THE WATER VAPOR NITROGEN PROCESS FOR REMOVING SODIUM FROM LMFBR COMPONENTS

M.D. CRIPPEN, C.W. FUNK, J.M. LUTTON
Hanford Engineering Development Laboratory,
Richland,
United States of America

ABSTRACT

Application and operation of the Water Vapor-Nitrogen Process for removing sodium from LMFBR components is reviewed. Emphasis is placed on recent efforts to verify the technological bases of the process, to refine the values of process parameters and to ensure the utility of the process for cleaning and requalifying components.

I. INTRODUCTION

Water and water based techniques are widely used for cleaning sodium from industrial equipment. The potential aggressiveness of the sodium-water reaction has lead to a variety of procedures for control. Methods applied depend to some extent on the results desired.

Development of the HEDL Water Vapor-Nitrogen process has emphasized two factors both keyed to safe and simple maintenance requirements for FFTF and future LMFBR components:

1. Relatively complete sodium removal.
2. Straightforward requalification of cleaned components.

Operating conditions for WVN processing have been generally defined in previous work.(1) Recent efforts have concentrated on refining the techniques used, establishing, on a sound basis, recommended process parameters; and ensuring freedom from effects that would limit reuse.

II. PROCESS EXPERIENCE

A large base of experience exists for water based processes and has been summarized in Reference 1. These processes have generally been successfully applied to large components, although in a few cases extreme process conditions have damaged components.

Typically, steam lance cleaning, a common approach, suffers from the inability to control conditions leading to high temperatures and equipment distortion. Efforts to control sodium-water reaction rates have used dilution approaches such as concentrated NaOH solutions and inert carrier gases.

Experience has shown that a variety of moisture in inert gas techniques can be successfully applied.(1) The HEDL Water Vapor-Nitrogen process has emphasized economical removal of sodium from large LMFBR components in a closed vessel to contain radioactivity. This process uses nitrogen, at less cost than argon, to inert the large volume of the vessel required to process the primary pump, Intermediate Heat Exchanger (IHX), or In-Vessel Handling Machine (IVHM). The WVN process uses water in the gaseous state (71°C; 160°F) to penetrate restricted access cavities. The reaction rate is controlled by delivering the water vapor in metered concentrations (1 to 15 vol%) to limit the rate of the reaction and to avoid excessive temperatures from too rapid heat release.

The process has been applied in small scale laboratory apparatus, in pilot plant equipment and in a full scale plant facility, the Alkali Metal Cleaning Facility (AMCF). Specific applications have been reviewed in Reference (1).

The HEDL pilot plant, the Sodium Removal Development Apparatus (SRDA) has been used both for development and service work. Mock-ups of the FFTF In-Vessel Handling Machine (IVHM) and Intermediate Heat Exchanger (IHX) were processed through 3 cycles of sodium wetting, cleaning and reinsertion in sodium. These studies demonstrated both the efficacy of the process for relatively complete sodium removal and the benign effect of the process on requalification. Complex assemblies from other development programs have also been processed. These include a view port-valve assembly which was heavily frosted, impairing its function; the assembly was successfully returned to service after cleaning. The Closed Loop In-Reactor Assembly (CLIRA), which contained many complex, deep crevices was also cleaned successfully with the exception of one 380 mm (15 in) deep inverted annular crevice in which the access clearance was only 12.7 µm (0.0005 in). The SRDA equipment has also been successfully adapted to clean a Fermi secondary pump and an instrumented FFTF fuel assembly using the component outer walls as the process "vessel".

The AMCF facility was successfully applied to remove sodium from the IVHM, and from an instrumented fuel assembly. Several mock-up assemblies and model sodium pools were successfully processed in the course of checking out and qualifying the AMCF system. One minor difficulty occurred in the IVHM cleaning. The orientation plug of the component contains a baffle assembly to which access is quite difficult. A small amount of undrained sodium on these plates did not react during vapor processing and produced a pressure pulse of about 3.5 x 10^3 Pa (5 psi). In subsequent testing of a mock-up assembly in SRDA, it was shown that this problem could be resolved by more extended process times or by increasing the moisture concentration toward the end of the cycle. Pressure pulsing was also demonstrated to be helpful.

III. PROCESS OPERATION

In the WVN process, sodium is reacted by introducing water vapor into a recirculating flow of nitrogen. The reaction rate is limited by metering the water vapor concentration in the nitrogen feed, initially at 1 vol%, subsequently at 5 vol% and ultimately at saturation. The hydrogen concentration in the discharge is monitored for control purposes. The inlet gas temperature is controlled to maintain a consistent feed temperature of 71°C (160°F). When the hydrogen concentration indicates that the sodium reaction is complete the rinse operation is initiated.

The surface reaction product is removed by flooding the reaction vessel with hot (82°C; 180°F) deionized water. At the same time the effluent hydrogen concentration is monitored for an increase that would indicate the presence of additional residual sodium. This hot water rinse is especially effective in removing sodium from crevices, but requires 1) extended rinse times (at least 160 hr) to allow for diffusion of the reaction products from the crevice, and 2) repeated rinse cycles to reduce final sodium hydroxide concentrations to very low levels, as indicated by conductivity measurements (final value < 2 µohm^{-1} cm^{-1}).

