon dioxide was supplied in liquid form from AGA Gases, Inc. The distilled water used to humidify the carbon dioxide was obtained from the Argonne National Laboratory Chemistry Division.

3.2 Equipment

The test chamber used for the experiment was constructed of carbon steel and measured 59.01 cm in diameter, 62.38 cm in height, and had an internal volume of 0.1709 m³. It was covered with a stainless steel plate that had six entry ports. Each entry port was instrumented with four thermocouples that could be used to monitor the temperature of individual samples placed beneath each entry port. Figure 2 shows the top of the test chamber cover plate.

The test system consists of a carbon dioxide dewar, a water column, the test chamber described above, a gas analysis cabinet, and an assortment of valves and instruments. A photograph of the test chamber is shown in Figure 2. A schematic of the experimental equipment is shown in Figure 3. A photograph of the experimental equipment is shown in Figure 4.

Humidified carbon dioxide was supplied to the test chamber by bubbling it through a water column that was connected to the test chamber. The water column was constructed of a clear acrylic pipe measuring 243 cm long and 9.53 cm in diameter. The water level in the pipe was maintained at approximately 195 cm above the bottom of the pipe. Carbon dioxide was introduced into the water column through a porous alumina filter stone at the bottom of the column. A Panametrics #MMS35-321-1-100 w/M2LR probe moisture monitor was connected to the gas space above the water level in the column and was used to measure the moisture content of the humidified carbon dioxide. The water column was very efficient and was able to humidify the carbon dioxide to 99% relative humidity.

To provide carbon dioxide to the test chamber, carbon dioxide was supplied from the dewar at a pressure of +70 kPa-gauge. Once the line pressure was established, a mass flow controller was used to more precisely control the gas flow rate. A pressure controller was used on the water column to maintain a pressure of +28 kPa-gauge in the water column gas space. A pressure controller was also used on the

gas exhaust outlet line of the test chamber to maintain a test chamber pressure of +1.25-3.75 kPa-gauge. Pressure controllers were used instead of back-pressure regulators for the test chamber because they could be more precisely monitored by computer.

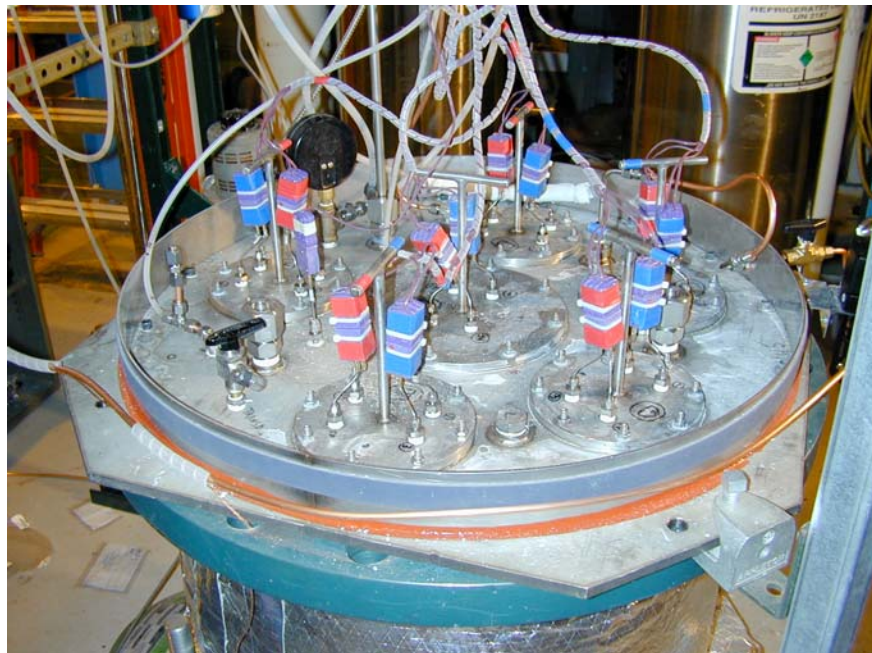


Figure 2. Top cover of test chamber showing entry ports and thermocouple connections.

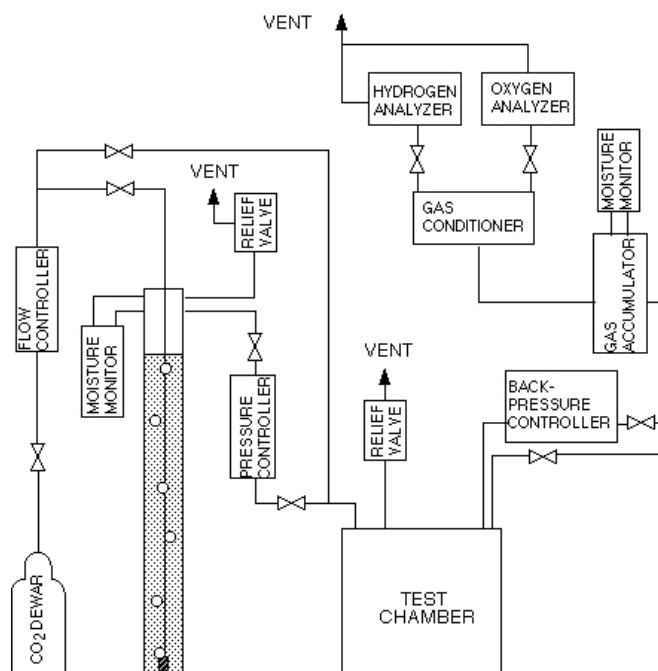


Figure 3. Schematic of water column, test chamber and supporting equipment.

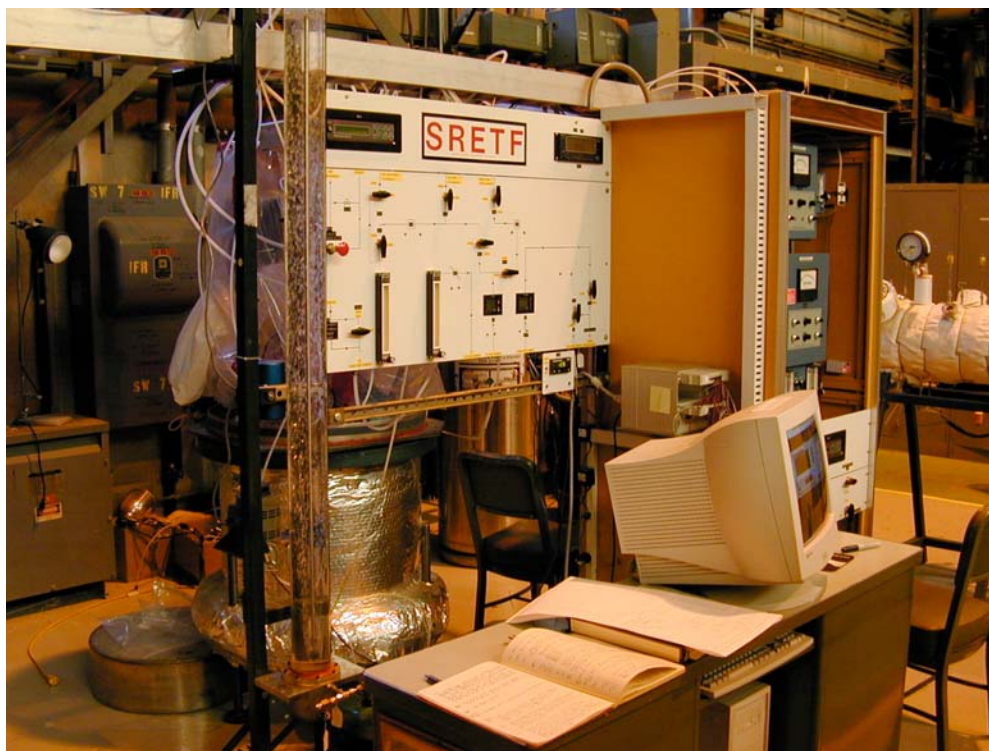


Figure 4. Photograph of water column, test chamber and instrument panel. SRETF means “Sodium Reaction Experimental Test Facility.”

Instrumentation for measuring the relative humidity, oxygen concentration, and hydrogen concentration in the test chamber exhaust gas was placed after the test chamber pressure controller on the exhaust line. Due to the flow rate requirements of the moisture monitor, a ballast tank or gas accumulator was used to provide enough gas volume so that the moisture probe sampling system would not disturb the pressure controller. The moisture monitor used here was the same kind as the one used to measure the humidity of the humidified carbon dioxide from the water column. Following the gas accumulator, a Clean Air Engineering Express SGC-4000 sample gas conditioner was used to remove moisture from the sampled exhaust gas stream prior to performing the oxygen and hydrogen concentration measurements. Moisture removal was accomplished by cooling the gas sample stream to about 1-4 °C, and collecting the condensate. A Teledyne Analytical Instruments #326RB oxygen monitor was used to measure the oxygen concentration in the gas sample stream and was set to measure in the mid-range of 0 to 1 vol%. A Teledyne Analytical Instruments #235B thermal conductivity analyzer was used to measure the hydrogen concentration in the gas sample stream. It was set to measure in the mid-range of 0 to 5 vol%.

The water column, the test chamber, and the gas lines were equipped with electrical resistance heaters, so that the temperature of the water column and test chamber could be changed. The lower temperature limit of the test equipment was established at ambient temperature, and the upper temperature limit was established at approximately 45 °C, which was the upper safe temperature limit for the instrumentation electronics. At all times, the test chamber temperature was maintained at +5 °C relative to the temperature of the water in the water column in order to avoid moisture condensation inside the test chamber.

