

FINAL DRAFT

FSV RESERVE SHUTDOWN ABSORBER MATERIAL EVALUATION

By

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## 1. SUMMARY AND CONCLUSIONS

On November 5, 1984, with the reactor shutdown for control rod drive inspection and maintenance, the Reserve Shutdown System (RSS) hopper of Control Rod Drive and Orifice Assembly (CRDOA) #21 was functionally tested in the Fort St. Vrain (FSV) hot service facility per the requirements of FSV Technical Specification SR 5.1.2c. The results of this test indicated that only one-half of the RSS absorber material in this CRDOA was released. Subsequent investigation determined that much of the material that failed to discharge from the hopper had bonded together as a result of the formation of boric acid crystals on the surface of the material. This event was reported to the NRC as Licensee Event Report (LER) No. 50-267/84-012.

The purpose of this report is to describe the event of November 5, 1984, subsequent investigations of the event, and the causes of the event. Both near-term and long-term corrective actions are presented. A brief review of the FSV reserve shutdown system is also provided.

Extensive analyses were conducted on RSS absorber material from CRDOA #21. It was concluded that the boric acid crystals were formed by moisture entering the RSS hopper and reacting with residual boron oxide in the RSS absorber material. It was concluded that the moisture entered the hopper through the CRDOA vent/purge line by breathing (changes in the primary system helium pressure) and/or by contamination of the purified helium purge system.

Corrective action to be taken consists of three elements. First, the RSS absorber material in all 37 hoppers will be replaced with new material. The new material, manufactured by Advanced Refractory Technologies (ART), has an order of magnitude lower residual boron oxide content than the original RSS absorber material. It is, therefore, much less susceptible to boric acid crystal formation. The new material is manufactured by a somewhat different process and with a different binder material than that used for the original material. Hence, the new absorber material differs from that described in FSAR Appendix A. The difference manifests itself in the new material having a

slightly lower bulk density. Qualification testing has been conducted on the new material to confirm that its lower density is acceptable and that the new material will perform in a manner consistent with all FSAR safety analysis assumptions. Based on the successful results of the testing program, it is concluded that use of the new material does not involve any unreviewed safety question as defined in 10CFR50.59.

Second, an expanded program of RSS functional testing will be incorporated in the FSV Technical Specifications. This testing will include testing of more RSS units during each refueling outage and chemical analyses of RSS absorber material for boron carbide and leachable boron content.

Third, efforts will be made to mitigate or prevent future moisture ingresses which could have an adverse impact on RSS absorber material performance. These efforts are discussed in a separate submittal: PSC's response to the NRC audit team inspection report of October 16, 1984.

As a result of the investigations and corrective actions taken it is concluded that the causes of this event are known and that the RSS can be expected to perform its function reliably during future operation.

## 2. RESERVE SHUTDOWN SYSTEM DESCRIPTION

The reserve shutdown system (RSS) provides a means of inserting sufficient negative reactivity into the core to ensure an adequate core shutdown margin from any reactor operating condition independent of the control rod system. The RSS is described in Section 3.8.3 of the FSAR.

The system features a storage hopper located between the control rod drive mechanism and the thermal shield at the lower end of each refueling penetration. Each hopper contains approximately 1.34 ft<sup>3</sup> of neutron absorber material composed of boronated graphite (graphite mixed with grains of boron carbide (B<sub>4</sub>C)) pressed into nominally spherical form. The RSS absorber material in Regions 1-19 is 7/16 inches in diameter and contains 20 weight percent (w/o) natural boron. The material in Regions 20-37 is 9/16 inches in diameter and contains 40 w/o natural boron. The absorber material is held inside the hopper by a graphite rupture disk.

A steel guide tube extends from the underside of each hopper to the top control reflector block of the associated core region. The guide tube engages the top reflector block, forming a clear passageway for the absorber material to fall from the hopper, through the guide tube, and into the core upon rupture of the rupture disk. The RSS absorber material can be recovered from the core after its release by use of a special vacuum tool.

Rupture of the hopper rupture disk and release of the RSS absorber material into the core is accomplished by pressurizing the hopper with helium to pressures well above primary coolant pressure. Each hopper is connected to a separate high pressure helium bottle (2200 psi nominal) by a pressurizing line that allows helium flow from the bottle into the hopper immediately above the rupture disk. These bottles have an alarm system associated with them that will actuate when the bottle pressure drops below about 1640 psig, at which time the bottles are replaced.

