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U.S. NUCLEAR REGULATORY COMMISSION
In the Matter of Entergy Nuclear Vermont Yankee LLC
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NRC Staff Other
IDENTIFIED on 7/21/08 Witness/Panel Hopenfeld
Action Taken: ADMITTED REJECTED WITHDRAWN
Reporter/Clerk MAC

R&D Status Report
NUCLEAR POWER DIVISION

John J. Taylor, Director

BWR WATER CHEMISTRY

Many of the stress corrosion problems in boiling water reactors (BWRs) result from the presence of a very small amount of dissolved oxygen in the reactor water. Radiolysis in the reactor core continually decomposes a small amount of the very pure water used in BWRs into free oxygen and hydrogen. Most of the gas is stripped from the water by the steam, leaving only trace amounts of oxygen and hydrogen dissolved in the reactor water. Although the amount of dissolved oxygen is only about 200 ppb, it is sufficient to facilitate stress corrosion cracking. Hydrogen water chemistry can reduce dissolved oxygen to a level that will no longer facilitate stress corrosion.

Pipe cracking in BWRs first came to the attention of U.S. electric utilities in 1974. This problem has resulted in costly repairs and lost operating time. The potential seriousness of the problem was recently emphasized by the discovery of cracks in large-diameter (26-in; 660-mm) recirculation piping at a domestic BWR. These cracks necessitated replacement of the complete recirculation piping system and will cost 12 to 18 months of operating time.

Earlier EPRI reports (*EPRI Journal*, September 1981, p. 6; November 1981, p. 18) have helped familiarize the industry with the various factors involved in pipe cracking. In most cases, cracks have resulted from intergranular stress corrosion cracking (IGSCC). This status report describes how changing reactor water chemistry can help prevent IGSCC.

Three conditions must be present simultaneously for IGSCC to occur: stress, a sensitized microstructure, and an environment (water chemistry and temperature) that will facilitate cracking. Theoretically, no pipe will ever crack if any one factor is completely eliminated. Eight pipe-cracking remedies have been developed: three that affect stress, three that affect sensitization, and two that affect environment (Table 1). By their very nature, all the stress and sensitization remedies are limited to the specific component to which they are applied. For example, induction heating stress improvement affects cracking in the pipe weld to which it is applied; it does not affect any other weld. Only the water chemistry remedies have the potential of protecting the whole system.

The water in a BWR is similar in purity to laboratory distilled water. It is converted into steam by reactor core heat, condensed into liquid again after passing through the turbine, and reconverted into steam on reentering the core. This process is repeated continuously.

During reactor operation, radiolysis in the reactor core continually decomposes a small amount of water to form free oxygen and hydrogen. Most of the oxygen and hydrogen is stripped from the water by the steam and is subsequently removed from the water circuit by special equipment in the condenser. However, about 200 ppb oxygen and 12 ppb hydrogen remain dissolved in the water in the core when the reactor is at the steady-state full-power operating temperature (288°C; 550°F). During reactor startups and shutdowns oxygen concentration varies with temperature (Figure 1). The important question of which temperature-oxygen combinations facilitate IGSCC has been answered in part under EPRI research (RP1332 and RPT115). The shaded IGSCC danger zone in the figure represents those combinations.

Reducing oxygen levels during reactor startups and shutdowns by deaeration has been highly publicized in the BWR industry. Although helpful during transients, this remedy does little, if anything, to reduce pipe cracking during steady-state conditions (RP1332-2, RPT112-1, RPT115-3, RPT115-4). Deaeration does not affect oxygen levels during steady-state operating conditions, which definitely facilitate IGSCC. The amount of time spent at steady state is about 140 times greater than the amount of time spent in startups. Therefore, to reduce IGSCC further, it is necessary to change water chemistry during steady-state conditions.

Table 1
CAUSES AND REMEDIES FOR BWR PIPE CRACKING

Cause	Remedy
Stress	Induction heating stress improvement
	Heat sink welding
	Last-pass heat sink welding
Sensitization	Solution heat treatment
	Corrosion-resistant cladding
	Alternative materials
Environment	Hydrogen water chemistry
	Impurity control

Hydrogen water chemistry

In hydrogen water chemistry, small amounts of hydrogen gas are added to the reactor feedwater. In the reactor core the added hydrogen recombines with oxygen and other radiolysis products to suppress the net amount of oxygen produced at the steady-state temperature (Figure 1).