All data measured by the laboratory instruments was recorded on a personal computer using Labview 6i software. Labview software is manufactured by National Instruments, Inc.

3.3 Sample Preparation and Chamber Loading

Kimex[®] graduated cylinders and flasks were used to contain the metallic sodium samples. Glass containers were used because it allowed for non-destructive measurement of the sodium height and the sodium bicarbonate layer thickness over time.

The sodium samples were prepared in an argon-purged glove box in the following manner. A mass of solid sodium from a standard commercial container (e.g., 0.454 kg can) was sliced into small pieces, which were then placed into an appropriately sized stainless steel beaker. The stainless steel beaker containing the solid sodium pieces and a Kimex[®] sample holder (e.g., beaker or graduated cylinder) were placed onto an electric hot plate and heated until the sodium in the stainless steel beaker had completely melted. The molten sodium was then poured into the Kimex[®] sample holder. After pouring the sodium sample, the electric hot plate was turned off and the sodium sample was allowed to cool to room temperature while still on the hot plate. After cooling, the sodium sample was placed into an argon-filled sealable plastic bag in preparation for removal from the glove box and transferal to the test chamber. Figures 5 and 6 show Kimex[®] beakers and cylinders that had been prepared using this procedure. Since the the glove box atmosphere was not oxygen-free and contained up to 1.5 vol% oxygen at times, the formation of a sodium oxide (white) layer on top of the sodium samples could not be prevented.



Figure 5. Kimex[®] beakers of various heights with metallic sodium. The white layer is sodium oxide.



Figure 6. Kimex[®] graduated cylinders filled with sodium.

The dimensions of the sodium samples varied between 1.27 cm and 6.50 cm in diameter and between 1.27 cm and 22.9 cm in sodium depth. Table 1 shows the sample name, sample diameter, sodium depth, and container depth for each sample. The difference between the container depth and sodium depth is the height of sample container not occupied by sodium metal.

Table 1. Kimex[®] Container Sodium Sample Dimensions

Sample Name	Diameter (cm)	Sodium Height (cm)	Container Height (cm)
A2	4.75	22.9	37.5
B1	6.51	2.54	2.54
B2	1.95	10.2	10.2
C1	6.51	3.81	3.81
C2	2.54	10.2	10.2
D1	6.51	5.08	5.08
D2	3.49	10.2	10.2
E1	6.51	7.62	7.62
E2	6.51	10.2	10.2
F1	6.51	1.27	1.27

In addition to the preparation of samples within Kimex[®] beakers and cylinders, five custom-made stainless steel (SS304) trays having the dimensions of 20.32 cm length, 3.18 cm width, and 1.27 cm height were also filled with sodium. Stainless steel plates having variously sized slits cut into them were bolted on top of the trays to simulate the behavior of sodium within restricted spaces and cracks. The slit dimensions are given in Table 2. The plates were not welded around the edges, and so there was not an airtight seal between the flat plate surface and the open edge of the trays. Top views of the sample trays can be seen in Figures 7 and 8.

Table 2. Metal Tray Slit Dimensions

Sample Name	Sodium Depth (cm)	Slit Height (cm)	Slit Width (cm)
B3	1.11	1.27	2.86
C3	1.11	2.54	2.86
D3	1.11	20.0	0.64
E3	1.11	20.0	1.27
F3	1.11	0.64	2.86



Figure 7. Metal Trays C3, D3, E3 from left to right.



Figure 8. Metal Trays F3 and B3 from left to right.

The following procedure was used to load the sodium samples into the test chamber. The test chamber was initially closed and purged with dry carbon dioxide. While this purge was taking place, a plastic glove bag with 4 glove ports was erected over the top cover of the test chamber. When the measured oxygen concentration inside the test chamber fell below 2.0 vol%, the sealable plastic bags containing the sodium samples were moved from the argon glove box to the test chamber cover, along with any required tools. The glove bag was then sealed to the top of the test chamber and purged with dry carbon dioxide. When the measured oxygen concentration in the glove bag fell below 2.0 vol%, the samples were removed from the sealable plastic bags. Thermocouples were pressed into the top of each sodium sample. Then the ports in the test chamber were opened and the samples were placed inside the test chamber. The ports were then sealed. The glove bag remained in place during the execution of the experiments.

3.4 Conduct of Experiment

All samples described above were placed into the test chamber and were exposed to humidified carbon dioxide for periods of time between 29 days and 219 days. Kimex[®] containers were placed in the chamber in a horizontal orientation, while the metal trays were placed in the sample in a vertical orientation. Figure 9 shows the exposure times of the samples placed into Kimex[®] containers (Samples A2, B1, B2, C1, C2, D1, D2, E1, E2, F1). The samples in the metal trays (Samples B3, C3, D3, E3, F3) were all uniformly exposed for a period of 29 days. In the figure the horizontal line at Day 16 shows where the flow rate of the humidified carbon dioxide was increased from 0.4 standard liters per minute to 0.8 standard liters per minute. The second horizontal line at Day 154 shows where the temperature of the water column was increased from ambient temperature (24-27 °C) to a set point of 40 °C. When the

water column was at ambient temperature, the temperature of the test chamber was maintained between 34 and 38 °C to prevent moisture condensation. When the water column temperature was increased to 40 °C, the test chamber temperature was increased to between 54 and 60 °C, also to prevent moisture condensation inside the chamber. Sample A2 was started at Day 61 and ended at day 280, and so the vertical bar for this sample does not align with the rest of the samples.

The samples were periodically removed from the chamber and examined for changes in sodium depth, sodium bicarbonate layer depth, and for cracks and other changes in the sample containers. The sample removal procedure was as follows. The test chamber gas was switched from humidified carbon dioxide to dry carbon dioxide. The glove bag above the test chamber was purged with dry carbon dioxide until the oxygen concentration in the glove bag fell below 2.0 vol%. The samples were removed from the test chamber and were measured and photographed, using the cover of the test chamber as a work table. After taking measurements and photographs of a particular sample, the sample was either loaded back into the chamber, or was removed from the experiment. Once all of the samples had been examined, the test chamber was sealed, and the flow of humidified carbon dioxide was re-started to resume the experiment.

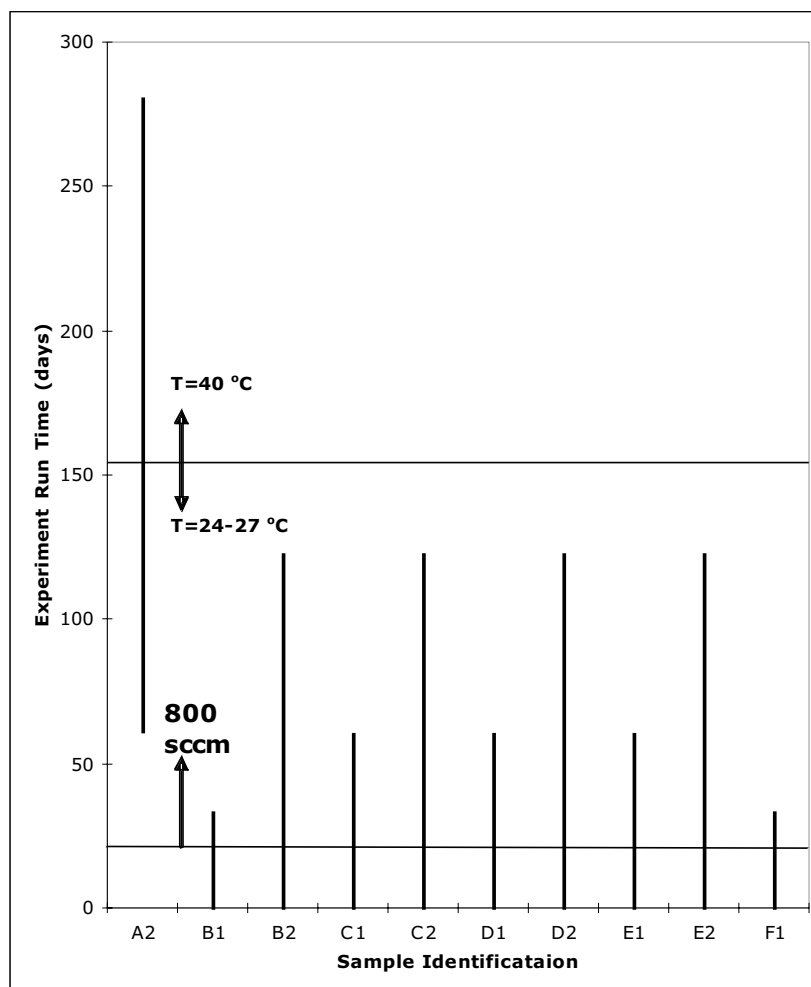


Figure 9. Exposure time of Kimex[®] sodium samples in test chamber.

3.5 Results and Analysis

During the experiment, no unstable temperature or pressure behavior was observed in the test chamber. At no time did the measured sample temperatures exceed the atmospheric temperature inside the test chamber, and no excess pressure changes were detected. Figure 10 shows the measured hydrogen concentration over the experiment time interval 0 to 150 days (beyond 150 days, the measured hydrogen concentration was very low). At no time did the measured hydrogen concentration exceed the safety threshold of 4 vol%. The sharp drops in measured hydrogen concentration below 0.2 vol% correspond to times when the flow of humidified carbon dioxide was stopped in order to examine sodium samples.