The RSS is designed to provide sufficient negative reactivity control to achieve hot shutdown conditions from any operating condition without movement of control rods. This condition can be met with two of the 37 RSS hoppers inoperable, providing for a total negative reactivity insertion of at least 0.088  $\Delta k$  in the equilibrium core.

### 3. RSS ABSORBER MATERIAL BONDING

#### 3.1. RSS FUNCTIONAL TESTING

FSV Technical Specification SR 5.1.2c requires off-line functional testing of a reserve shutdown system assembly to be performed in the hot service facility following each of the first five refueling cycles and at two cycle intervals thereafter. These tests consist of pressurizing the RSS hopper to the point of rupturing the disk and releasing the RSS absorber material.

On June 23, 1984, with reactor power at 23%, the plant protective system initiated an automatic scram upon sensing higher than normal pressure in the PCRV. Prior to the high pressure trip, an orderly shutdown from 40% power was in progress due to high primary coolant moisture levels. During the scram, 6 of the 37 control rod pairs failed to automatically insert. The six rod pairs were manually driven into the core within 20 minutes following the event. This event was reported to the NRC as Licensee Event Report (LER) No. 50-267/84-008 (Ref. 1).

Because moisture can potentially have an adverse effect upon the absorber material in the RSS hoppers (Refs. 2 and 3), the NRC requested that PSC perform the tests governed by SR 5.1.2c on two RSS units, one containing 20 w/o boron and one containing 40 w/o boron. The two shutdown hoppers selected for testing were CRDOA #26 (20 w/o boron) and CRDOA #21 (40 w/o boron).

During the testing of CRDOA #26 (20 w/o boron) all of the RSS absorber material was released from the hopper. However, during testing conducted on November 5, 1984, it was discovered that only about one-half of the 40 w/o boron RSS absorber material in CRDOA #21 was discharged from the hopper assembly. This event was reported to the NRC as LER No. 50-267/84-012 (Ref. 4).



An investigation was initiated to determine why a portion of the RSS absorber material was not released. Maintenance personnel performed a visual examination of the hopper internals using a boroscope. Examinations indicated that the rupture disk had ruptured cleanly, and the absorber material in the bottom half of the hopper had discharged. When the RSS hopper fill plug was removed, the absorber material at the top of the hopper was found to be in essentially normal condition. However, the absorber material in the middle of the hopper was found to be bonded together. The bonding of the material resulted in the material "bridging" across the middle of the hopper and being unable to fall to the bottom of the hopper and into the reactor core.

### 3.2. CAUSE OF RSS ABSORBER MATERIAL BONDING

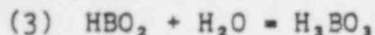
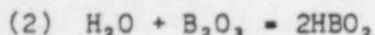
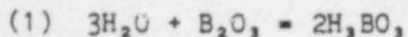
Samples of RSS absorber material (balls) were taken from the top, middle and bottom of the hopper of CRDOA #21 for examination and analysis. Crystals were found on occasional balls removed from the top and bottom of the hopper and extensive crystal growth was found on the balls from the middle section. Also, in the middle section several large clumps of RSS balls were found firmly stuck together by the crystalline substance. RSS balls from CRDOA #26 were also taken for analysis, although their appearance was completely normal.

RSS balls removed from CRDOA #21 and 26 were extensively analyzed to determine the composition of the crystals and the manner in which they were formed, and to determine if significant oxidation of  $B_4C$  had occurred. Scanning Electron Microscopy (SEM) and Debye-Scherrer X-ray analysis was performed on the crystals to determine their chemical constitution and possible source, and chemical analyses were performed to determine leachable boron and total boron content.

The Debye-Scherrer analysis of crystals obtained from the agglomerated balls in CRDOA #21 showed the crystals to be pure anhydrous boric acid,  $HBO_2$ . This is consistent with the observation of cubic crystals in the SEM. Small amounts of  $HBO_2$  would be expected since the as-manufactured balls were allowed by specification to contain up to 1% by weight of boric oxide,  $B_2O_3$ . The



boric acids (e.g., anhydrous, or metaboric acid,  $\text{HBO}_2$ , and orthoboric acid,  $\text{H}_3\text{BO}_3$ ) are hydrated boric oxide. The chemistry of the reactions of interest is:



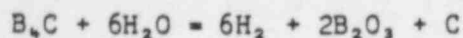
The boric acids,  $\text{HBO}_2$  and  $\text{H}_3\text{BO}_3$ , are both volatile at temperatures above  $212^\circ\text{F}$ , particularly in the presence of water vapor. Boric oxide is volatile in dry gas at temperatures above  $1800^\circ\text{F}$ .

