P. O. Box 361, Platteville, Colorado 80651

10-10-75

September 30, 1975

Mr. E. Morris Howard, Director
Nuclear Regulatory Commission
Region IV
Office Of Inspection and Enforcement
Suite 1000
Arlington, Texas 76012

IE FILE COPY

REF: Facility Operating License
No. DPR-34

Docket No. 50-267

Dear Mr. Howard:

Enclosed please find a copy of Unusual Event Report No. 50-267/75/18, Preliminary, submitted per the requirements of the Technical Specifications.

Very truly yours,

Frederic E. Swart
Superintendent, Nuclear Production
Fort St. Vrain Nuclear
Generating Station

FES/alk

cc: Mr. Roger S. Boyd

8311090037 751215
PDR ADOCK 05000267
S PDR

COPY SENT REGION IV

10644

REPORT DATE: September 30, 1975

UNUSUAL EVENT 75/18

OCCURRENCE DATE: September 24, 1975

FORT ST. VRAIN NUCLEAR GENERATING STATION
PUBLIC SERVICE COMPANY OF COLORADO
P.O. BOX 361
PLATTEVILLE, COLORADO 80651

REPORT NO. 50-267/75/18

Preliminary

IDENTIFICATION OF OCCURRENCE:

While removing the boron carbide balks from the Reserve Shutdown hopper assembly of CRD SN 28 from core region 13, it was noted that there was a light deposit of while crystals on the surface of several of the balls. Since the presents of the crystals did not affect the operability of the Reserve Shutdown Syste, this was defined as an unusual event.

CONDITIONS PRIOR TO OCCURRENCE:

	Steady State Power		Routine Shutdown
	Hot Shutdown		Routine Load Change
X	Cold Shutdown		Other (specify)
	Refueling Shutdown		
	Routine Startup		

The major plant parameters at the time of the event were as follows:

Power	RTR	0	MWth
	ELECT	0	MWe
Secondary Coolant	Pressure	N/A	psig
	Temperature	N/A	°F
	Flow	N/A	#/hr.
Primary Coolant	Pressure	0	psig
	Temperature	120	°F Core Inlet
		120	°F Core Outlet
	Flow	1 Circ. @ 4000 RPM	#/hr

3. Determine the effect, if any, they have on the performance of the Reserve Shutdown System.

4. Determine the effect, if any, they have on the core components and core performance if they are transported from the hopper assembly.

Not all of the analysis and tests have been completed, but there is sufficient evidence to indicate that the crystals are a boric acid residue, that they originated in the Reserve Shutdown hopper and the majority are still retained there, and that they will not affect the satisfactory operation and performance of the Reserve Shutdown System.

The following is a summary of the tests and inspections performed to date and some of the detailed results obtained.

Identification of Crystals

Chemical analysis at three different laboratories have indicated the crystals to be distilled boric acid. X-ray diffraction has shown them to be either hydrogen borate, HBO_2 or boric acid crystal, H_3BO_3. The crystals on the surface of the hopper were all H_3BO_3 while those on the boron graphite balls contained some of both. Trace amounts of other material, Fe, Si and Mg were also found.

Cause and Origin

The majority, greater than 99 percent, of the boron in the reserve shutdown balls is contained as B_4C, but trace amounts are present as B_2O_3. The measured amount of B_2O_3 in the as built balls was determined by batch sampling to be ~0.15 w/o of the ball weight.

Some time in January of this year, water was inadvertantly admitted into the PCRV (Abnormal Occurrence Report #50-267/75/7-A). Subsequent to the water ingress, water was removed from the PCRV through the helium purification coolers of the helium purification system from January 23 through February 15. During the process, the moisture level in the PCRV was nearly saturated, in excess of 10,000 ppmv. The reactor pressure was cycled between 50 and 250 psia a number of times essentially creating a pumping action in order to pull or squeeze the water from the PCRV liner insulation. The reactor was then pumped down and evacuated to less than 10 mm of Hg to complete the water removal. This was completed on March 10 and the reactor taken critical on March 17 to establish the integuity of the fuel and core components and insure that the water had been completely removed.