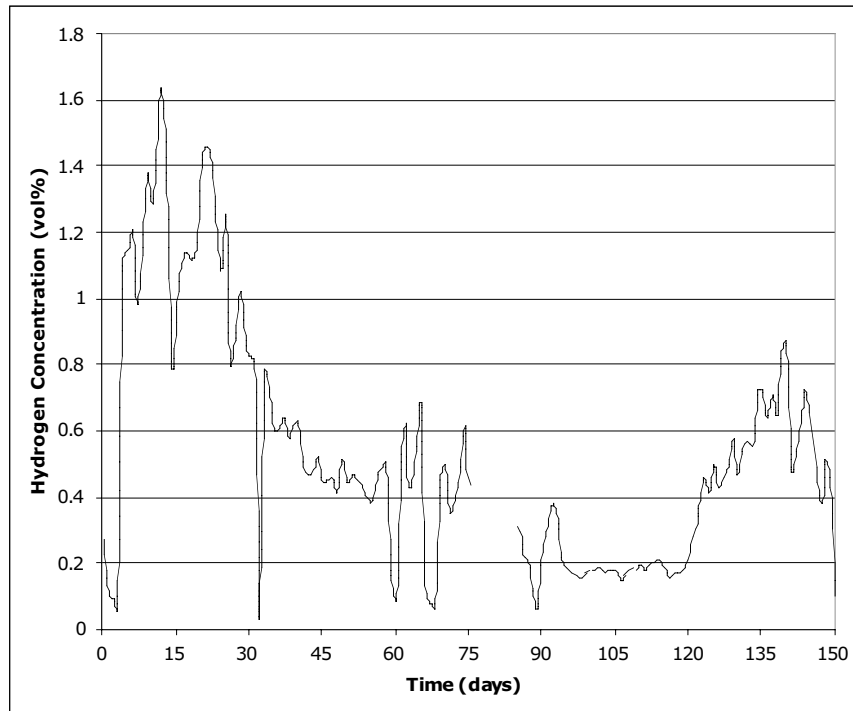


Figure 10. Measured hydrogen concentration in vol% for time interval 0 to 150 days in the test chamber.

As the humidified carbon dioxide reacted with the sodium samples, a layer of white material accumulated on the exposed surfaces of the sodium. The material that formed was solid and had some structural coherence, but did not have much mechanical strength and crumbled readily into a powder when disturbed. The material was porous and had a low packing fraction. Evidence of this physical behavior is seen in Figure 11, which shows a layer grown high enough to over flow the sample container.

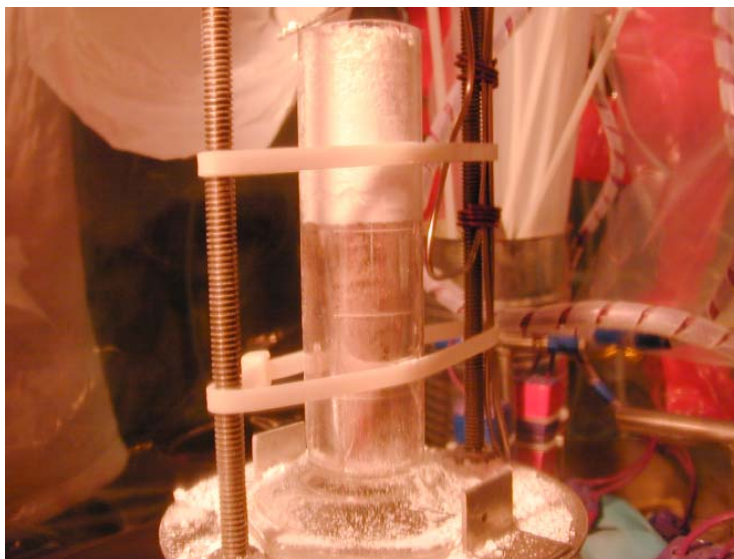


Figure 11. Sample C2 after 84 days of exposure.

Five chemical samples were taken of the layer from various sodium samples and were analyzed by X-ray diffraction and standard acid-base titration with 0.1 M hydrochloric acid. The X-ray diffraction tests showed that, qualitatively, the layer was composed entirely of sodium bicarbonate, NaHCO_3 . By titration, the chemical samples were found to be 91 ± 3 wt% sodium bicarbonate and 4 ± 2 wt% sodium carbonate. The identity of the balance of the mass was not identified in the chemical tests, and it is possible that there is no other chemical constituent present, since the sum of the two measurements is statistically indistinguishable from 100 wt%.

No quantitative data was obtained from the exposure of the sodium samples in the metal trays, but physical observation of the metal tray samples (B3 through F3) after the first 29 days of test chamber operation showed that the sodium bicarbonate layer is compressible, is less dense than sodium, and has some mechanical strength. Figure 12 shows the damage that has occurred to the stainless steel cover on Sample B3. The metal cover plate was not welded around the edges, and humidity was able to penetrate all along the edges of the plate where it contacted the tray. Subsequent reaction and expansion of the layer pushed out the plate and bent it outward, except where it is bolted in place. Similar results were obtained for all of the other stainless steel tray samples too. A destructive examination of one of the trays showed that all of the sodium had been consumed during the treatment period. Although no information was obtained about how easy it is to treat sodium through predefined cracks, seams, or narrow spaces, it was useful to see how the expansion of the sodium bicarbonate layer can create mechanical stresses.

Quantitative data could be obtained on the expansion of the sodium bicarbonate layer from the Kimex[®] samples, and the observations recorded on sodium depth reacted and sodium bicarbonate layer height are shown in Table 3.



Figure 12. Tray B3 after 29 days of exposure (shown in vertical alignment). The wire in the center is a thermocouple.

According to the observations made in the laboratory and the information recorded in the table, the sodium bicarbonate layer is less dense than the metallic sodium. The sodium undergoes an increase in volume when it is converted into sodium bicarbonate. It is this volume increase that caused the sample containers B2, C1, D1, E1 and E2 to break during the test and that deformed all of the cover plates on samples B3, C3, D3, E3, and F3. Figures 13 and 14 show Sample B2 after 90 days of exposure and Sample E2 after 123 days exposure. The expansion of the bicarbonate material caused the Kimex[®] containers to crack and split longitudinally. The cracks exposed unreacted sodium metal, and crack growth was accelerated by the growth of more sodium bicarbonate at the crack openings.

Table 3. Measured Sodium Reaction Depth and Sodium Bicarbonate Layer Depth

Sample	Time (days)	Na Depth Reacted (cm)	NaHCO ₃ Layer Depth (cm)
A2 (at 24-27 °C)	0	0.00	0.00
	9	0.65	3.80
	29	1.45	7.60
	62	2.40	12.2
	91	2.90	14.5
A2 (at 40 °C)	125	3.80	19.1
	153	4.75	20.6
	181	5.25	19.8
	219	5.50	21.0
B1	0	0.00	0.00
	33	2.50	6.40
B2	0	0.00	0.00
	33	2.20	2.90
	61	3.80	3.80
	90	5.10	5.10
	123	-- fractured --	
C1	0	0.00	0.00
	33	2.55	5.10
	61	-- fractured --	
C2	0	0.00	0.00
	33	2.55	3.30
	61	3.80	4.45
	90	4.45	4.45
	123	5.40	6.35
D1	0	0.00	0.00
	33	2.70	6.35
	61	-- fractured --	
D2	0	0.00	0.00
	33	2.55	2.85
	61	3.80	5.10
	90	4.75	5.70
	123	5.70	6.65
E1	0	0.00	0.00
	33	2.55	5.10
	61	-- fractured --	
E2	0	0.00	0.00
	33	2.20	6.35
	61	3.20	6.35
	90	3.65	7.80
	123	-- fractured --	
F1	0	0.00	0.00
	33	1.27	N/A

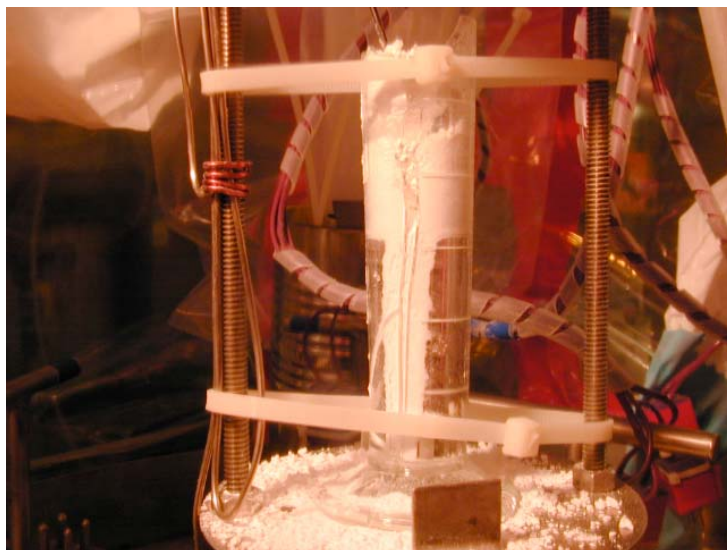


Figure 13. Sample B2 after 90 days exposure.



Figure 14. Sample E2 after 123 days exposure.

The degree of expansion is best determined by examining the ambient temperature data for Sample A2. Sample A2 is unique because the sample container was only partially filled with sodium, leaving a void space 14.6 cm high above the sodium to contain the expanding sodium bicarbonate layer. All of the other sample containers had been filled to the top of their containers with sodium during the initial preparation (see Figures 5 and 6), so that when the sodium bicarbonate layer grew beyond the confines of the container walls, excess material tended to fall out of the container and fall to the bottom of the test chamber. Figure 15 was obtained by plotting the sodium bicarbonate layer depth data versus sodium reacted depth for Sample A2 from 0 to 91 days.