The final step in the RSS absorber material manufacturing process is high temperature heat treating at temperatures around  $3400^\circ\text{F}$ . This step reduces the oxide content to low values and eliminates virtually all volatile boric acids. Small amounts of boric oxide remain (perhaps because of oxidation during cooldown), however, and product specifications are necessary to ensure the oxide content is acceptably low. In the case of the original RSS absorber material, which was installed in the reactor in 1973 and is still in place today, the procurement specification allowed up to 1.0% by weight of boric oxide, (i.e., one percent of the total RSS ball weight).

Based on the original specifications, a hopper containing 80 lbs of absorber material could contain up to 0.8 lbs of  $\text{B}_2\text{O}_3$ . Since the hoppers are always relatively cool, i.e., less than about  $700^\circ\text{F}$ , this  $\text{B}_2\text{O}_3$  would be immobile because of its low volatility. In the presence of moisture, however, boric acids would form and tend to volatilize from the bottom of the hopper where it is relatively hot ( $700^\circ\text{F}$ ) and condense in cooler portions of the hopper. At the top of the hopper the temperature is around  $200^\circ\text{F}$ . It is believed that water vapor or perhaps some liquid water entered the hopper of CRDOA #21 and reacted with the boric oxide to form boric acid. This reaction most likely occurred in the bottom of the hopper where the ambient temperature is highest and where the water entered. Over an extended period of time (the hoppers have been loaded since 1973) the condensation and growth of boric acid

crystals would occur in the most favorable temperature zone of the hopper. This appears to be the middle of the hopper where during reactor operation temperatures are around 300 to 500°F.

It is also possible that over an extended period of time, oxidation of the B<sub>4</sub>C could contribute some additional boric oxide per the following reaction:



Tests at GA on a bed of RSS balls exposed to 0.1 atm of water vapor at 700°F (simulating the highest expected temperature in the hopper during reactor operation) indicate that less than 1% of the B<sub>4</sub>C in the bottom of the hopper could have converted to oxide. Therefore, oxidation could not have significantly affected the B<sub>4</sub>C content of the RSS absorber material in the hopper.

Assuming the bottom 1/4 of the hopper (where the temperature range is 600 to 700°F) experienced 1% oxidation of the B<sub>4</sub>C, about 0.1 lbs of boric oxide would be formed in the hopper, which could already contain up to 0.8 lb. It is concluded, therefore, that although oxidation of B<sub>4</sub>C could have occurred, it was not the major contributor to the oxide or boric acid content of the hopper.

There are three ways that moisture could get into the RSS hoppers. In each case, the moisture would enter at the bottom of the hopper. First, water vapor in the primary coolant could diffuse either through the graphite rupture disk and/or through the CRDOA vent/purge line, which communicates with the primary system. Second, water vapor could get in by what will be referred to here as "breathing." Breathing occurs via the vent/purge line due to changes in the primary system helium pressure. Third, water vapor, or in fact liquid water, may have gotten into the purified helium header and hence into the RSS hoppers.

Based upon the information available at this time, the first possibility seems to be the most unlikely. This thesis is based upon the following reasoning. First, diffusion calculations have shown that no significant

diffusion of water vapor into the hopper can occur through the relatively impervious graphite rupture disk or through the 9-ft-long vent tube. Second, gamma counting the RSS absorber material revealed no fission products. It is reasoned that if diffusion from the primary coolant occurred, then during reactor operation diffusion of radioactive xenon and krypton should have also occurred, leading to deposition and buildup of long lived daughter products, such as Cs-137 whose half-life is 30 yrs. Since none was found, diffusion is considered unlikely as the means of water getting into the RSS hopper.

However, the absence of Cs-137 in the hoppers does not rule out the breathing phenomenon. Breathing due to pressure changes has occurred numerous times during reactor shutdowns when water vapor concentration in the helium is often high and when the fission gases are not present. Calculations show that the breathing phenomena could account for a large portion of the moisture necessary to react with the available  $B_2O_3$ . For example, assuming 1 w/o  $B_2O_3$ , 90 grams of water is all that is required to react with all the  $B_2O_3$  in a hopper. Assuming a water vapor concentration of 100,000 ppmv (at 1 atm of total pressure), each pressurization of the PCRV in which the pressure doubles could introduce about 1 g of  $H_2O$  into each hopper. However, the total amount of water that could be introduced by each such pressurization is limited by the CRDOA purge flow, which is activated at a PCRV pressure of about 50 psia and precludes any additional moist primary coolant from entering the hopper. Therefore, pressurization from near atmospheric (~12 psia) to 50 psia or more could introduce about 2 g of water into each hopper. If it is further assumed that all the water chemically reacts inside the hopper, then a total of 45 such pressurizations of the PCRV could introduce sufficient water (90 g) into each hopper to react with all the  $B_2O_3$  present.

