PURITY OF EBR-II PRIMARY COVER GAS

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EBR-II Project

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ABSTRACT

The primary cover gas of Experimental Breeder Reactor II (EBR-II) is continuously monitored for oxygen, nitrogen, and hydrogen content. A program was started in March 1968 to identify the sources of these impurities and to reduce their level in the cover gas. At that time, the nitrogen concentration averaged about 6000 ppm with short-term levels as high as 20,000 ppm; the hydrogen concentration was occasionally as high as 400 ppm. Nitrogen (from air) was found to be introduced primarily through the argon cooling system of the fuel-unloading machine and through the fuel-holddown packing gland during fuel-transfer operations in the primary tank. The principal source of hydrogen (moisture) was traced to inadequate drying of the interbuilding fuel-transfer cask (or coffin). Modifications of equipment have significantly reduced the frequency and magnitude of inleakages of impurities.

I. INTRODUCTION

The investigation discussed in this report was started in March 1968 as part of an effort to formulate specifications for the primary cover gas in liquid-metal-cooled fast breeder reactors. Nitrogen buildup was of particular interest because nitridation of stainless steel is known to occur at high temperatures and high nitrogen concentrations, and, unlike hydrogen and oxygen, nitrogen is removed from the primary system only by dilution by an argon purge into the primary tank.

The first phase of the investigation was to identify the major sources of impurities in the EBR-II cover gas. Comparisons of variations in impurity levels with plant logs indicated that significant inleakage of impurities occurred during fuel-handling operations. The various sources are discussed in Sec. II.

As the investigation progressed, results indicated that the nitrogen in the cover gas was not a serious problem insofar as nitridation of reactor materials is concerned. However, the introduction of oxygen and hydrogen into the cover gas was obviously detrimental to coolant purity, so plant improvements were made to reduce the volume of air inleakage to the primary cover gas. Nitrogen was used as a "tag" to evaluate the improvements, because it is the only impurity not removed from the cover gas by reaction with the liquid sodium coolant.

Plant improvements were made over a relatively long period of time and only when compatible with the schedule for reactor operation. The importance of reactor operation, the complexity of the EBR-II facility, and the lack of accurate measuring devices in some components of the system have made some interesting tests impractical to complete. However, air inleakage to the primary tank has been reduced considerably.

The primary cover gas is argon. Makeup gas does not exceed the following maximum allowable impurity levels (in ppm by volume): H_2O , 13; nitrogen, 20; carbon-bearing gases, 5; hydrogen, 1. The primary cover-gas system has a total geometrical volume of about $1.8 \times 10^7 \text{ cm}^3$. Figure 1 shows the flow diagram for the argon distribution system; the system is completely described in Refs. 1-5.

Cover-gas purity is monitored by a Beckman Model 320-D gas chromatograph attached to the supply of the fission-gas monitor (FGM) as shown in Fig. 2. A gas sample is analyzed once every 4 min, and the results are recorded on a strip-chart recorder.

II. NITROGEN CONTAMINATION

A. Behavior of Nitrogen Concentration under Various Plant Conditions

1. Purge of Primary Cover Gas

The primary cover gas is purged with fresh argon occasionally to reduce: excessively high nitrogen concentrations; radioactivity levels; or the nitrogen level to a very low value for system studies on air inleakage.

Fig. 1. EBR-II Argon Distribution

TO:

- (a) PRIMARY-TANK MANUAL PRESSURE-CONTROL STATION
- (b) IBC PURGE
- (c) ACS MAKE-UP
- (d) PRIMARY-TANK ANNULUS
- (e) FGM FLUSH GAS

FGM-PORT
PURGE

TO BASKET BLAND
AND TRANSFER-
ARM BELLOW

SERVICE LINE FOR
SHUTDOWN COOLERS
NO. 1 & 2

OPERATING-FLOOR
MANIFOLD

TO RSCL

TO PRIMARY-
COOLER SAMPLING
STATION

TO PRIMARY-
SYSTEM GAS
CHROMATOGRAPH

REACTION-
CONTAINMENT
SHELL

SODIUM-BOILER-
BUILDING SUPPLY

PIC

PI

PA

PI

PA

PI

ARGON SUSPECT
TO CHIMNEY STACK

FI

FI

FI

PI

PI

FR

ARGON SUPPLY
FROM FEF

EMERGENCY ARGON-
BOTTLE SUPPLY MANIFOLD

ARGON-GAS
TOTALIZER

ARGON-GAS
TOTALIZER

N.C.
NEX TRAP

ARGON
COMPRESSOR

FILTER

TRAP

ARGON RETENTION
TANK

RUPTURE
DISK

RAD
DET

ion System

2

Fig. 2. EBR-II Fission-gas Monitor (FGM) System

Two methods are used to purge the primary cover gas. In the first method, the cover gas is exhausted to the stack at a rate of about 6 cfh ($47 \text{ cm}^3/\text{sec}$). Makeup comes from a combination of the purge to the primary-pump seals and the flow to the primary tank from the floating-head tank through the N-1 nozzle (see Fig. 1). Figure 3 shows the nitrogen concentration as a function of time for a typical purge. This purge, as with all other purges of the primary cover gas, was terminated before the nitrogen concentration reached a definite equilibrium value.