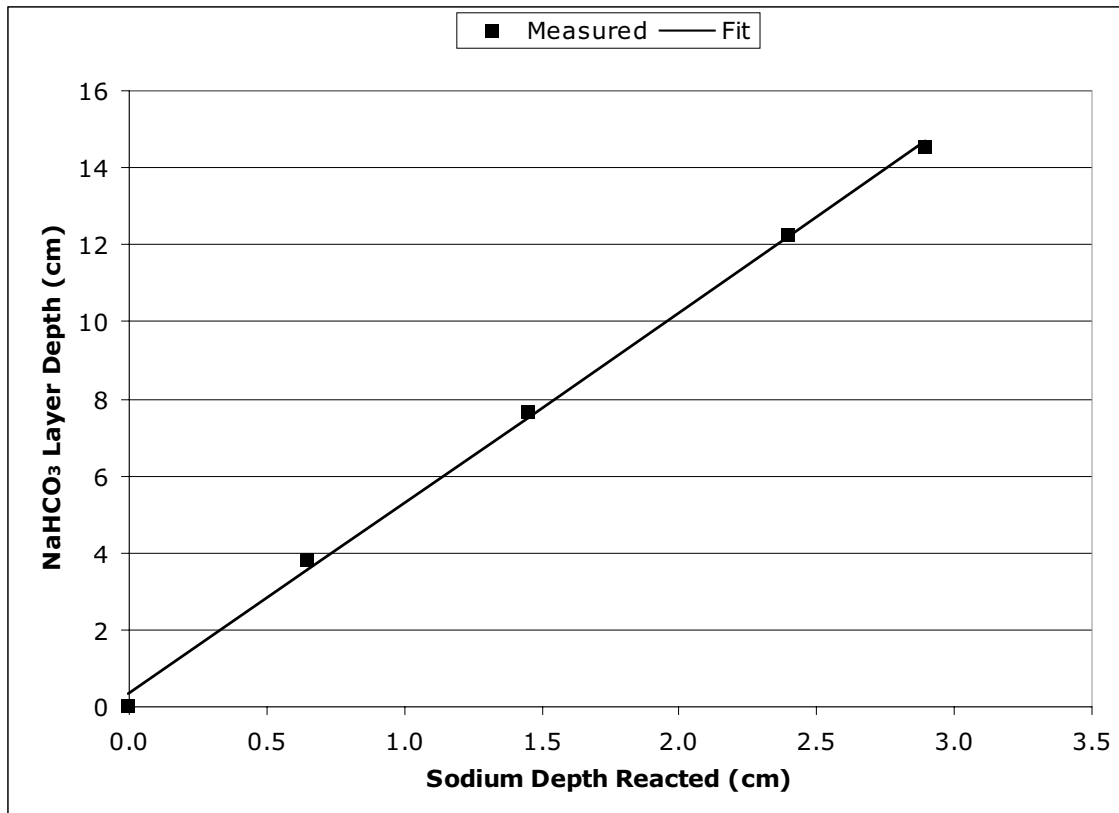


Figure 15. NaHCO₃ layer depth versus sodium depth reacted for Sample A2 at ambient conditions.

The equation of the line, $y = (4.95 \pm 0.11)x + (0.29 \pm 0.20)$, has a correlation coefficient of $r^2 = 0.999$. The intercept of the equation is almost zero, which is consistent with a zero layer thickness when no sodium has reacted (sample may have a positive offset from initial formation of thin oxide layer on the sodium surface). The equation shows that for every centimeter of sodium that has reacted, approximately 5 cm of layer were created.

The expansion in volume arises from two causes. The first cause is the change in molar volume that occurs when sodium is converted into sodium bicarbonate. Sodium metal has a molar volume of 23.5 cm³ per mole, while sodium bicarbonate has a molar volume of 38.2 cm³ per mole. This equates to a 1.6-fold expansion when the sodium is converted into sodium bicarbonate. The second cause is the creation of void space in the sodium bicarbonate. Assuming that the total expansion factor is approximately 5, then the void fraction of the sodium bicarbonate layer is approximately 0.7. The molar change plus the creation of void space generates the 5-fold expansion in the volume.

Figure 16 shows a plot of all of the layer depth versus sodium depth data given in Table 3. The sodium reaction rate was calculated in a discrete manner by dividing the difference between observed sodium reaction depths by the difference between observation times, as shown in Equation 16.

$$\text{rate} = \frac{D_i - D_{i-1}}{t_i - t_{i-1}} \quad (16)$$

In the equation D is the depth of sodium reacted for observation “i” or “i-1”, and t is the observed time in days for observation “i” or “i-1.” In the figure, it is apparent that the rate of sodium reaction decreases with increasing sodium bicarbonate layer depth. Note that there are two symbols used in the figure. The diamonds are used to shown which observations were recorded at ambient temperature, and which observations were recorded at elevated temperature.

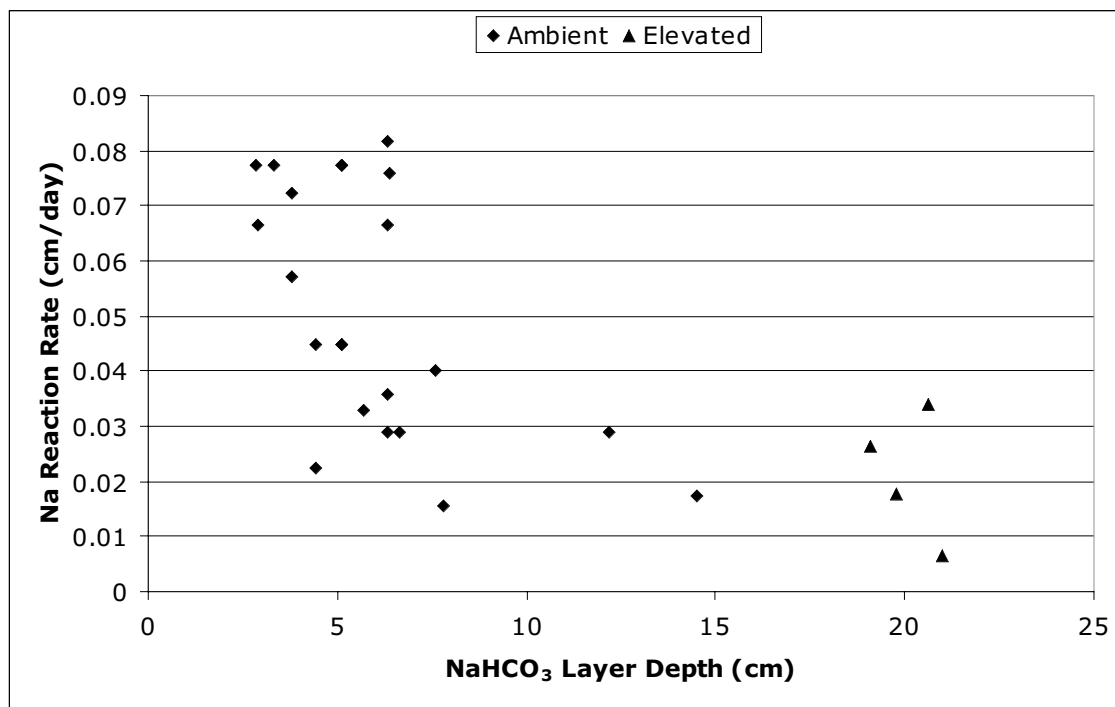


Figure 16. Reaction rate versus sodium bicarbonate layer depth, based on data in Table 3.

The data in Figure 16 are not so precise, and there is much scatter. One explanation of the cause of the scatter may be that the measurements were obtained only at discrete times, and the height of the sodium bicarbonate layer can fluctuate as it grows up and beyond the confines of the containers. This may result in unsteady sodium reaction rates as the layers grow, and then fall out of the containers. Also, the sodium bicarbonate layers in each sample do not all have the same density, and can undergo compression if the layer is unable to expand easily upward out of the sample container. As a result, layer height may not be related in a simple manner to the rate of sodium reaction in each sample.

It is certain, though, that layer height is correlated with reaction rate, and that thicker sodium bicarbonate layers are correlated with slower sodium reaction rates. It is also clear that the correlation is non-linear.

If it is assumed that the sodium bicarbonate layer provides just a resistance barrier to the diffusion of water to the sodium surface, then the reaction rate would be expected to be inversely proportional to the layer thickness. Figure 17 shows another plot of the sodium rate data, except that the sodium reaction rate is plotted against the inverse sodium bicarbonate layer thickness.