It may be concluded from this scoping calculation that if breathing occurs during periods of very high moisture content, then a substantial portion of the water necessary to react with all  $B_2O_3$  in the hopper could be introduced.

The third possible source of water is through the purified helium purge system. Scenarios which could possibly result in water being introduced into all, or selected, hoppers have been investigated. The results of the

investigation are reported in PSC's response to the NRC audit team inspection report of October 16, 1984.

### 3.3. SIMILARITY TO PREVIOUS EVENT

The recent observation of boric acid crystals on the RSS absorber material from CRDOA #21 is quite similar to observations made in 1975, when boric acid crystals were discovered on RSS absorber material in CRDOA #28, 37, 11, 21, and 27 following the ingress of more than 4,000 gallons of water into the PCRV (Ref. 2). The crystals observed in 1975 had an almost identical appearance with those observed in 1984. However, in 1975 no bridging occurred, and the absorber material dropped cleanly during the functional test. Investigations at that time led to similar conclusions, namely that water entering the bottom of the hopper reacted with residual boric oxide forming boric acid, which volatilized and condensed or recrystallized in cooler parts of the hopper. Two species of crystals were found, namely  $H_3BO_3$  and  $HBO_2$ , the particular species depending upon the temperature of crystallization and the water vapor concentration.

The investigations in 1975 included an experiment in which a bed of RSS balls were heated from below with boiling water. Steam from the water leached boric oxide from the bottom layers of balls which condensed as orthoboric acid ( $H_3BO_3$ ) on the upper layers. The balls were found to be bonded together; however, the slightest movement or vibration easily separated them.

The principle differences between the 1975 and 1984 events are: (1) the absorber material has now spent an additional 9 years in the hoppers and (2) prior to the 1975 event the reactor had not yet started up; therefore, the time-temperature-moisture histories are quite different.

### 3.4. BORON CONTENT OF ORIGINAL RSS ABSORBER MATERIAL

A number of chemical analyses for leachable boron and total boron content were also performed on RSS absorber material from the hoppers of CRDOA #21 and 26. These were done to determine whether oxidation of  $B_4C$  had occurred during the last ~12 years in the hopper and whether any significant loss of boron

from the material had occurred. The analyses were performed independently at GA Technologies (GA) and at Advanced Refractory Technologies (ART). For RSS absorber material taken from CRDOA #21, GA measured 0.65 grams B/cm<sup>3</sup> and ART measured 0.67 grams B/cm<sup>3</sup>. These results are in excellent agreement with the specified value of  $0.66 \pm 0.03$  gm B/cm<sup>3</sup> for 40 w/o material. For RSS absorber material taken from CRDOA #26, GA measured 0.31 gm B/cm<sup>3</sup> and ART measured 0.35 gm B/cm<sup>3</sup>. These measurements are also in excellent agreement with the specified value for 20 w/o material, i.e.,  $0.32 \pm 0.03$  gm B/cm<sup>3</sup>.

Thus, it is concluded that there has been no measurable loss of B<sub>4</sub>C due to oxidation (followed by hydrolysis) in either CRDOA #21 or 26. This is a significant finding in that it means that if the crystallized RSS absorber material is dropped into the reactor, it will contribute the required negative reactivity as assumed in the FSAR. (The RSS absorber material in an RSS channel is neutronically black to thermal neutrons. It would require more than a 10% loss of boron to change the reactivity worth of the reserve shutdown system by 1% of its original worth.)

#### 4. CORRECTIVE ACTION

##### 4.1. REPLACEMENT OF RSS ABSORBER MATERIAL

The RSS absorber material discharged from CRDOA #26, during its successful functional test, was in excellent condition; it had the same appearance as it did when originally procured. Therefore, there is no evidence that all RSS hoppers have been affected by the formation of boric acid crystals. Nevertheless, all hoppers will be emptied, the original RSS absorber material will be discarded, and the hoppers will be reloaded with fresh absorber material. This will be accomplished during the refurbishment of each CRDOA prior to reactor re-start.

