NRC FORM 366
(7-77)

U. S. NUCLEAR REGULATORY COMMISSION

LICENSEE EVENT REPORT

CONTROL BLOCK: | - | | | | | | (1) (PLEASE PRINT OR TYPE ALL REQUIRED INFORMATION)

| 0 | 1 | P A T M I 1 (2) LICENSEE CODE | 0 0 - 0 0 0 0 0 - 0 0 (3) LICENSE NUMBER | 4 1 1 1 1 (4) LICENSE TYPE | (5) CAT

CON'T
| 0 | 1 | REPORT SOURCE L (6) | 5 0 0 0 0 2 8 9 (7) DOCKET NUMBER | 0 2 1 1 8 3 (8) EVENT DATE | 0 6 0 6 8 3 (9) REPORT DATE

EVENT DESCRIPTION AND PROBABLE CONSEQUENCES (10)

0 2 During long term cold shutdown, the PORV was removed for a special inspection to
0 3 ensure that corrosion found in a previously installed PORV had not occurred with
0 4 the existing PORV. The pilot valve disc was found stuck open and the main valve
0 5 disc was found stuck closed. Additionally, yellow deposits were found on the
0 6 valve body inlet (Sulfur). The RCS has been open to atmospheric pressure so no
0 7 over pressure protection has been required. Public health and safety remain
0 8 unaffected. This is reportable per Tech. Spec. 6.9.2.A.9.

0 9	SYSTEM CODE	CAUSE CODE	CAUSE SUBCODE	COMPONENT CODE	COMP SUBCODE	VALVE SUBCODE
	C A (11)	E (12)	D (13)	V A L V E X (14)	F (15)	B (16)

(17) LER/RO REPORT NUMBER	EVENT YEAR		SEQUENTIAL REPORT NO.		OCCURRENCE CODE	REPORT TYPE		REVISION NO.
	8 3	—	0 0 3	/	0 1	T	—	0

ACTION TAKEN	FUTURE ACTION	EFFECT ON PLANT	SHUTDOWN METHOD	HOURS (22)	ATTACHMENT SUBMITTED	NPRD-4 FORM SUB.	PRIME COMP. SUPPLIER	COMPONENT MANUFACTURER
X (18)	A (19)	Z (20)	Z (21)	0 0 0 0	Y (23)	Y (24)	N (25)	D 2 4 3 (26)

CAUSE DESCRIPTION AND CORRECTIVE ACTIONS (27)

1 0 Cause of corrosion is attributed to acid sulfur compounds. See attachment for
1 1 details of transport mechanism. Corrective actions included: Additional inspec-
1 2 tion on other components also connected to pressurizer steam space, PORV internals
1 3 replaced leak and functionally tested and reinstalled. Other components were also
1 4 cleaned.

1 5	FACILITY STATUS	% POWER	OTHER STATUS (30)	METHOD OF DISCOVERY	DISCOVERY DESCRIPTION (32)
	X (28)	0 0 0 (29)	NRC Order	C (31)	Special Component Inspection

1 6	ACTIVITY RELEASED	CONTENT OF RELEASE	AMOUNT OF ACTIVITY (35)	LOCATION OF RELEASE (36)
	Z (33)	Z (34)	N/A	N/A

PERSONNEL EXPOSURES

1 7	NUMBER	TYPE	DESCRIPTION (39)
	0 0 0 (37)	Z (38)	N/A

PERSONNEL INJURIES

1 8	NUMBER	DESCRIPTION (41)
	0 0 0 (40)	N/A

LOSS OF OR DAMAGE TO FACILITY (43)

1 9	TYPE	DESCRIPTION
	D (42)	PORV was corroded - Internals required replacement

PUBLICITY

2 0	ISSUED	DESCRIPTION (45)	NRC USE ONLY
	N (44)	N/A	

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LER 82-011/99X-0

LER 83-003/01T-0

I. Recap of LER's

A Power Operated Relief Valve (PORV 1) was removed from the TMI-1 Plant in 1981. This valve was sent to Wyle Laboratories in 1982 for modification and recertification. Upon disassembly corrosion of some internal parts was observed and reported to GPUN. Examination of the parts revealed that the corrosion occurred while the valve was in a closed state. It appeared likely that the valve would not have functioned properly as a result of the corrosion. This condition was not reportable under specific Technical Specification requirements, but was reported in LER 82-011/99X-0.