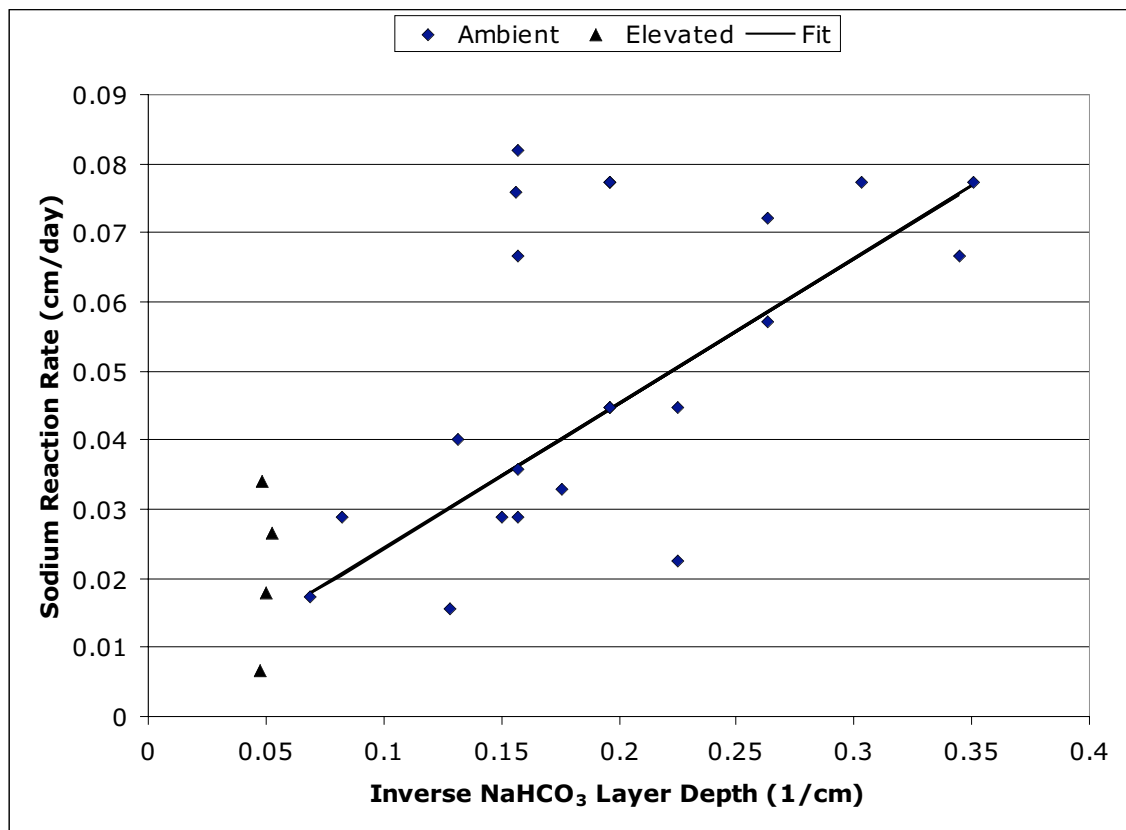


Figure 17. Measured sodium reaction rate versus inverse sodium bicarbonate layer thickness.

The plot shows that a line with a reasonable fit can be placed through the measured data, with the exception of some outliers. The equation of the line is $y = (0.210 \pm 0.039)x + (0.002 \pm 0.009)$ and has a correlation coefficient of $r = 0.797$. The intercept of the line is statistically indistinguishable from zero, which is consistent with the expected boundary condition of a zero reaction rate with infinite layer thickness.

If future experiments were conducted, then it would be beneficial to either increase the frequency of the inspection periods (e.g., weekly instead of monthly), or install a window in the test chamber, so that the sodium reaction depths and sodium layer depths could be observed and measured more frequently without having to open the test chamber.

3.6 Experimental Conclusions

The deactivation of residual sodium metal can be performed safely and in a controlled manner with humidified carbon dioxide. The use of humidified carbon dioxide to deactivate residual sodium results in the transformation of sodium metal into a solid, powdery white colored material that is primarily composed of sodium bicarbonate. A decreasing sodium reaction rate appears to be correlated with an increasing thickness of the sodium bicarbonate layer. Expansion of the sodium bicarbonate layer can result in the breakage of glassware and the deformation of sheet metal in confined spaces. For the

sample with the longest exposure, a reaction depth of 5.5 cm of sodium was achieved, with demonstrated penetration of water vapor through 21 cm of sodium bicarbonate.

4. EBR-II SECONDARY SODIUM SYSTEM

This section describes the sodium deactivation work that was accomplished on the EBR-II secondary cooling system during the EBR-II Plant Closure Project. Work on this system was used to qualify the humidified carbon dioxide deactivation technique on a full-scale system, and to gather safety and performance information so that the technique could be applied to the deactivation of residual sodium within the EBR-II primary cooling system.

4.1 EBR-II Plant Closure Project

The Experimental Breeder Reactor II (EBR-II) is a sodium-cooled fast breeder reactor that operated from 1964 until 1994. The reactor used metallic alloy fuel and a pool-type design. For this design, the reactor was placed into a large tank and submerged in a pool of sodium metal. Sodium metal from the pool was pumped through the core of the reactor and out again to the pool to remove the heat of nuclear reaction. The sodium pool and its accompanying pumps, cold traps, etc. are known as the primary sodium system and the tank that contains the primary sodium system is called the primary tank. An intermediate heat exchanger (IHX) was used to transmit the thermal energy from the sodium pool to a secondary loop containing liquid sodium. The secondary loop along with its supporting equipment is called the secondary sodium system. Thermal energy from the secondary loop was used to produce steam, which drove a steam turbine to produce electrical power. The reactor was capable of producing 62.5 MW-thermal and 19.5 MW-electric. When operating, the reactor's primary tank contained approximately 340 m³ of sodium metal, and the secondary cooling system contained approximately 130 m³ of sodium metal.

After the reactor was shut down in 1994 as a result of a congressional mandate, the United States Department of Energy (DOE) ordered that the bulk sodium be drained from the primary and secondary cooling systems and that the reactor be placed into a "a radiologically and industrially safe condition" in preparation for later treatment and decommissioning activities. Though EBR-II was always considered to be in such a state, this terminology applied to an end condition that could be maintained indefinitely with a minimum of supervision and maintenance personnel.

Work to achieve this end condition was done under the EBR-II Plant Closure Project, which was active between 1999 and 2002. This effort included the removal or dismantling of non-essential electrical systems, the powering down of obsolete equipment, the creation of "lay-up" plans or historical documents that record the definition, function, end state, and path forward for treatment or decommissioning of every sub-system within the EBR-II facility, and the initial deactivation of residual sodium within the EBR-II secondary and primary sodium systems.

During the EBR-II Plant Closure Project, initial deactivation of the residual sodium was performed by using humidified carbon dioxide. A different terminology was used at that time, and the deactivation process was referred to as "residual sodium passivation." Since the deactivation process creates a solid carbonate layer on top of the residual sodium, an analogy was made between this "oxide" layer, and the formation of oxide layers on other metals, such as aluminum. In the case of aluminum, for example, the oxide layer that forms on the surface passivates it, and prevents any further reaction of oxygen with the metal underneath. In the case of sodium, the carbonate layer does not prevent any further reaction of carbon dioxide with the residual sodium metal underneath, and so technically does not passivate the residual sodium, but it does provide a resistance barrier to gaseous diffusion and would slow down the reaction of gaseous reactants with the sodium underneath. Such a resistance barrier would be useful in the case that uncontrolled leakage of moisture occurs into any of the EBR-II sodium systems

during the potentially long period of time between the finish of the EBR-II Plant Closure Project and the resumption of residual sodium deactivation. By adopting the term “passivation” and placing a thin layer of carbonate on the residual sodium surfaces in the EBR-II sodium systems, the Project was able to achieve an added level of safety that was acceptable to the Department of Energy (DOE) in regard to the stored residual sodium, so that the EBR-II sodium systems could be placed in a steady state condition indefinitely while awaiting further resources (i.e., funding, personnel) to continue full sodium deactivation.

4.2 EBR-II Secondary Cooling System Description

The EBR-II secondary cooling system was used to transport the thermal energy from the EBR-II primary tank to the steam system, which drove EBR-II’s power turbine and served as a heat sink. Molten sodium was pumped through the tube-side of the IHX, located in the EBR-II primary tank, and then into a network of pipes and steam generators, located in the Sodium Boiler Building adjacent to the EBR-II containment dome. The steam generators were used to remove the thermal energy from the EBR-II secondary cooling system and convert water into steam.

As part of the EBR-II sodium clean-up effort, the secondary cooling system was drained of sodium, and the IHX was physically isolated from the rest of the system by cutting and sealing the connections. Before the sodium was drained, the secondary cooling system contained approximately 130 m³ of sodium. After draining, the system was estimated to contain approximately 400 liters of residual sodium. The largest pools of residual sodium resided in the bottom of the superheaters and evaporators, though smaller amounts were present in pipe dead legs, pipe elbows, and low areas in horizontal pipes. After draining the bulk sodium from the system, it was allowed to cool to ambient temperature.

After cooling, the secondary sodium cooling system was modified from its original configuration in order to perform the initial sodium deactivation. First, a carbon dioxide header was installed in the basement of the Sodium Boiler Building to channel the flow of dry or humidified carbon dioxide in seven different directions. Second, modifications were made to the secondary sodium cooling system to allow for the creation of 14 different gaseous flow paths. The flow paths were not isolated, however, and there was a certain degree of overlap in the flow paths due to the highly interconnected nature of the secondary sodium cooling system components. Figure 18 shows a simplified schematic of the secondary sodium cooling system after the modifications had been performed. In the figure, key operational units (e.g., north evaporator, surge tank) and valves (e.g., 520, 560a) of the system have been identified. The flow paths were created by opening and closing the valves indicated in the figure. Table 4 shows the names of the flow paths, and the valves that were opened to create the flow paths, with all other valves closed unless otherwise indicated in the table. Third, a vent line was installed at a central location, so that all of the exhaust lines could be purged. Also, a hydrogen monitor, an oxygen monitor, and a gas-conditioning unit, all identical to the ones used for the laboratory experiments, were installed on the vent line. The vent line was equipped with a shut-off valve, but was generally left open to the atmosphere during sodium deactivation work.

To monitor the exhaust gas during the residual sodium deactivation process, the vent manifold was equipped with a hydrogen monitor, an oxygen monitor, and a gas-conditioning unit. The Teledyne Analytical Instruments #235B thermal conductivity conductor (hydrogen monitor) was calibrated for a range of 0 to 5 vol% hydrogen in carbon dioxide. The Teledyne Analytical Instruments #326RB oxygen monitor was set to the low range of 0 to 1 vol% and was used to watch for air in-leakage during deactivation. The Clean Air Engineering Express SGC-4000 sample gas conditioner was used to remove

moisture from the sampled vent gas by cooling the gas stream and reducing the dew point of the gas to between 4.4 and 7.2 °C.