The second method of purging the primary cover gas is to first establish that the argon in the argon cooling system of the fuel-unloading machine (FUM-ACS) is of high purity and then mix the gas in the FUM-ACS with the primary cover gas. (Figure 4 shows the argon-system piping for the FUM-ACS.) This purging method reduces impurity levels very quickly by dilution, but the limited volume in the FUM-ACS places a limit on the amount of impurity reduction that can be achieved in one mixing operation. The gas in the FUM-ACS can be cleaned up and again mixed with the primary cover gas, but this procedure is seldom used.

2. Restricted Fuel Handling

Restricted fuel handling, the mode of operation in which sub-assemblies are exchanged between the reactor storage basket and the inter-building coffin (IBC), is usually performed during reactor operation. Normally, one subassembly is loaded into the primary tank and one removed per day while fuel handling is in progress.

The first definite pattern observed in monitoring the cover-gas impurities was numerous step increases in the nitrogen concentration. The plant log books showed that the step increases coincided in time with restricted fuel-handling operations. Comparison of data from the gas chromatograph with entries in the fuel-handling log indicated that the major in-leakage occurred when the fuel transfer port was opened, but some minor increases were observed during the time the argon from the FUM-ACS was routed through the transfer port for cleaning up the sodium adhering to the port. There was no nitrogen increase during a special test of repeated opening and closing of the transfer port. This discounted the possibility of air leakage past the seals of the transfer-port valves and indicated that the increases were due to air contamination in the FUM-ACS.

Fig. 3. Nitrogen Concentration in EBR-II Primary Cover Gas during a Purge of Approximately 10 cfh

Fig. 4. Flow Diagram of Argon Cooling System for Fuel-unloading Machine

Gas purity in the FUM-ACS is monitored with an oxygen meter. At the beginning of this study, operating procedures called for purging the FUM-ACS until the oxygen meter registered 40 ppm before the fuel transfer port was opened. Any sodium in the system would greatly reduce oxygen content, would have less effect on hydrogen concentration, but would have almost no effect on nitrogen concentration. Thus, the oxygen meter would give a false indication that purging was complete, and nitrogen would be transferred to the primary tank when the transfer port was opened.

Operating procedures were changed to require a purge of an additional 15 min after the oxygen meter reached 40 ppm. This change in procedures reduced the frequency of step increases in nitrogen during restricted fuel handling from a rate of about 45% to a rate of about 14% of the transfers.

Figure 5 shows the nitrogen concentrations in the primary cover gas during three subassembly transfers. These data illustrate nitrogen behavior during (a) a large step increase, (b) a small step increase, and (c) no increase.

During the first part of this study, there was a considerably higher probability of nitrogen being introduced into the primary tank during the first fuel transfers after a FUM-ACS cooldown than during subsequent fuel transfers with a hot FUM-ACS. However, the change in purging procedure has made the probability of nitrogen introduction about equal for these two conditions.

3. Unrestricted Fuel Handling

Unrestricted fuel handling is performed to refuel the reactor with fresh subassemblies. It includes the transfer of subassemblies between the reactor core and the storage basket, and all operations are done under the sodium surface within the primary tank. Movement of the rotating plugs, fuel gripper, and holddown is required to complete a transfer of a subassembly to or from the reactor core. The reactor is shut down during unrestricted fuel handling.

Before January 1971, a gradual increase in nitrogen concentration was always observed during unrestricted fuel handling. Figure 6 shows a typical increase. Air inleakage during raising and lowering of the gripper and/or the subassembly holddown was considered to be the most likely

Fig. 5. Nitrogen Concentration in EBR-II Primary Cover Gas during Restricted Fuel Handling:
 (a) Large Step Increase, (b) Small Step Increase, (c) No Increase

Fig. 6. Typical Behavior of Nitrogen Concentration in EBR-II Primary Cover Gas during Unrestricted Fuel Handling: Before Modification of Subassembly Holddown

source of nitrogen. The holddown was the prime suspect, because there appeared to be the possibility of a pumping action during its operation, which would force air through the mechanical packing gland into the primary tank. Also, the holddown was becoming sticky, which indicated that sodium oxide was building up on the mechanism.