It has been postulated that while the PCRV was being dried out, particclarly during the first phase when the moisture level was high and the reactor pressure cycled, that a significant amount of water saturated helium was introduced into the Reserve Shutdown hopper through the vent to the reactor coolant. During this time, the gas temperature was maintained between 150 and 250°F. At these temperatures, the water vapor leached B_2O_3 out of the Reserve Shutdown balls in the form of boric acid.

$$3H_2O + B_2O_3 \rightarrow 2H_3BO_3 \quad 300°F \leq T > 100°F$$

DESCRIPTION OF OCCURRENCE:

During the modification of the 37 Control Rod Assemblies to minimize the bypass of primary coolant flow from the orifice valve, CRD SN 028 was being converted for use in an outer core region. This conversion requires replacing the control rods and the reserve shutdown balls contained in the RSD hopper. In the outer 18 core regions, reserve shutdown balls containing 40 w/o boron are used instead of those containing 20 w/o boron. After the lower weight boron balls had been removed from the hopper, it was noted that several of these had a white crystal deposit.

This white crystal appeared to be firmly attached to the boron graphite balls and varied significantly in the quantity deposited on each of the balls. In the initial analysis which was later supported by results from a random sample of 500 balls, less than 5 percent had the majority of their surface covered, about 25 percent had noticeable traces, and the remainder had no apparent traces. These white crystals were water soluble.

Later inspection of the reserve shutdown hopper and balls of four other CRD assemblies also showed similar deposits. Not only was the deposit found on the reserve shutdown balls, but the top surface of the hopper had a similar crystalline coating. One of the five hoppers inspected showed traces of the deposit on the side wall of the hopper tangential to the CRD wall. The deposit appears similar in quantity and characteristics for those presently inspected.

CRD SN 028 from core region 13
CRD SN 037 from core region 2
CRD SN 011 from core region 21
CRD SN 021 from core region 30
CRD SN 027 from core region 22

APPARENT CAUSL OF OCCURRENCE:

_____ DESIGN	* Unusual Service Cond. Including Environ.
_____ MANUFACTURE	_____ Component Failure
_____ Installation/Const.	_____ Other (specify)
_____ Operator	_____
_____ Procedure	_____

* See Analysis Section for Detailed description of cause.

ANALYSIS OF OCCURRENCE:

A thorough investigation has been initiated since first observing the crystals to:

1. Identify the chemical composition, form, and quantity of crystals found in the RSD hoppers.

2. Determine the cause and origin of the crystals.

In the saturated environment, some liquid H_3BO_3 settled with water in the bottom of the hopper, while the vapor permeated the entire hopper. Some vapor condensed on the top of the hopper or at the cold wall on the side tangential to the CRD wall. Liquid drops of H_3BO_3 and H_2O fell upon the upper layers of the balls in the hopper and depending upon temperature crystallized at H_3BO_3 or HBO_2.

$$H_3BO_3 \rightarrow HBO_2 \pm H_2O \text{ at } T > 300°F$$

As the reactor coolant was dried out, the crystals remained on the reserve shutdown balls and the hopper wall. During the last stage of PCRV dryout, evacuation to 10 mm of Hg, some H_3BO_3 was converted to the anhydrons boric acid, HBO_2.

This postulation agrees with the distribution of crystalline deposit as seen in the reserve shutdown hoppers on four inspected. But it has been further observed by a laboratory experiment in which a reserve shutdown hopper and the respective conditions were simulated. The results were identical to those already described.

In this experiment, distilled H_2O was vaporized at 250°F below a bed of reserve shutdown balls. The water saturated vapor in the closed system condensed on the top surface (150° to 200°F) and dripped back onto the walls. After about 30 hours the balls were examined and found to have white crystalling deposits spattered on the surface. The system was dried out by venting to the atmosphere. The white spots on the ball surfaces remained and were identified to be H_3BO_3.

Quantitative Evaluation

The simulation experiment demonstrates that boron can be leached by water vapor from B_2O_3 that was present in the balls after manufacture. The total amount of B_{203} present in the PSC reserve shutdown balls (as Manufactured) averaged to be: Boron present as B_2O_3 - 0.15% of the compact weight. This amounts to 60 grams of leachable boron per hopper.

A quantitative analysis was made on the random sample of balls taken from the first reserve shutdown hopper inspected. The results of that analysis are shown below:

Total Boron 20.8 % of ball wgt.