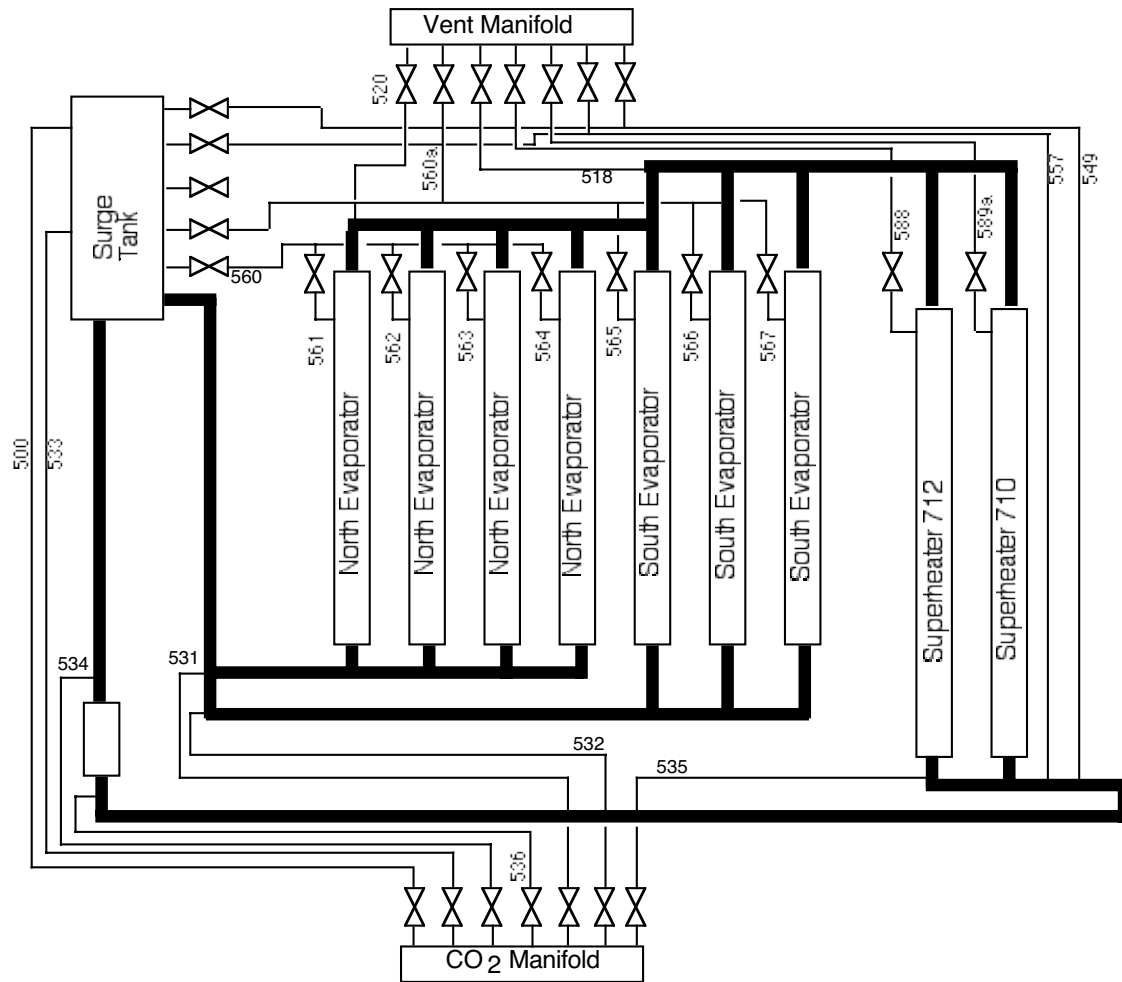


Figure 18. EBR-II Secondary Sodium Cooling System, as modified for residual sodium treatment.

Table 4. EBR-II Secondary Sodium Cooling System Valve Configuration, by Pathway

Path Name	Path #	Open Valves
Initial Purge with Dry CO ₂	1	All Valves Open
Surge Tank to Yard Lines	2	ACO-500, AV-549
Superheater 712	3	ACO-535, AV-588
Secondary Flow Path to Yard Lines	4	ACO-535, AV-549
Line Na2-34-557	5	ACO-535, AV-557
Major Purge – Superheaters and Evaporators	6	ACO-535, AV-518
Superheater 710 Purge	7	ACO-535, AV-589a
Surge Tank	8	ACO-531, AV-560, AV-560a
North Evaporators (4 units)	9	ACO-531, AV-520
South Evaporators (3 units)	10	ACO-532, AV-518
Line Na2-31-534	11	ACO-534, AV-557
Line Na2-31-536	12	ACO-536, AV-557
Final Treatment of Surge Tank to Yard Lines	13	ACO-500, AV-549
Final Treatment Evaporators, Superheaters, Line Na2-34-520	14	ACO-533, AV-520
Final Purge with Dry CO ₂	1	All Valves Open

4.3 Carbon Dioxide Humidification Cart

To deliver humidified carbon dioxide to the secondary sodium cooling system, a humidification cart or station was designed and fabricated. The cart (so called because the equipment is placed on a pushcart) is designed for a supply flow rate of 134 standard liters/minute of carbon dioxide. To provide this flow rate, the humidification cart requires a regulated carbon dioxide supply (approximately +138 kPa-gauge) from a dedicated source. A 170-liter clear acrylic water tank is used to contain the liquid water that is used to humidify the carbon dioxide. In the bottom of the tank are four stainless steel sintered metal sparging elements. The carbon dioxide gas stream flows through these sintered elements and bubbles through the water tank. A portion of the humidified gas flows through a Panametrics #MCHTR-1 with remote moisture probe monitor to measure the relative humidity of the outgoing gas stream. The relative humidity is displayed on a digital indicator on the cart control panel. A by-pass line around the water tank allows the operator to control the relative humidity of the gas stream by controlling the relative flow split between dry and humidified carbon dioxide. The cart also contains other valves, mechanical flow meters and pressure indicators. A schematic of the cart is shown in Figure 19, and photographs of the cart are shown in Figure 20.

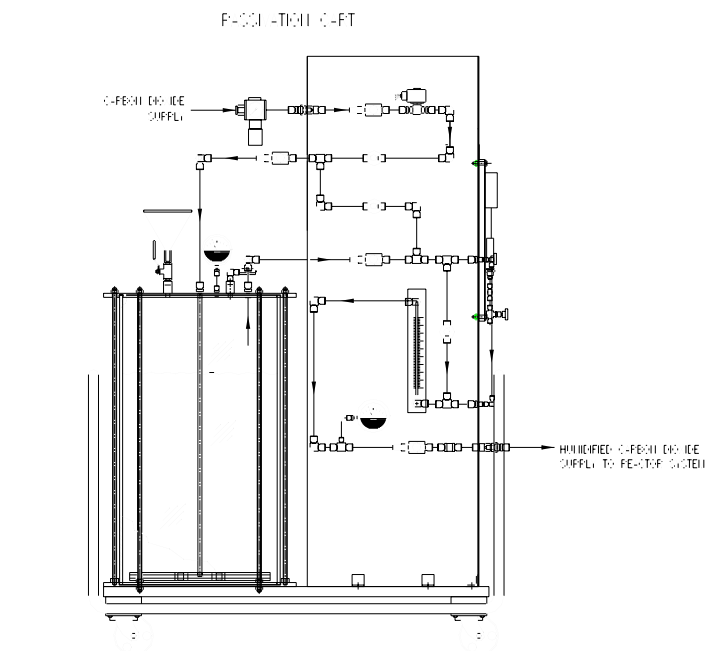


Figure 19. Schematic of carbon dioxide humidification cart.

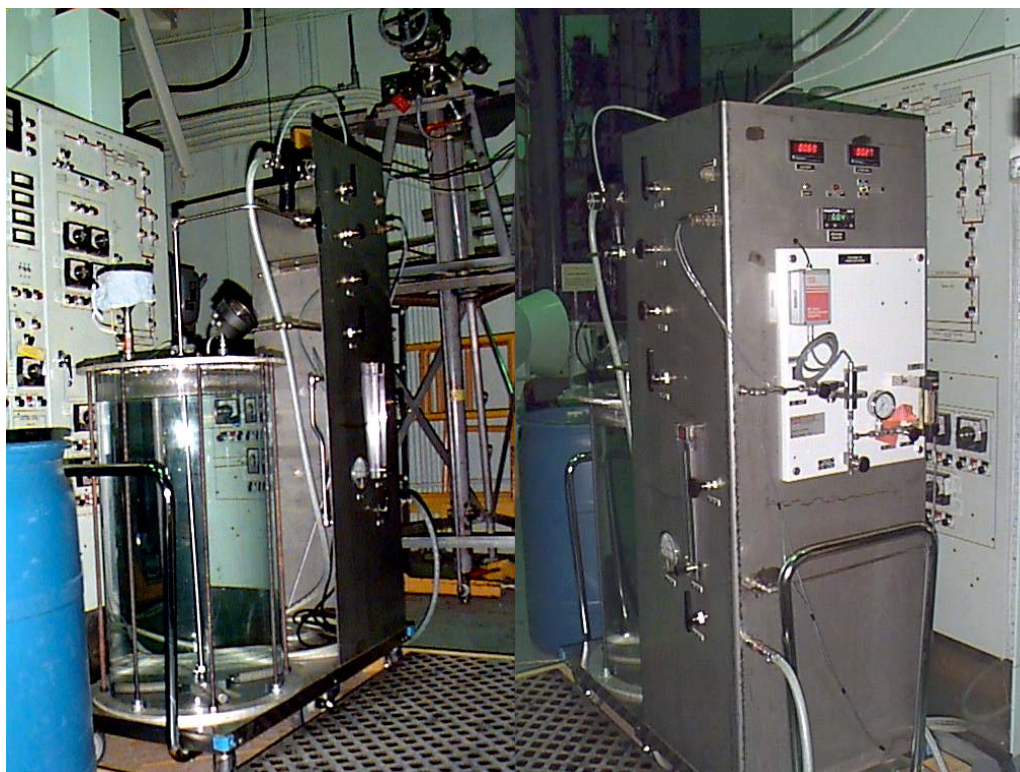


Figure 20. Carbon dioxide humidification cart, from two vantage points.