The subassembly holddown was modified during the scheduled long reactor shutdown for maintenance at the end of 1970. Relief holes were drilled in the shroud tube to eliminate the possibility of pumping action during operation. (This is the same modification that was successfully made to the gripper when considerable sticking of that unit was experienced in 1963.) There have been no observed increases in nitrogen concentration during unrestricted fuel handling since this modification was completed.

4. Reactor Operation

There has been a gradual decrease in nitrogen concentration during most periods of reactor operation. Figure 7 is typical of the trend that has been observed. Of course, restricted fuel handling is usually done during periods of reactor operation, so step increases in nitrogen concentration are often superimposed on the long-term gradual decrease.

The nitrogen decrease during reactor operation is undoubtedly due to dilution of the primary cover gas by makeup argon. However, the lack of precise measuring devices in the gas system and the fluctuations in rate of argon makeup for the primary cover gas during plant operation and maintenance make an accurate quantitative description impossible to achieve.

There are essentially two ways in which the primary cover gas can be diluted with fresh argon. First, any leakage from the primary tank is replaced with plant argon. This argon is fed to the receiver tank, but it eventually reaches the primary tank through the purge to the primary-pump seals (see Fig. 1). A total of 8-10 cfh ($63-79 \text{ cm}^3/\text{sec}$) flows from the receiver tank, through the primary-pump seals, and into the primary tank, but most of this amount of flow returns from the primary tank to the receiver tank, via the floating-head tank.

The rate of leakage of gas from the primary system, and hence the rate of makeup, is not constant. Maintenance and replacement of seals, etc. can have a significant effect on the leakage rate. For instance, a test

Fig. 7. Typical Nitrogen Concentration in EBR-II Primary Cover Gas during Reactor Operation

conducted in July 1968 indicated a leakage rate of about 10 cfh ($79 \text{ cm}^3/\text{sec}$) during reactor operation and no fuel handling. In comparison, a test conducted in March 1971 under the same operating conditions indicated a leakage rate of about 1 cfh ($8 \text{ cm}^3/\text{sec}$). Although there is considerable uncertainty in the data, they do show that the leakage rate is not constant.

The second way in which the primary cover gas can be diluted occurs during restricted fuel handling. The FUM-ACS is purged during each startup and often contains argon of higher purity than that in the primary tank. There is an exchange of gas between the FUM-ACS and the primary tank during fuel handling, which results in a small improvement in the quality of the primary cover gas.

5. Leakage through the FUM-ACS and FGM Systems

Both the FUM-ACS and FGM systems pump gas from the cover-gas plenum and then discharge the gas back into the same space (see Figs. 1 and 2). The suction sides of the FGM pumps and the FUM-ACS turbines (when the system is valved into the cover gas) are under negative pressures. A leak in the suction side of either system results in air being pumped into the primary cover gas, which causes a rapid increase in the nitrogen concentration. Although the systems are normally sealed, a few leaks have occurred. Causes of the leaks were either: failure of a component (e.g., rupture of a diaphragm of a FGM pump), which caused the system to open to the atmosphere; or improper sealing around vapor traps and aerosol filters that had been installed as replacements.

To ensure system integrity, mandatory leak-checks are now required after maintenance. In addition, an alarm has been added to the primary-gas chromatograph, and procedures have been changed to make possible early detection of air inleakage into either system.

6. Miscellaneous

Long reactor shutdowns are scheduled periodically for plant maintenance. The primary gas system is usually opened for one reason or another, and large step increases in nitrogen concentrations are sometimes observed. However, the nitrogen level is usually decreased quickly by the high purge rate that results from the increased leakage from the "open" system.

The pressure of the primary cover gas was increased from 1-1/2 to 2-1/2 in. H₂O as a special test during a short period of unrestricted fuel handling. Although the results were inconclusive, the rate of nitrogen buildup was less than the average rate of increase observed during unrestricted fuel handling. No further tests were made with increased cover-gas pressure, because the nitrogen buildup during unrestricted fuel handling was effectively eliminated by modifying the subassembly holddown (see Sec. II.A.3).

The rotating-plug seals are cleaned periodically to remove dross that accumulates in the troughs. There has been speculation that air was forced into the seal alloy during cleaning and was bubbling up on the inside of the seal trough. Review of the data from the gas chromatograph showed that there were no significant nitrogen increases that could be attributed to air inleakage during cleaning of the seals.

B. Summary of Data from the Gas Chromatograph

Figures 8-13 show the average daily concentrations of nitrogen in the primary cover gas for the period March 21, 1968, through April 4, 1971. For orientation, the general plant conditions are shown above the plots.