##### 4.1.1. Replacement RSS Absorber Material Fabrication

The RSS absorber material is fabricated from B<sub>4</sub>C powder, graphite flour, and a binder. The original material was fabricated by Union Carbide Corporation (UCC) using a hot molding process with coal tar pitch (Barret #30) as the binder. Coal tar pitch is now known to be a source of carcinogens; therefore, a different binder and molding process was employed in fabricating the new material. The new material was manufactured by Advanced Refractory Technologies (ART) by cold molding using an organic binder system or a phenolic resin as the binder. In this respect, the new material is different from that described in FSAR Appendix A. The organic binder system consisted of Norlig NH (supplied by Reed Lignon Corporation, a subsidiary of American Can Co.) and Avicel (supplied by FMC Corporation). The phenolic resin used was Sherman-Williams, 60% solids. All of these binders are reduced to a carbonaceous residue at the temperatures used in the final heat treatment of the RSS material. Some of the new material was manufactured in 1982 by Eagle-Pitcher Industries, the Specialty Materials Division of which was subsequently purchased by ART. The remainder was made by ART in 1982 to 1985.



The original UCC-fabricated RSS absorber material was final heat treated in an inert atmosphere at  $3400 \pm 100^{\circ}\text{F}$  for a minimum of two hours. The absorber material fabricated in 1982 and 1983 by ART (or Eagle-Picher Industries) was heat treated by baking in an inert atmosphere at a target temperature of  $3956^{\circ}\text{F}$  ( $2180^{\circ}\text{C}$ ) for more than 15 minutes. Some early production lots were heat treated at a lower temperature, i.e.,  $3812^{\circ}\text{F}$  ( $2100^{\circ}\text{C}$ ), then refired at the target temperature of  $3956^{\circ}\text{F}$  ( $2180^{\circ}\text{C}$ ) to enhance their impact strength. The RSS absorber material fabricated by ART in 1984 and 1985 was final heat treated in an inert atmosphere at a temperature between  $2600^{\circ}\text{F}$  and  $3500^{\circ}\text{F}$  for a minimum time of 60 minutes, of which at least 15 minutes were at  $3400 \pm 100^{\circ}\text{F}$ . In each of the above cases, the final heat treatment accomplished the intended objectives of (1) reducing impurity levels to ensure being within product specification limits, (2) stabilizing final product volume, and (3) yielding a material strength meeting the product specification. Measurements and testing on the final product material demonstrated that these objectives were indeed achieved.

#### 4.1.2. Replacement RSS Absorber Material Characteristics

The RSS absorber material in the hoppers at the time of the recent functional tests had been in place since 1973. The replacement material is expected to have a relatively longer reliable functional lifetime. That is, it is relatively less susceptible to moisture induced agglomeration by the hydrolysis of residual (initial)  $\text{B}_2\text{O}_3$ . The basis for this expectation is founded upon the observation that the initial  $\text{B}_2\text{O}_3$  content of the new absorber material is very much lower than the initial  $\text{B}_2\text{O}_3$  content of the original material.

A review of the quality assurance records for RSS absorber material manufacture shows that the initial  $\text{B}_2\text{O}_3$  content of the replacement material is lower by a factor of 20 for the 20 w/o material and by a factor of 10 for the 40 w/o material (See Appendix A). This order of magnitude reduction in initial  $\text{B}_2\text{O}_3$  concentration in the new material contributes to it having a longer reliable functional lifetime relative to the original material.



The new RSS absorber material differs from the original RSS material in that its bulk density is slightly lower. The new material bulk density is on the order of ~1.4 to ~1.6 gm/cc as compared to the original material bulk density of ~1.7 to ~1.8 gm/cc. While the new material meets the specification requirements for impact strength, it was considered prudent, in view of the lower bulk density of the material, to test the new material's high temperature structural integrity. Accordingly, both the 20 w/o and 40 w/o material manufactured by ART were tested for plastic deformation at high temperatures. Both RSS material made using phenolic resin as binder as well as material made using the organic binders were fully tested. | 1

The RSS absorber material high temperature strength is an important consideration because under the conditions of Design Basis Accident No. 1, permanent loss of forced circulation (LOFC), the column of RSS absorber material experiences very high temperatures (up to 5400°F) after it is released into the core. These temperatures, coupled with the fact that the weight of the material on the top of the column will provide compressive loads to the material below, can lead to compaction (i.e., slumping) of the material and hence a reduction in the height of the column of absorber material. In the criticality calculations that support the FSAR LOFC accident analysis, it was assumed that the RSS absorber material filled the RSS channel to a height even with the top of the active core. The RSS hoppers each contain a volume of absorber material sufficient to fill each RSS channel to a height of just over 22 in. above the top of the active core. Thus, slumping of the column of RSS absorber material up to 22 in. would be acceptable and within the bounds of what was assumed in the FSAR. As discussed in FSAR Appendix D, the measured high temperature strength of the UCC absorber material was such that the RSS column slumping would be negligible.