The second PORV (PORV-2), which had been installed in 1981 as the replacement for the one identified above, was inspected in February 1983. This inspection was performed to ascertain valve condition in light of the corrosion observed in PORV-1. Some internal parts of PORV-2 were found to be corroded. Also, small yellow deposits (later identified as 99% pure elemental sulfur) were found inside the main valve body. The corrosion observed was similar to that of PORV-1 but less severe. It was judged, however, that the corrosion was sufficient to have prevented proper valve functioning. This condition was reported under Technical Specification 6.9.2.A.9 in LER 83-003/01T-0. It is noted that the block valve was found fully capable of performing its isolation function.

This follow-up report describes the actions taken by GPUN to identify the cause of the corrosion, the corrective actions taken, and preventative and monitoring actions to be performed.

II. Evaluation of Condition & Cause

PORV-1

A. Leading Circumstances to the Occurrence

A PORV, Serial No. BL08905, was installed at the beginning of the second cycle (March 1976). In February 1979 this valve was removed from service and refurbished onsite by a Dresser Industry service man. At this time, several parts were replaced but no excessive corrosion was noted on the surfaces of these parts. Following refurbishment, the valve was reinstalled and was removed from service in April 1981. Both PORV and Block Valve operated satisfactorily during HFT in March 1979 in both open and closed positions. In August 1982, this valve was shipped to Wyle Laboratories for modification and recertification.

B. Description of Occurrence

On August 11, 1982, GPU Nuclear Corporation was notified by Wyle Laboratories that the PORV was corroded and pitted. Wyle took photographs and wrote a description of what had been observed. Unfortunately, prior to testing and inspection at Wyle Laboratories, the PORV was thoroughly cleaned with Radiac Wash. Thereafter, the corroded PORV parts excluding the valve body, which exhibited superficial pitting in several areas, were sent to Babcock & Wilcox for failure analysis. Highlights of the failure analysis are as follows:

1). Inconel X750 springs showed severe pitting and general corrosion.

2). The Inconel 600 pilot seat bushing was severely pitted.

3). In general, the 12% Cr martensitic stainless steel parts were severely pitted and corroded. Also, cracking was observed on the guide retained plug.

4). 304 stainless steel parts exhibited superficial corrosion.

5). Some sulfur was found but its source was uncertain since Radiac Wash residue contains sulfur.

6). A B&W literature survey indicated that the type of pitting observed is usually caused by chlorides and/or sulfur.

C. Root Cause of Occurrence

The B&W failure analysis was unable to determine the root cause of corrosion. To ensure that the corrosion found in this PORV had not occurred in the in-service PORV, a special inspection was performed on the existing PORV and Block Valve. The inspection results are reported in LER 83-003 along with subsequent failure analysis results.

II. Evaluation of Condition & Cause - continued

PORV-2

A. Leading Circumstances to the Occurrence

In April 1981 the PORV, Serial No. BS03989, was installed on the pressurizer. Both PORV and Block Valve operated satisfactorily during HFT in September 1981 in both open and closed positions. TMI-1 records indicate that the Block Valve internals have not been inspected since 1976. During the week of February 7, 1983 both valves were removed for a special inspection to confirm that corrosion reported to the NRC by LER 82-011 on an equivalent model of this valve was not occurring.

B. Description of Occurrence

Removal and disassembly of the PORV and Block Valve were completed on February 10, 1983. The pilot disc, pilot spring and pilot seat bushing were found corroded such that the pilot disc was stuck in the full open position. The PORV disc was found corroded and stuck to the guide in the closed position. Additionally, small yellow deposits were found on the internal surfaces of the PORV and in the Block Valve cavity.

The following is a summary of the as-found conditions of the internal parts:

1) The pilot disc spring and main disc spring (Inconel X750) were corroded.

2) The pilot seat bushing (Inconel 600 material) was corroded and stuck to the pilot disc, pilot disc spring and lower spindle.

3) The pilot disc, lower spindle, guide retaining plug, main disc, and lock plate (12% Cr martensitic stainless steel materials) were corroded.

4) The guide (Stellite 6 material) was stuck to the main disc.

5) The retaining lock plate screw (304 stainless steel) showed orange and black discoloration.

6) The bottom of the bellow piston (316L stainless steel material) showed orange and black discoloration.

7) The internal surfaces of the PORV and the Block Valve Body (316 stainless steel material) showed no evidence of corrosion damage.