B as HBO_2/H BO_3 on surface	0.1 wt % of ball wgt.
B as B_2O_3 remaining in ball	0.1 wt % of ball wgt.
B as HBO_2 on surface of "worst" ball	0.5 wt % of ball wgt.
B as B_2O_3 remain in "clean" ball	0.1 wt % of ball wgt.

The quantitative analysis showed that most of the B_2O_3 within the balls remained within the balls, thus: only a fraction of the B_2O_3 was leached out to form the crystals observed. In addition, the total boron concentration and analysis of clean balls taken from the same hopper show that no B_4C was converted to a leachable form. At the temperature of interest, no B_4C reaction was expected to take place.

If we assume that boron remaining as B_2O_3 inside the ball was 0.1% of ball weight for all balls in the hopper, and that the original concentration of B as B_2O_3 in the balls was 0.15%, the boron leached out would be 0.05% of 40 kg or 20 gm of

boron per hopper. However, clean balls from the middle of the hopper showed boron remaining as B_2O_3 inside the balls to be 0.15% indicating that boron may not have been leached out of all balls in the hopper. There is also uncertainty in the boron present and B_2O_3 in the original balls because of the variation between manufactured lots. The data definitely show that boron was leached out of the upper and lower levels of balls in the hopper and that the limit of this leached boron was 1/3 of the total leachable boron.

It is estimated that approximately 2-5 grams of boron may be present as crystals on balls and that another 2-5 grams may be deposited as crystals in the hopper. The upper limit of boron present as boric acid crystals in any one hopper is estimated to be 15 grams boron (natural enrichment).

Effect on Performance of RSD System

Since the majority of boron in the balls is present as B_4C (>99%) and it was confirmed in the quantitative analysis that this was not affected, very little of the boron has been removed from the balls. The minimum boron loading in any hopper is 5400 gms and it has been estimated that only 15 gms has been leached out. With this heavy boron bonding, the reserve shutdown column is neutronically black to thermal neutrons and consequently even a 1% loss in boron content would not change the reactivity worth. Therefore, from the reactivity control consideration, no change is expected.

Some tests were done in the laboratory to determine if bonding was possible. Boric acid crystals were grown over a stack of balls by dripping boric acid solution onto them and heating in a furnace. A significant amount of crystals were formed between adjacent balls, but the crystals were so weak that the load was broken with only the slightest movement of the specimen dish. Every attempt to form a strong bond between the balls proved to be negative.

As a final test, it is planned to deliberately drop a loaded bonded with reserve shutdown balls containing the crystals to insure that the performance is not adversely affected. An attempt is being made to select a hopper containing the maximum amount of crystals.

Effect on Core Components and Performance

There is a substantial amount of evidence to believe that the crystals have been pretty much contained to the reserve shutdown hopper.

1. In the quantitative analysis, the boron deposited and present on the surface of the balls agrees closely to that expected from the before and after quantity of B_2O_3 present in the balls.

2. In working on the CRD assembly modification, the only significant amount of crystals noted has been either on the balls , inside the RSD hopper, or in the colder portions of the line leading from the hopper.

3. The reactor was taken critical on March 17, 1975 after the PCRV had been dried out and no significant abnormalities were noted. The expected critical position was within 0.001 Δk of the actural critical position.

However, more tests are being made to investigate any potential transport mechanism from the RSD hopper. In addition, further experiments are in progress to determine the stability of these crystals for a viriety of reactor core environments should the balls be dropped in the core for an emergency shutdown.

CORRECTIVE ACTION:

In addition to demonstrating that the presence of the boric acid crystals in the reserve shutdown hopper does not adversely affect either the RSD system performance or the core performance, action has been taken to prevent further formation of the boric acid crystals. Further formation is prevented by limiting the water content in the PCRV atmosphere. (See corrective action for Abnormal Occurrence Report #50-267/75/7-A).

FAILURE DATA/SIMILAR REPORTED OCCURRENCES:

None

PROGRAMMATIC IMPACT:

None

CODE IMPACT:

None

Submitted By: Roger A. Heller for
Harvey W. Hillyard, Jr.
Technical Services Supervisor

Reviewed By: Larry Brey for
Dick Nirschl
GAC Fuels Div. Representative

Approved By: Frederic E. Swart
Frederic E. Swart
Superintendent, Nuclear Production