High temperature qualification testing was performed to ascertain the degree of slumping that could occur with the ART material. Samples of both the 20 w/o and 40 w/o material manufactured by ART were tested in the same manner as the original RSS absorber material (Ref. 5). This testing was conducted at GA Technologies using a high temperature induction furnace capable of extended operation at temperatures up to around 6000°F, and a resistance furnace capable of extended operation at temperatures up to about 4550°F.

At temperatures below  $-4352^{\circ}\text{F}$  ( $-2400^{\circ}\text{C}$ ), the ART material was found to slump a negligible amount, i.e., 0-2%. This is as expected since the eutectic temperatures for boron concentrations below 70 w/o is  $-4352^{\circ}\text{F}$  ( $-2400^{\circ}\text{C}$ ). Below this temperature the whole  $\text{B}_2\text{C}$ -graphite system is solid, and thus one expects good stability up to the eutectic temperature. The 40 w/o RSS absorber material is used only in the outer 18 refueling regions of the FSV core, where the temperatures calculated for the hypothesized LOFC accident do not reach  $-4352^{\circ}\text{F}$  ( $2400^{\circ}\text{C}$ ). Thus, the 40 w/o ART material is clearly acceptable for use in the FSV reactor.

The 20 w/o RSS absorber material is used in the inner 19 refueling regions. Of these, the central refueling region (refueling region No. 1) experiences the most severe LOFC temperatures; the maximum calculated temperature for the LOFC accident is  $5400^{\circ}\text{F}$ . Hence, the 20 w/o ART absorber material was tested over a temperature range of  $-4440^{\circ}\text{F}$  to  $5970^{\circ}\text{F}$  ( $-2450^{\circ}\text{C}$  to  $3300^{\circ}\text{C}$ ). Over this range of temperatures the ART material slumped more than that reported for the UCC material in the FSAR. However, based upon the measured temperature dependence of the magnitude of the slumping in conjunction with the calculated maximum core axial temperature distribution given in the FSAR for the LOFC accident, the maximum slump of the RSS column as a whole was determined to be about 16 in., which is less than the 22 in. which would result in the top of the RSS column falling below the top of the active core. Thus, the impact of the slumping of a column of ART absorber material is fully within the bounds of what was assumed in the FSAR LOFC accident analysis. This is particularly true in view of the fact that the compressive load used during these high temperature tests was larger than that which the absorber material would actually experience. Hence, the ART-manufactured 20 w/o material has been shown to be acceptable for use in the FSV reactor.

#### 4.1.3. Silver-Colored Spots

An inspection of replacement 20 w/o RSS absorber material on hand in the Fort St. Vrain warehouse revealed occasional random silver-colored spots on the surfaces of some of the balls. This material was manufactured in 1982 and 1983 by Advanced Refractory Technologies, Inc. The silver-colored spots,

typically 1/8-in. diam, have been observed only on some of the material that was subjected to a second heat treatment (i.e., was re-fired) to enhance the material's impact strength. Only a relatively few production lots were re-fired in this manner.

Because of the earlier observation of boric acid crystals on the agglomerated absorber material from CRDOA #21, there was initially a concern that these silver-colored spots were boron oxide or boric acid crystals. This concern was subsequently found to be unwarranted. The spots were analyzed for oxide content by leaching and by scanning electron microscopy followed by energy dispersive X-ray techniques. These analyses showed that the silver-colored spots are not boric oxide nor boric acid crystals. Rather, the spots are in fact an allotrope of boron carbide. Boron carbide crystallization on the surface of the balls occurs whenever they are heated to or near the melting point of the  $B_4C$ -C eutectic,  $\sim 4334^\circ F$ . The spots are caused by recrystallization of boron carbide during cooldown.

The boron dispersion in the RSS balls with silver-colored spots was also analyzed to confirm that the boron was distributed uniformly throughout the ball. Optical micrographs and ion probe maps were examined to make this determination. Based upon the examination of these data it was concluded that the boron is indeed uniformly dispersed in a manner completely within the bounds of what was assumed for the reactor physics calculations in support of FSAR safety analyses.

Based upon the above evaluations of the physical and chemical state of the RSS absorber material with silver-colored spots, it was concluded that the performance of this material in the reactor will be acceptable and that the silver-colored spots will have no adverse impact upon its performance.

#### 4.1.4 CONCLUSION

The boron balls, manufactured in 1982 - 1985 under their respective specifications, do not involve an unreviewed safety question.