4.4 Secondary Sodium Cooling System Preparation

Prior to beginning sodium deactivation, the secondary sodium cooling system contained an argon atmosphere. Argon was used as the cover gas for the primary and secondary sodium cooling systems in EBR-II during the reactor's operation because it is not flammable and does not chemically interact with the sodium, even at high temperatures. Though the deactivation process could have been performed without initially purging the argon from the system, it was felt that it would be safer to mimic the laboratory experiments, and convert the atmosphere inside the secondary sodium cooling system to predominately carbon dioxide before introducing moisture and initiating the deactivation process.

To convert the internal atmosphere to carbon dioxide, all of the valves shown in Figure 18 were opened, and dry carbon dioxide was used to flush the system. Carbon dioxide flowing at a rate of 134 slm (5 scfm) was introduced into the CO₂ manifold using the carbon dioxide deactivation cart shown in Figure 20, and the mixed argon/carbon dioxide gas was vented out of the vent manifold. The vent manifold is connected to a stack that is open to the atmosphere. The choice of 4 days for the gas purge was made by assuming that the total volume of the secondary sodium cooling system was approximately 110,000 liters and that the gases were well-mixed inside the system, and then calculating how long it would take to remove greater than 90% of the argon inventory in the system by the purge. While it is likely that the system was not well-mixed, the calculation provided a defensible guideline for performing the purge.

Completeness of the purge was indicated indirectly by an offset in the hydrogen concentration meter. The hydrogen meter was not calibrated using an argon atmosphere, and so read 0.5 vol% hydrogen in pure argon. After performing the carbon dioxide purge for 4 days, the reading had declined to 0.25 vol%, which indicated that perhaps some argon was still present in the system. Later, shortly after beginning the deactivation process with humid carbon dioxide, the offset in the meter declined to a steady 0.08 vol%, where it remained for the duration of the deactivation process. Once the hydrogen meter had reached a steady offset, it was assumed that all of the argon had been purged from the system.

4.5 Deactivation of the Secondary Sodium Cooling System

The deactivation of residual sodium within the secondary sodium cooling system was performed in two phases. During the first phase, each of the 12 flow paths were exposed to humid carbon dioxide for a relatively short period of time (from a couple of days to a couple of weeks) in order to react the most accessible residual sodium. During the second phase, a more concentrated deactivation of the residual sodium within the Superheater 712 pathway was performed because the superheater was known to contain a deeper pool of residual sodium, and the Project wanted to perform a visual examination of the deep pool after treatment.

During the performance of each treatment phase, the flow of carbon dioxide through the carbon dioxide humidification cart was maintained at 134 slm. The temperature of the water in the carbon dioxide humidification cart was not heated, and the water remained at ambient conditions. The average absolute air pressure during the deactivation process was 0.83 atm. The measured relative humidity of the humid carbon dioxide prior to entering the secondary sodium cooling system was between 65% and 75%. Ambient temperature varied between 15 and 21 °C.

4.5.1 Phase One Treatment

Figure 21 shows the measured hydrogen concentration during Phase 1, and Table 5 shows the exposure times and the calculated amount of residual sodium reacted for each flow path listed in Table 4 during Phase 1. The calculated amount of sodium reacted is based on a hydrogen mass balance. Although no mass flow meter was installed on the vent manifold to measure the mass flow of gas, some assumptions were made to allow for an approximate calculation of the mass of hydrogen leaving the system through the vent manifold. Once the mass flow rate of hydrogen was determined, the rate could be integrated over time using a 3-minute measurement interval to get the total mass of hydrogen generated, and then this amount could be related to the total amount of sodium reacted. To perform this calculation, it was assumed that the exhaust gases were ideal, the pressure is 0.83 atm, the temperature is 15.5 °C, and that the only constituents of the exhaust gas were what could be measured or deduced – hydrogen, oxygen, and carbon dioxide. While it is certain that there was water vapor in the exhaust gas too, no accounting was made of the water vapor, and the gas leaving the exhaust manifold was assumed to be dry. The amount of sodium reacted that was calculated in this manner was compared to the potential amount of sodium that would have reacted based on the amount of water that was evaporated from the carbon dioxide humidification cart as a cross-check.

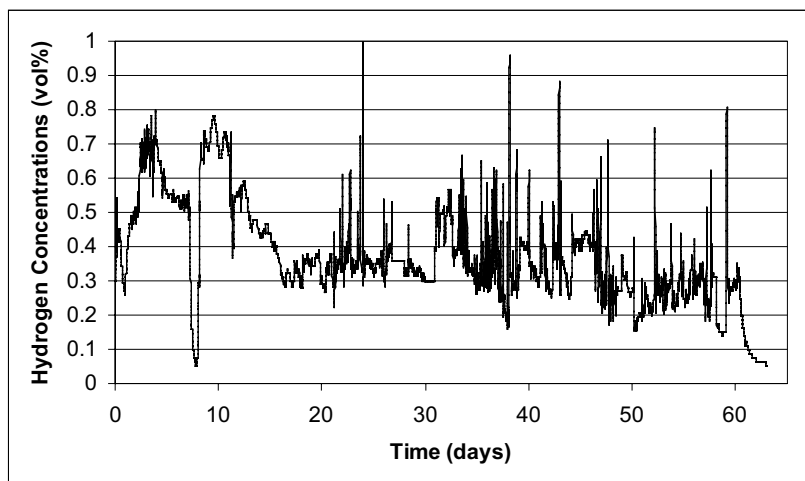


Figure 21. Measured hydrogen concentration during Phase One treatment of the EBR-II Secondary Sodium Cooling System.

During the conduct of the deactivation process, the treatment method appeared to work smoothly and predictably, with no detected uncontrolled reactions. The large spikes in Figure 21 are not due to sudden increases in hydrogen, but were due to the changeover from one flow path to another. When these switches were made, gas flow was temporarily stopped, and the hydrogen collected near the detectors, causing a noticeable rise in the measured hydrogen reading. Measured hydrogen concentrations remained at all times below the safety limit of 4 vol%, and never actually exceeded 1 vol% during deactivation.

During Phase One, approximately 115 liters of water were evaporated from the carbon dioxide humidification cart. This amount of water is sufficient to react up to 145 kg of sodium. Since only 92 kg were reacted according to an integration of the hydrogen concentration data, some water must have been lost from the system through the vent manifold. This water loss was confirmed by the observation that water was frequently collected from the sample gas conditioner unit, which indicated that the dew point of the gas leaving the system exceeded the temperature set point of the gas conditioner, 4.4-7.2 °C.

Table 5. Phase One Treatment Times and Calculated Sodium Amounts Treated

Path Name	Treatment Time (days)	Sodium Reacted (H ₂ basis)
Surge Tank to Yard Lines	19.0	32
Superheater 712	12.1	21
Secondary Flow Path to Yard Lines	6.9	10
Line Na2-34-557	2.2	2
Major Purge – Superheaters and Evaporators	1.9	2
Superheater 710 Purge	4.1	6
Surge Tank	1.0	1
North Evaporators (4 units)	4.7	7
South Evaporators (3 units)	1.3	1
Line Na2-31-534	1.0	1
Line Na2-31-536	1.0	1
Final Treatment of Surge Tank to Yard Lines	3.8	4
Final Treatment Evaporators, Superheaters, Line Na2-34-520	2.2	3
Final Purge with Dry CO ₂	2.8	1
Total	64.0	92

4.5.2 Phase Two Treatment

In Phase Two, deactivation of the Superheater 712 pathway was resumed, and treatment time was extended for another 72 days. According to an integration of the measured hydrogen data, another 90 kg of sodium metal was consumed. Approximately 110 liters of water were evaporated from the carbon dioxide humidification cart during the conduct of Phase Two, which is consistent with the amount of water evaporated from the cart during Phase One for a similar period of time and amount of sodium reacted.

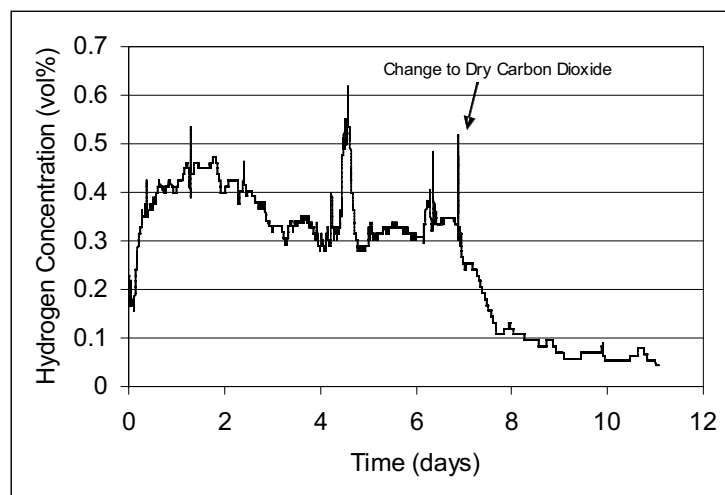


Figure 22. Measured hydrogen concentration during initial stage of Phase Two treatment.