Although hydrogen water chemistry experiments were conducted over 20 years ago in several early Norwegian and U.S. test reactors, the concept was not further developed until 1979, when the Swedish utilities and ASEA–Atom conducted a short eight-hour test of hydrogen water chemistry at Oskarshamn-2 and demonstrated that hydrogen water chemistry was economically feasible. In 1981 the Swedes conducted a second test at Oskarshamn-2 for four days and obtained detailed water chemistry measurements. These tests showed that hydrogen water chemistry lowered the oxygen concentration to levels that would no longer be expected to facilitate stress corrosion. However, no actual in-reactor corrosion tests were performed. In June 1982 DOE funded

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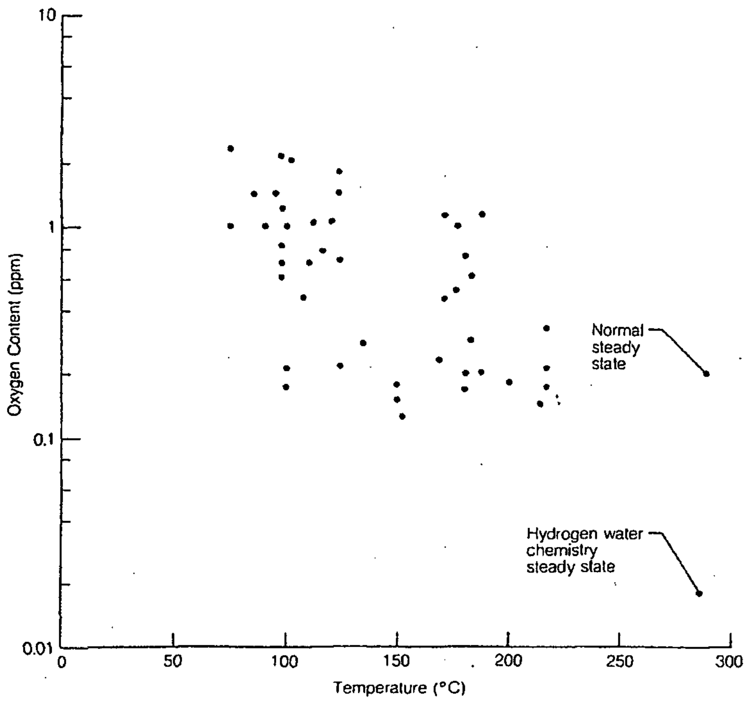
Figure 1 The shaded area represents the temperature-oxygen combinations that facilitate IGSCC in high-purity water. The data points are examples of temperature-oxygen combinations that have been measured in operating BWRs during startup, shutdown, normal steady state, and hydrogen water chemistry steady state.



a 30-day hydrogen water chemistry experiment at Commonwealth Edison Co.'s Dresden-2 plant. During this experiment, EPRI sponsored in-reactor stress corrosion tests that helped confirm hydrogen water chemistry as a powerful antidote for stress corrosion problems (RP1930-2). A $1 million EPRI laboratory research project on hydrogen water chemistry, which has been in progress for two years, supports this conclusion (RP1930-1).

The combined results of the in-reactor and laboratory IGSCC tests show that the oxygen level must be suppressed to 20 ppb to eliminate IGSCC completely. For example, during the Dresden-2 test, a severely sensitized sample of stainless steel was tested under extreme stress and strain, and absolutely no IGSCC was detected. In laboratory tests on full-scale pipes the growth rates of preexisting cracks have been slowed by a factor of 10 as a result of hydrogen water chemistry. If no cracks are present before hydrogen treatment of water, no new cracks are expected to start.

To achieve an oxygen level of 20 ppb during the Dresden-2 test, it was necessary to add 1.5 ppm hydrogen to the feedwater and to use pure oxygen in the off-gas system instead of air. The total cost of both hydrogen and oxygen was less than $1000/day. If a BWR had a 70% capacity factor and a remaining lifetime of 20 years, the total would be about $5 million. Equipment installation would cost an additional $1 million. In contrast, replacement of a complete recirculation piping system is estimated to cost on the order of $500 million, including the cost of replacement power.