An evaluation was made to determine whether the probability of an occurrence or the consequences of an accident as previously analyzed in the FSAR was increased. In addition, the probability of occurrence or the consequences of a malfunction of equipment important to safety was also evaluated. In the case of RSS material manufactured in 1982 and 1983, five changes were examined. These are outlined below.

- (1) BORON CONTENT: Since the density has been lowered, the boron wt% of the sphere has been increased slightly, maintaining the boron content of the sphere. The increase in tolerance for boron density does not affect the total amount of boron to be inserted into the core. The average boron density from the lot would remain constant; thus the proper amount of boron (as assumed in an LOFC, FSAR sections 14.10 and D.1, and in a Rod Withdrawal Accident, FSAR Section 14.2) can be deposited in the core. The reactivity worth (FSAR 3.5.1) of the reserve shutdown system has not been changed.
- (2) CHEMICAL PURITY OF FINISHED PRODUCT: The specification requires metallic impurities to be less than 1.5%. Temperature strength tests on balls containing 2 wt% indicate they are acceptable for use in the FSV reactor. The presence of approximately 1.5% metallic impurities will have no effect on the performance of the material.
- (3) DENSITY CHANGE: The density of the boron balls will be lowered to 1.35 g/cc for the 7/16" balls and to 1.50 g/cc for the 9/16" balls. The flow of the balls and the insertion of the necessary boron upon activation of the Reserve Shutdown System remains unchanged. The size of the balls or columns has not changed; therefore, the possibility of bridging discussed in Section 3.8.3.2 (and FSAR Section A.10) has not been increased.
- (4) BINDER: Eliminating the possibility of using a coal tar pitch binder is an effort by the vendor to create a stronger, better product. This change was added after problems were occurring with the coal tar pitch binder which is a carcinogenic substance.
- (5) HEAT TREATMENT: The increased temperatures for heat treatment of the balls is also an effort to increase the strength of the balls and therefore make a better product. It was determined that the high temperatures do not affect the ability of the balls to perform their absorption function when dispersed into the core, and shut the



reactor down in an emergency situation. The increased heat treatment temperatures do not degrade the thermal characteristics of a column of boron balls in the core (LOFC and Rod Withdrawal Accidents).

In the case of RSS material manufactured in 1984 and 1985, two further changes were made. The amount of allowable B2O3 was decreased, and the heat treatment was changed. All of the aforementioned changes are in the manufacturing process of the RSS material and do not impact FSAR accidents or their respective consequences. FSAR Section 3.8.3 evaluates the consequences of a boron ball from the reserve shutdown system being retained in the core or entering a helium circulator or steam generator. The probability of these two accidents occurring is not increased by a change in the specifications to the boron balls. The size and final boron carbide (B4C) content of the balls has not been changed. The final tests and chemical analyses have not been changed. If a boron ball were to become lodged somewhere in a steam generator, the result of the chemical reactions with the steam generator materials would remain the same since the boron (and graphite) concentrations in the balls has not changed. Other consequences of a boron ball in steam generator or helium circulator (e.g. balls in contact with steam generator tubes) would not increase since the size and chemical composition is similar.

The consequences of a Rod Withdrawal Accident (FSAR Section 14.2) or a Loss of Forced Cooling Accident (FSAR Sections 14.10 and D.1), where it is required to activate the reserve shutdown system, would not be increased. The reactivity worth of the reserve shutdown system, has not been changed and therefore is still sufficient to shut the reactor down and hold it at a subcritical level. The boron balls will still maintain the required level of integrity when subjected to the high temperature encountered during an LOFC.

The ball size has not been changed and the ball diameter to duct size ratio discussed in FSAR Section 3.8.2 are not affected. Therefore, the possibility of balls lodging in the channels to the reactor core has not been increased.

In the case of all approved RSS material manufactured from 1982-1985, the changes made to the manufacturing specifications do not create the possibility of an accident or malfunction of a different type than any evaluated previously in the FSAR. The concentrations of B2O3 are less than the original RSS material. B2O3 can form volatile boric acids on the ball under high temperature and high moisture conditions, which can form a white crystal which could cause the boron balls to stick together. Therefore, decreasing the impurity concentration would decrease the possibility of the reserve shutdown system malfunctioning due to the boron balls sticking together.

The heat treatment temperature change will not have adverse effects on the boron balls. The ball strength is still adequately increased and the strength is verified by the impact tests required in the specifications. Heat treatment will still drive out impurities and reduce volume changes. The decrease in density will not impose greater loads on the Reserve Shutdown system. The Specification changes do not change the design intent of the boron balls, degrade their thermal or neutronic characteristics, or affect the operation of the reserve shutdown system.