After the first seven days of treatment, a blockage formed in one of the lines being used to exhaust the reacted gases (see Figure 22). A blockage was indicated by a sudden increase in outlet pressure on the carbon dioxide humidification cart. The carbon dioxide humidification cart was changed from humid carbon dioxide to dry carbon dioxide for four days, and then the flow of carbon dioxide was stopped. An examination of the flow route by breaking pipe lines and pressure testing eventually revealed that the blockage occurred in a narrow section of pipe having an inner diameter of less than 4 cm. Upon inspection, it was discovered that the line near the elbow had filled with a white material, presumably sodium bicarbonate, which blocked the flow of exhaust gas from the superheater. Rather than cutting out the blocked section, the decision was made to choose an alternate gas exhaust path and to resume treatment, and the blockage was allowed to remain in place.

Once carbon dioxide flow was resumed, treatment of the superheater continued for another 60 days, as shown in Figure 23. In the figure, a large spike is seen in the hydrogen concentration. This spike is not a sign of sudden runaway reaction, but rather indicates a point at which a power surge occurred, which tripped off the flow of carbon dioxide to the process. Once normal flow was once again restored, the measured hydrogen concentration fell back within the expected range.

No end point was reached in the treatment process, and residual sodium still remains in the superheater. Treatment was stopped on the superheater because sufficient information had been collected to certify that the treatment process was safe and verify that the equipment and instrumentation were reliable enough to monitor the treatment process. Further treatment will be needed to fully react all of the residual sodium within the superheater.

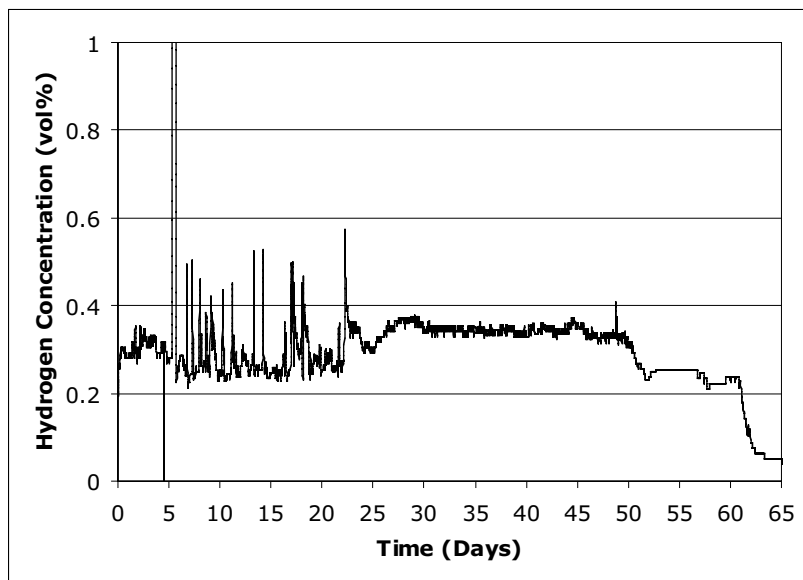


Figure 23. Measured hydrogen concentration during final stage of Phase Two treatment.

4.5.3 Visual Inspection Results

Following the shutdown of residual sodium treatment operations in Superheater 712, holes were drilled in the side of the superheater to determine the level of unreacted sodium in the bottom of the superheater. Prior to drilling the holes, the approximate level of the residual sodium was determined by tapping the side of the superheater with a hammer. A change in pitch of the hammer taps indicated the approximate sodium level. The approximate residual sodium level was determined to be 29.2 cm above the bottom of the shell side of the superheater. After tapping the sides with a hammer, three 3 mm diameter holes were drilled at this location. The first hole was drilled 2.5 cm above the sodium level and revealed only white powder. The second hole was drilled 2.5 cm below the sodium level and revealed solid sodium metal. The third hole was drilled at the sodium level and revealed a solid mixture of white powder and sodium metal. These observations indicate that the carbonate material accumulates on the exposed surface of sodium metal and does not significantly penetrate the sodium layer beneath the surface.

Following the initial survey, more holes were drilled in the superheater to determine the height of the carbonate layer above the sodium. Additional holes showed that the height of the carbonate layer was between 11.4 cm and 14.0 cm above the sodium surface. If an expansion factor of five is assumed, as was measured in the laboratory, then this would correspond to a depth of 2.5 cm of sodium reacted.

The last examination that was made was to determine if the carbonate material lying on top of the sodium layer was produced locally, or whether it was moved to that location from somewhere else in the system by gravity or by pressure differences (i.e., pushed by carbon dioxide flows). To answer this question, a 1.3 cm diameter hole was drilled above the level of the carbonate in the superheater and a boroscope was inserted to perform a visual inspection. This visual inspection revealed that the carbonate layer had grown in the form of carbonate stalagmites. These stalagmites grew up between the open spaces between the heat exchanger tubes. The stalagmites were solid in appearance but proved to be very brittle and powdery when mechanically disturbed. Very little loose powder was observed. It was concluded that the carbonate material was generated locally and did not accumulate there by other means.

A visual inspection was performed on a closed 20.3 cm diameter pipe tee located far downstream from the superheater. The pipe tee was known to contain sodium to a depth of 13 cm prior to beginning the residual sodium deactivation work. It was observed that a growth of carbonate material had occurred in this pipe tee, and that the height of the growth was between 10 and 13 cm, which compares with the height of the carbonate material observed inside the superheater.

From these observations, it was concluded that the humidified carbon dioxide distributed itself well throughout the EBR-II secondary sodium cooling system network, and that it can be expected that much of the residual sodium throughout the system may have reacted to a similar extent. Also, it was concluded that much more time would be needed to react the deeper pools of residual sodium using this technique, since the depth reacted over the total accumulated treatment time of 84 days (Phase One plus Phase Two) only resulted in sodium reacted to a depth of approximately 2.5 cm.

4.5.4 Chemical Analysis of the Carbonate Layer

Samples of the carbonate material obtained from Superheater 712 were analyzed in the laboratory. Titration of the samples using 0.1 M HCl revealed that the samples were indistinguishable from sodium bicarbonate, based on a comparison of pH titration curves to a standard. This result is

consistent with the chemical reactions presented in Section 2 and with the chemical analysis results obtained during the laboratory experiments described in Section 3.

4.6 Current State and Future Treatment Options

Since the completion of Phase Two treatment, the system has been maintained under a carbon dioxide blanket with no active gas flow. A positive gauge pressure is maintained, and carbon dioxide is supplied at a rate that is just sufficient to counter the leak rate of carbon dioxide out of the system.

Once a week the system is monitored for hydrogen and oxygen to watch for uncontrolled water-sodium reactions or air in-leakage. Hydrogen and oxygen have not been detected in the carbon dioxide cover gas since monitoring began.

Two different treatment processes are recommended to completely remove or treat the remaining residual sodium within the EBR-II Secondary Sodium Cooling System. The remaining residual sodium will either be reacted in place, or the component or section containing the residual sodium will be physically removed from the system and treated elsewhere.

Initially, it will be necessary to remove the larger sodium pools by melting and draining. Most of the larger pools are contained in the bottom of the superheaters and evaporators. In each of these components, a drain connection can be welded to the vessel just above the lower tube sheet. Then, the vessels can be individually heated and the sodium drained into suitable containers. Pools contained in larger diameter piping may also be drained in this manner.

Narrow pipe sections, dead end pipe legs, and other such parts of the system may require complete removal from the system to reach the residual sodium. For parts or sections removed from the system, the sections will be cut into smaller pieces and the residual sodium will be reacted by exposing it to a liquid water spray in the site's Sodium Component Maintenance Shop (SCMS). The SCMS is equipped with a large reaction chamber that is capable of treating up to 2.3 kg of sodium at a time in any configuration. The by-product of the treatment process is a caustic solution. The caustic solution is recycled and used continuously until the concentration level reaches between 5 and 15 wt% hydroxide, at which time it is removed from the treatment system, solidified in drums using Aquaset (stabilizing absorbent material), and disposed. The structural metal parts that remain after removing the residual sodium are disposed as low level radioactive waste or scrap metal. If necessary, additional reaction chambers, or chambers that can handle larger volumes of sodium metal at any one time can be designed and built in the future to increase the treatment rates.

Treatment in place will involve further use of humidified carbon dioxide and possibly humidified nitrogen or steam-and-nitrogen, as decided on a case-by-case basis. The choice of technique will depend upon many factors including funding, safety, degree of isolation, rate of treatment desired, and so on.

Following deactivation of the residual sodium by humidified gas, all remaining sections will be flushed with liquid water. This flushing operation may have to be repeated several times to react any remaining residual sodium and dissolve all sodium reaction chemical by-products (i.e., sodium hydroxide, sodium bicarbonate). It is expected that this flushing will generate between 50,000 and 60,000 liters of solution which will require further treatment (i.e., neutralization, encapsulation, etc.).

Instead of directly treating and disposing the waste solution, the waste solution may be saved and used to help flush the EBR-II Primary Cooling System when it is ready for such a treatment step.

Further engineering planning is needed to evaluate which parts of the system will require further draining, removal, or treatment-in-place before any sodium deactivation is resumed on this system. Such treatment operations will be carried out in the context of the overall residual sodium treatment in the larger EBR-II complex, and will be pursued in a coordinated manner with treatment and removal of residual sodium in the EBR-II Primary Cooling System.

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