Although the stress corrosion benefits from hydrogen water chemistry are expected to be very high, at least one negative side effect exists. The amount of the radioactive isotope nitrogen-16 (N-16) in the steam will increase. The N-16 is formed in the reactor core by the nuclear reaction: oxygen-16 + neutron $\longrightarrow$ nitrogen-16 + proton. Under normal water chemistry conditions the N-16 reacts with dissolved oxygen to form nitrate (NO_3^-), which is soluble in the reactor water.

Under hydrogen water chemistry conditions there is not enough dissolved oxygen to react with the N-16 to form NO_3^-; the N-16 combines with the hydrogen to form ammonia, NH_3. Ammonia is a volatile gas and is therefore removed from the water by the steam. The N-16 is a very unstable isotope and decays with a half-life of 7.11 s, giving off high-energy gamma rays. Because more N-16 ends up in the steam when hydrogen water chemistry is used, the steam lines and steam turbine will emit more gamma radiation than when normal BWR water chemistry is used. At Dresden-2, the amount of N-16 gamma radiation increased by a factor of 5 during the hydrogen water chemistry test. The turbine is heavily shielded and therefore the increase in N-16 did not significantly increase the radiation dose rate to plant personnel. In general, the N-16 side effect was manageable during the tests at Dresden-2. When maintenance crews had to enter an area where N-16 radiation was high, the hydrogen injection was stopped, and N-16 radiation levels quickly returned to normal. After the maintenance crew left the area, the hydrogen injection was resumed.

The major uncertainties about hydrogen water chemistry revolve around the possibility of long-term negative side effects. The two most important concerns are the hydrogen embrittlement of the nuclear fuel cladding and the redistribution of corrosion products (radiation buildup) within the plant. Although the best technical judgment available indicates that the possibility of either of these effects becoming unmanageable is extremely remote, there is no data base on which to build firm conclusions. At least one fuel cycle with hydrogen water chemistry will be required before a recommendation can be made to the utilities. EPRI is developing a long-term in-reactor test program to address these major uncertainties.

Control of Impurities

Although reactor water contains impurities in small amounts (at the ppm or ppb levels), BWRs generally operate with high-purity water. For example, NRC guidelines specify that reactor water chloride (Cl) concentration be kept below 0.2 ppm and the conductivity below 1 μS/cm during plant operation. A solution containing 1 ppm of sodium chloride (NaCl) would have a conductivity of about 2 μS/cm and a Cl concentration of 0.6 ppm. Therefore, 1 ppm of NaCl would exceed the NRC specifications. The results of EPRI research projects have shown that maintaining water purity may be just as important as controlling oxygen levels (RP1563-2, RPT115-3, RPT115-6). Impurities increase the size of the IGSCC danger zone.

In accelerated laboratory IGSCC tests as little as 1 ppm of certain impurities eradicated hydrogen water chemistry benefits. To benefit from hydrogen water chemistry, utilities will have to control both oxygen levels and conductivity. Reactor water with only 20 ppb oxygen and a conductivity in the vicinity of 0.2 μS/cm may eliminate any possibility of IGSCC. EPRI has recently stepped up its research to understand the role of impurities in an effort to produce cost-effective water chemistry guidelines. *Project Manager: Michael Fox*

VALVE RESEARCH

The primary goal of valve research in EPRI's Nuclear Power Division is to reduce the amount of plant unavailability attributable to valves in LWR power plants. These R&D activities seek to improve valve maintenance practices and valve performance and reliability and thus reduce the cost of producing electricity. EPRI's initial effort in this area was an assessment of industry valve problems conducted in the mid 1970s (NP-241). It was found that nuclear plant unavailability attributed to valves, valve actuators, and associated control circuits represented approximately three forced outages per plant per year, with an average outage duration of about two days. The value of such unavailability is significant. A study reported in the June 1982 EPRI Journal *(p. 18) indicates that a 1% availability improvement in base-load coal and nuclear generating units combined would represent savings of $2.2 billion nationwide over the seven-year study period.*

In the initial assessment of industry valve problems, which was conducted by MPR Associates, Inc., the concept of key valves evolved. These are valves whose malfunction can result in a forced plant outage, a power reduction, or an extension of a planned outage. It is basically to these valves that the EPRI research effort is directed.