C. Studies on Nitridation

Ruther⁶ demonstrated that nitriding of stainless steel in nitrogen-blanketed sodium could occur and conducted a series of ex-reactor experiments to evaluate the nitriding potential under conditions approximating those in the primary tank. The results of his experiments indicate that only insignificant nitriding would be expected at a temperature of 700°F and a nitrogen concentration of a few thousand parts per million in argon cover gas.

The auxiliary gripper plug is the only EBR-II component that has been examined for evidence of nitridation after a long residence time in both the primary sodium and the cover gas. The plug was fabricated from Type 304 stainless steel and had been in the primary tank for approximately 70 months. Samples filed from the surface of the plug analyzed 0.03 wt % nitrogen below the sodium/gas interface, 0.063 wt % at the interface, and 0.071 wt % above the interface. Thus, there apparently has been very

Fig. 8. Nitrogen Concentration in EBR-II Primary Cover Gas: March 1968-September 1968

Fig. 9. Nitrogen Concentration in EBR-II Primary Cover Gas: October 1968-March 1969

Fig. 10. Nitrogen Concentration in EBR-II Primary Cover Gas: April 1969-September 1969

Fig. 11. Nitrogen Concentration in EBR-II Primary Cover Gas: October 1969-March 1970

Fig. 12. Nitrogen Concentration in EBR-II Primary Cover Gas: April 1970-September 1970

Fig. 13. Nitrogen Concentration in EBR-II Primary Cover Gas: October 1970-March 1971

little nitridation of stainless steel components in the primary tank, either above or below the sodium level.

III. HYDROGEN AND OXYGEN CONTAMINATION

Hydrogen concentration in the primary cover gas is usually within the range of 10-20 ppm. Oxygen is usually below the level of detectability of the gas chromatograph.

When step increases in the nitrogen concentration were first observed during restricted fuel handling, corresponding peaks of as high as 400 ppm in hydrogen concentration occurred. It was noted, however, that the hydrogen peaks (or spikes) usually occurred when the IBC was used to transfer fuel to or from the primary tank via the FUM. This fact indicated that the hydrogen could be coming from moisture retained in the IBC after it had been dried in the Fuels and Examination Facility. To reduce the moisture carry-over, an air preheater was installed in the IBC drying system, and operating procedures were changed to require that the IBC be dried with heated air until the moisture content drops below 500 ppm.

Although the improved drying procedure has substantially reduced the magnitude and frequency of the hydrogen peaks, concentrations of hydrogen as high as 150-200 ppm are observed when the air and/or moisture enters the primary tank during restricted fuel handling.

Oxygen peaks as high as 200 ppm also have been observed mainly during restricted fuel handling. High oxygen concentration is observed at only one datum point on the chromatograph recorder, which indicates that the oxygen is removed from the cover gas by the molten sodium within 8 min. The hydrogen concentration is reduced exponentially, but does not reach equilibrium for 8-10 hr. Figure 14 shows typical spikes in hydrogen and oxygen concentrations observed on two separate occasions.

IV. CONCLUSIONS AND RECOMMENDATIONS

Impurity levels encountered in the primary cover gas have not been detrimental to the reactor components. There has been very little nitridation of components either above or below the sodium level.

Fig. 14. Typical Increases in Hydrogen and Oxygen Concentration in EBR-II Primary Cover Gas When Fuel Transfer Port Is Opened

Nitrogen concentration has been reduced considerably since close monitoring of impurity levels in the cover gas began in 1968. The primary gas system appears to be quite tight, and air inleakage during fuel handling has been greatly reduced. It appears as though the average nitrogen concentration can be maintained between 2000 and 3000 ppm, a concentration that would not cause deterioration of any of the components in the primary system.

Oxygen that enters the primary cover gas through air leakage is of some concern. Although the amount of oxygen contamination is not large enough to significantly affect the oxide concentration of the bulk sodium, oxidation of sodium on surfaces of primary components penetrating the cover gas can occur. A certain quantity of sodium oxide is also retained in the cover gas as aerosol, and a portion of this aerosol is deposited on the exposed surfaces of the primary components. Additional amounts are carried into the FUM-ACS and FGM systems. Deposition and gradual buildup of sodium oxide (in combination with sodium) on the working clearances of the primary pumps, gripper, holddown, etc. can eventually result in rubbing and binding of these components. A more immediate problem is the plugging of lines, vapor traps, and aerosol traps of the FUM-ACS and FGM systems with sodium oxide. The frequent replacement and cleaning of the affected units increases the downtime of these critical systems.

Continued close monitoring of the cover-gas impurities is planned. A continuing effort is being made to further reduce all sources of air leakage into the primary tank. Planned activities are installation of well-characterized samples in the cover gas as long-term nitridation monitors and addition of accurate measuring devices to provide a means of determining the rate of leakage from the primary gas system.

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