Testing has repeatedly demonstrated the effectiveness of using the hydrogen evolution rate for feedback control of the reaction in large scale systems.

In the late stages of the processing, when the hydrogen evolution rate approaches the sensitivity of the detector (> 5 ppm), increasing the water concentration has been shown to be effective, both to speed up the reaction and to indicate the presence of remaining sodium. Pressure pulsing has also been shown to be effective in improving access of the reacting gas to deep cavities. This approach was applied in a series of tests on a baffle plate assembly where relatively large quantities of sodium were present.(5) These tests also verified the approximately linear dependence of reaction rate on moisture content which had previously been established only in the laboratory.

When the reaction is judged to be complete, the moisture content should be raised to a high value, at least 15%, to ensure that no further significant reaction is occurring. To be doubly safe, the hot water rinsing stage can be started with only a small volume of water at 80°C (176°F) or higher, which is aggressively sparged with nitrogen to produce 100% relative humidity conditions.

Because the WVN process involves contact of the component with concentrated NaOH solution (50 to 75%) in the temperature range from 71°C (160°F) to 93°C (200°F), HEDL has conducted extensive stress corrosion cracking (SCC) studies to evaluate risks involved and to develop component requalification criteria. The most important result of the SCC work has been the definition and extension of the threshhold curve to long times at modest temperatures. At 93°C (200°F) the threshhold time for the initial indication of cracking phenomena is greater than 30 days and is approximately 70 days at 71°C (160°F)(6).

A number of tests involving multiple processing with subsequent reinsertion in sodium have demonstrated complete freedom from SCC so that no limits have been found to the repeated use of the WVN process in a service environment as long as operating specifications are properly followed.

IV. OPERATIONAL CRITERIA

Under normal circumstances, a well drained component has large areas of surface films of sodium. The initial reaction rate with water vapor, even at concentrations as low as 1%, is immeasurably fast, although this rate rapidly declines as the sodium surface becomes covered with reaction product. At the outset of WVN processing the primary concern is to prevent dangerous concentrations of hydrogen in the process gas, conservatively specified as 4% which is the lower flammability limit if the gas contains at least 6% oxygen. After an hour or so, the hydrogen output drops to a low level and the regular processing conditioning of 5% moisture and 71°C (160°F) can be established. A large body of data has been accumulated demonstrating that these conditions lead to generally stable reactions and provide a reasonable optimum.(2) At this stage of the process, the reaction is slow, occurring in two stages:

1. Water condensation into a concentrated sodium hydroxide solution:
   $H_2O(g) + (NaOH)\cdot(H_2O_x) \rightarrow (NaOH)\cdot(H_2O_{x+1})$
2. Sodium reaction with this solution:
   $Na + (NaOH)\cdot(H_2O_{x+1}) \rightarrow (NaOH)_2\cdot(H_2O_x) + 1/2\ H_2$

with the overall rate being controlled by the water condensation rate. The sodium surface recession rate, R, has been determined to be:

$$R = 0.046\ (C_{H_2O})^{1.2}\ \text{mm/hr at } 70\text{-}98°C$$

for C_{H_2O} expressed as volume percent moisture. The rate has a small negative temperature coefficient because of the increase of solution aqueous tension with temperature.(3,4)

The caustic solution formed by the reaction readily drains from the hardware and the reaction can be controlled by varying the vapor concentration. However if the component configuration retains the caustic solution over a reacting pool of metal, instabilities can develop because of the additional diffusion time connected with the thick, intervening layer of caustic solution. If instabilities occur, they are signaled by oscillations in the hydrogen evolution that have a period of hours. Raising the temperature decreases the condensation rate and thereby stabilizes the systems.

The rinse phase of the process is of considerable importance because it can provide effective removal of sodium from all but the narrowest crevices, as well as removing residual caustic from cleaned surfaces. Cleaning of "contact surfaces", such as bolt threads often occurs but is generally unpredictable. For well defined crevices 25.4 μm (0.001 in) wide, or larger, the depth of cleaning increases with the logarithm of the time. A depth of 60 mm (2.4 in) of sodium can be removed from a 25.4 μm crevice in about 10 hours, while a depth of 90 mm (3.6 in) requires 100 hours. The rate increases rapidly with increasing width, so that in a 180 μm (0.007 in) crevice only about 12 minutes are needed to clean to a 90 mm depth.

Experience with the process and limited optimization studies have led to the conclusion that a high rinse temperature, in the 80° to 95°C range, along with multiple immersions gives best results. Rinse water conductivity has been generally used as an effectiveness criterion. The actual value of the conductivity attainable will vary with the total system. A final value to be used as a criterion must be selected based on experience with the particular system. Furthermore, it is desirable to specify a minimum time period, typically 4-12 hours, during which conductivity stays below a pre-selected value, or does not increase by more than a set amount such as 25%.

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