The study concluded that only a small percentage (5–10%) of the total valve population in a nuclear power plant is applied in such a way that failure would result in a forced outage. It should be noted that these key valves are not necessarily safety-related valves. No major differences were found between PWRs and BWRs regarding the causes (seat leakage, stem leakage, actuator malfunction) of valve-related shutdowns.

The study also concluded that forced outages attributable to valves are underreported because of an umbrella or shadowing effect—situations where a valve requires maintenance or repair work during an outage attributed to another system or component. Thus, although the valve could be considered a contributing cause of the outage, this is not reflected in the reported data.

Nuclear plant data collection and evaluation systems originally had many shortcomings. As a result of improvements in these systems, data quantity and usefulness have been increased. Other existing sources of information remain to be assimilated, however, to achieve a comprehensive view of the problem. EPRI's limiting-factors analysis studies, the findings of which are published in four reports (NP-1136 through NP-1139), provide further insight into the causes and the magnitude of nuclear plant availability losses attributable to valves.

On the basis of the efforts described above, two areas were selected for initial EPRI R&D attention: the seat leakage performance of main steam isolation valves (MSIVs) in BWRs and valve stem packing improvements for both PWR and BWR application.

Figure 2 presents a cutaway view of a representative MSIV with the valve bonnet and the actuator removed. Two identical MSIVs are installed in series in each BWR steam line. Technical specifications for BWR plants establish maximum allowable seat leakage rates for MSIVs and require the periodic testing of each valve to verify that this requirement is met.

Work was initiated in early 1979 with Atwood and Morrill Co., Inc., a manufacturer of MSIVs, and General Electric Co., the nuclear steam supply system contractor for BWR plants, to develop a comprehensive test program on MSIV seat leakage performance (RP1243-1, RP1389-1). The goals were first to identify the factors that affect the valves' capability to meet the seat leakage criteria imposed by the local leak rate test (LLRT) and then to identify and verify the effectiveness of corrective actions for improving valve leakage performance.

The program evaluated the effects of such factors as local residual stresses from valve installation welding; forces and moments applied by the connecting pipe; mechanical cycling; thermal cycling; excessive wear and corrosion of critical valve surfaces; and poorly controlled maintenance practices. Of the factors investigated, corrosion of the valve seating surface (or changes in the friction coefficient) and inadequate maintenance practices were found to be the most significant contributors to the seat leakage problem. Program results are reported in NP-2381 and NP-2454.

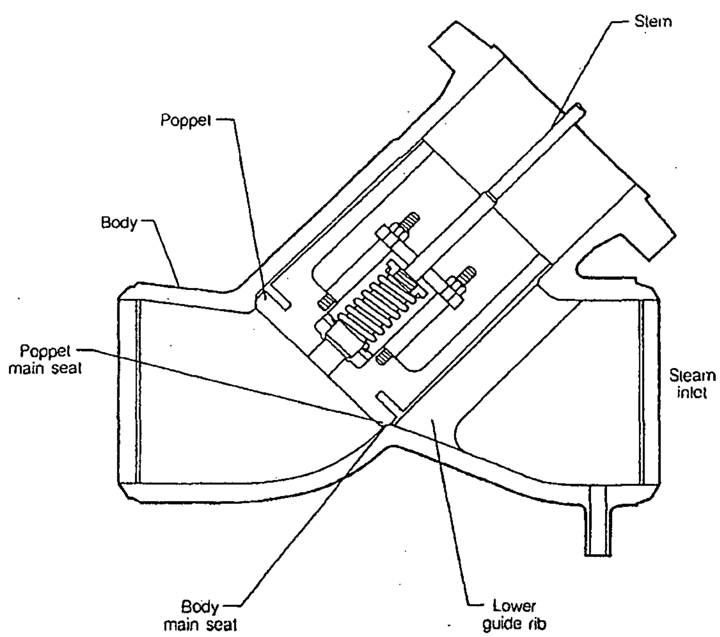


Figure 2 BWR main steam isolation valve. EPRI has sponsored a test program to determine the factors that affect valve seat leakage performance and to evaluate ways to improve this performance.