8) The Block Valve disc (304 stainless steel material hardfaced with Stellite 6 material) showed no evidence of corrosion damage.

9) The Block Valve Stem (17-4 PH material) showed no evidence of corrosion damage.

II. Evaluation of Condition & Cause - continued

Selected PORV parts, representing the various materials of construction for the valve internals, and the yellow deposits from both valves were sent to Battelle Memorial Institute for metallurgical and chemical analysis. Highlights of the Battelle study are detailed below:

1) The yellow deposits were identified as 99% crystalline sulfur.

2) The pilot disc was stuck in the open position due to the buildup of corrosion products.

3) The guide was stuck to the main disc by a wedging effect created by corrosion products. A 2000 pound load applied to the disc face could not move the disc inside the guide.

4) In general the main disc, lower spindle and pilot disc were pitted. In addition, minor cracking was associated with some of the pits in the main disc.

5) Patches of intergranular attack were present at the inside diameter surface of the bushing.

6) The guide showed no evidence of corrosion damage.

7) The pilot disc spring was pitted and corroded.

8) The bottom of the piston was slightly corroded.

9) No corrosion attack was present on the billows, a semi-austenitic stainless steel (19 Cr, 4 Ni).

10) Sulfur was found in all corrosion products ranging in concentrations from 5 to 30 wt %.

11) No chlorides were detected in the corrosion products.

12) Corrosion product identification revealed nickel sulfides and sulfates, iron sulfides and sulfates, elemental crystalline sulfur and alpha iron oxide hydroxide. The latter compound is only stable at low temperatures ($< 150^{\circ}F$).

C. Root Cause of Occurrence

The root cause of the corrosion has been attributed to acid sulfur compounds. A gaseous sulfur transport mechanism has been proposed by Battelle to explain the presence of corrosion in the PORV. The mechanism involves the decomposition of thiosulfate into gaseous sulfur species, probable sulfur dioxide or hydrogen sulfide, during those periods when sodium thiosulfate was introduced into the reactor coolant system. These gases would subsequently be transported to the PORV where they would form corrosive solutions such as sulfurous acid or sulfuric acid. The corrosive solutions would be formed by the condensation of water vapor in the presence of sulfur gases and/or the absorption of sulfur gases by thin films of water.

II. Evaluation of Condition & Cause - continued

D. Previous Events of a Similar Nature

The PORV, Serial No. BL08905, which was removed from service in 1981 exhibited similar corrosion (perhaps a little more severe in some areas). See LER 82-011. Decontamination of those corroded parts had removed any chemical evidence which might have indicated the cause of corrosive attack on that valve. However, in light of the current metallurgical findings, it is now believed that the corrodent responsible for the corrosion of this valve very likely was a sulfur species.

III. Additional Follow-On Inspections

The PORV is installed on a pressurizer nozzle connected to the steam space. Additional inspections were performed of other components and piping which also connect to the steam space. These were followed by a manned entry of the pressurizer for further inspection and cleaning. The following describes the results of these inspections:

Two safety valves are connected to nozzles in the pressurizer upper head. Until 1982, these were separated from the pressurizer by a loop seal in the piping. Both valves and the two sections of loop seal piping were visually examined for corrosion. Safety Valve RC-RV-1A was found to have no corrosion on either the nozzle (347SS) or disc (Inconel-X-750). Wipe samples were obtained of white deposits and a black film found on the valve inlet. Safety Valve RC-RV-1B was found to have no corrosion on the nozzle but had small, shallow pits on the disc face; the seating surfaces were not damaged. Wipe samples were obtained of the yellow deposits found in the area. Analysis of both sets of wipe samples is pending, but is expected to show sulfur concentrations analogous to those found on the loop seals. Inspection of the loop seal piping (304 SS) revealed no corrosion but the wipe samples did contain sulfur. The steam zones of both pipes and the water line of pipe A had less than 400 $\mu g/ft^2$ while the water line and submerged zones of loop B had about 2000 $\mu g/ft^2$. The reason for the difference between the two loop seals is not known but may indicate that one of the loop seals was lost at some point. The deposit analysis results correlate with the valve inspection results.

The pressurizer vent valve (RC-V17) was inspected since this valve also is connected to the pressurizer steam space through the vent piping. Inspection of this valve revealed small shallow pitting on the valve disc (410 SS) but not to a degree which could affect valve function or integrity. The pressurizer spray valve (RC-V1) was also inspected. RC-V1 is normally flooded, but would have been exposed to the pressurizer gas space after spray was terminated upon shutdown. This valve was found to have sulfur deposits on the pressurizer side of the valve but no corrosion.