In conclusion, samples of RSS material manufactured from 82-85 have undergone qualification testing at G.A. Technologies. The balls were placed in a furnace and subjected to high temperatures in order to emulate hot loss-of forced circulation accident conditions. The tests showed that the performance of the balls was acceptable and that the slumping of a column of ART absorber material is fully within the bounds of what was assumed in the FSAR LOFC accident analysis. Based upon the total evaluation of the new RSS absorber material described in this section, it is concluded that the new absorber material is fully acceptable for use and does not constitute an unreviewed safety question as defined in 10CFR50.59.

#### 4.2. LONG-TERM CORRECTIVE ACTION

While near-term corrective action consists of replacing the original RSS absorber material in each hopper with new material, long-term corrective action to prevent recurrence is also required. In this regard, PSC's efforts are directed at RSS surveillance and at mitigation or prevention of moisture ingress. Efforts to mitigate or prevent moisture ingress are discussed in PSC's response to the NRC audit team inspection report of October 16, 1984.

With regard to RSS surveillance, PSC is committing to an expanded program. Technical Specification SR 5.1.2c currently requires off-line functional testing of one RSS assembly to be performed following each of the first five refueling cycles and at two cycle intervals thereafter. PSC will expand this surveillance program to include functional testing of two RSS assemblies, one containing 20 w/o boronated material and one containing 40 w/o boronated material, at the end of every refueling cycle up to the end of plant life. The absorber material from the tested hoppers will be visually examined for evidence of boric acid crystal formation and chemically analyzed for boron carbide and leachable boron content. Failure of an RSS assembly to perform acceptably during functional testing or evidence of extensive boric acid crystal formation will be reported to the NRC.

Technical Specification SR 5.1.2c will be changed to include these new surveillance commitments. The revised SR 5.1.2c will be included in the Technical Specification Upgrade Program acceptance review package which is currently scheduled for submittal to the NRC on April 1, 1985 (Ref. 6).



## 5. REFERENCES

1. Letter, Don Warembourg (PSC) to E. H. Johnson (NRC), P-84227, July 23, 1984.
2. Fort St. Vrain Unusual Event Report No. 50-267/75/18A, December 15, 1975.
3. Letter, Robert A. Clark (NRC) to C. K. Millen (PSC), June 18, 1976 (Operating License Amendment No. 13).
4. Letter, J. W. Gahm (PSC) to Robert Martin (NRC), P-84515, December 4, 1984.
5. "Public Service Company of Colorado 330-MW(e) High-Temperature Gas-Cooled Reactor Research and Development Program, Quarterly Progress Report for the Period Ending December 31, 1969," GA-9875, January 30, 1970.
6. Letter, O. R. Lee (PSC) to Eric H. Johnson (NRC), "Technical Specification Upgrade Program," P-84530, December 14, 1984.

APPENDIX A  
RESIDUAL  $B_2O_3$  CONTENT OF RSS ABSORBER MATERIAL

As discussed in Section 4.1.2, a review of the quality assurance records for RSS absorber material manufacture shows that the residual  $B_2O_3$  content of the replacement material manufactured by ART is lower than that of the original material manufactured by UCC. The nominal residual  $B_2O_3$  content is summarized in Table A-1, which shows that the ART material  $B_2O_3$  content is lower by about a factor of 20 for the 20 w/o material and a factor of 10 for the 40 w/o material.

As noted in Table A-1, the residual  $B_2O_3$  content is expressed as a percent of total RSS ball weight. It should be noted that in report GA-A13742, "Status Report on Reserve Shutdown System," which was transmitted to NRC in 1975 via Ref. 2, residual  $B_2O_3$  levels in UCC material were reported in terms of the weight percent (w/o) of boron in the form of  $B_2O_3$ . Thus, for 20 w/o absorber material a residual  $B_2O_3$  concentration of 0.48 w/o was reported as being 0.15 w/o boron in the form of  $B_2O_3$ . In some instances in GA-A13742, this quantity of  $B_2O_3$  was simply (and misleadingly) reported as being 0.15 w/o. The corresponding actual  $B_2O_3$  level of 0.48 w/o is consistent with the value reported in Table A-1 for 20 w/o material (i.e., 0.46 w/o).

TABLE A-1  
B<sub>2</sub>O<sub>3</sub> RESIDUAL CONTENT (w/o)\*

	20 w/o Boron	40 w/o Boron
UCC material	0.459	0.815
ART material**	0.021	0.068

\*Percent of total RSS ball weight.

\*\*Material manufactured in 1982-83.