The manned entry into the pressurizer included visual inspection of the spray piping and nozzle, the shell internal surfaces, attachment welds for the ladder, and the pressurizer heaters. There was no evidence of significant corrosion on any of the internal parts. There was a reddish-brown film in some areas as well as yellow deposits in the upper dome region. Analysis of these materials is pending but is expected to show high sulfur concentrations in the yellow deposit and some level of sulfur contamination in the brown film. Ultrasonic testing of welds in the internal spray piping also showed no defects.

III. Additional Follow-On Inspections - continued

Welds in the one-inch vent piping near the pressurizer were radiographed and did not shown any defects. Ultrasonic testing and radiography performed in March 1982 showed the spray line thermal sleeve and surge line nozzle safe end (Inconel 600 and 316 SS) to have no indications.

The conclusion drawn from these inspections is that, with the exception of minor pitting not affecting system integrity or function, the damage is confined to the PORV internal parts.

IV. Corrective & Preventative Actions

PORV-2 was disassembled as discussed above and examined for corrosion. The valve body was cleaned to remove any residual sulfur and dye penetrant tested. All of the PORV internal parts were replaced during reassembly.

The reassembled valve was nitrogen leak tested and functionally tested prior to reinstallation. The block valve (RC-V2) was also cleaned prior to reinstallation. All other valves were functionally undamaged and no corrective actions were required.

The pressurizer internal surfaces were cleaned by hydrolazing at the time of the manned entry. Visual examination following hydrolazing showed that the corrosion products and yellow deposits had been removed. The PORV discharge tail pipe and reactor coolant drain tank were also cleaned at this time.

Removal of residual sulfur from the remaining portions of the Reactor Coolant System will be completed prior to plant heat-up. This, in combination with the pressurizer hydrolazing and elimination of the sodium thiosulfate additive, will minimize the potential for recurrence of sulfur assisted corrosion. Reactor Coolant sulfate levels will be monitored to assure early detection and prompt elimination of potentially corrosive conditions. In addition, a follow-up inspection of the PORV will be performed in conjunction with the first post-operation OTSG eddy current examination. (Per Topical Report 008 Rev. 2, Appendix A Section III.B)

LER 82-011/99X-0
LER 83-003/01T-0

V. Summary & Conclusion

Licensee Event Reports 82-011/99X-0 and 83-003/01T-0 reported finding corrosion of the internal parts of two TMI-1 PORV's. The PORV's were installed sequentially and covered the operating periods April 1976 to April 1981 and April 1981 to February 1983. Both valves exhibited similar corrosion of the internal martensitic, Inconel 600 and Iconel X-750 parts; austenitic parts were not affected. General corrosion and pitting attack were the predominant corrosion form with some localized islands of IGA observed.

Examination of the corrosion products and deposits from the second PORV revealed that the corrosion was due to attack from a acid sulfur species. The corrosion most likely occurred at low temperature although the sulfure transport may have occurred either hot or cold. A detailed determination of the responsible corrodant could not be made for the first PORV but the similarity of the attack strongly suggests that a similar mechanism was acting. Thiosulfate in the Reactor Coolant appears to have been the source of the corrosive species.

Extensive inspections were performed of other components connected to the pressurizer and of the pressurizer internals. Corrosion in these other components was limited to some isolated cases of minor pitting which did not affect system function or integrity. Thus, it was concluded that all significant attack was confined to the PORV.

Corrective measures were undertaken to restore the PORV to operable status. The valve body was cleaned and thoroughly inspected. All valve internal parts were replaced. This final valve assembly was tested and has been reinstalled. The block valve, although not corroded, was similarly cleaned and inspected prior to reinstallation.

Residual sulfur has been or will be removed from the Reactor Coolant System (RCS) to minimize the potential for recurrence. In addition to cleaning the PORV and block vlave, the pressurizer internal surfaces, the PORV discharge tail pipe and the reactor coolant drain tank were hydrolazed. The remainder of the RCS is to be cleaned as one of the final steps in the OTSG repair process.

Frequent chemistry monitoring will be employed to provide early detection and elimination of potentially corrosive environments. In addition, to assure that the corrosion is not continuing, the PORV will be inspected in conjunction with the first post-operation OTSG eddy current testing.