COMBUSTION ENGINEERING 0-MCC-86-007

FT. CALHOUN
SECONDARY CHEMISTRY REVIEW

DECEMBER, 1986

QA Status: Verified

The safety related design information combined in this document has been reviewed and satisfies (where applicable) the items contained on check-list(s) 2, ______, and ______ of the Quality Assurance of Design Manual. This review is so certified.

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Fort Calhoun Secondary Chemistry Review

Introduction

Following the May, 1984, tube rupture incident, the reactor coolant inlet temperature, Tc, at Fort Calhoun was decreased from the original operating value of 545°F to the range 537-538°F. Now, after nearly two cycles of operation at reduced temperature, the staff of Fort Calhoun has proposed to return the reactor coolant inlet temperature to the original operating value. Combustion Engineering, Inc. has been requested to endorse this proposed action. This report has been prepared to provide the basis for such endorsement.

The rationale for the original action of reducing temperature was an implied correlation between ID-initiated Coriou SCC which is highly dependent on temperature and OD-initiated caustic SCC. All chemical and physical processes depend on temperature to a greater or lesser extent; however, in view of the following discussion, CE considers this reduction in temperature, conservative.

OD-initiated caustic SCC along with IGSCC and the related phenomenon, IGA, are affected by impurities which concentrate in various locations along the OD of alloy 600 tubing. For this reason Combustion Engineering, Inc. considered it prudent to evaluate the quantities and characteristics of impurities which have concentrated in the various crevices and other dry-out locations in the Fort Calhoun steam generators.

Description of Review

In this review, an attempt was made to form a qualitative judgement regarding whether there had been an improvement (i.e. a reduction) in impurity hideout since the tube rupture incident. This was accomplished by observing the recovery of impurities during four gradual shutdowns and two trips. Of these incidents, one gradual shutdown occurred prior to the tube rupture and the remainder were subsequent. The circumstances surrounding these shutdowns varied, but in most cases blowdown was continued at between 10,000 - 15,000 lb./hr. per generator. The events reviewed are listed in Table 1. So far as CE is aware, these were the only shutdowns from one year prior to the tube rupture incident to the present.

Table 1

3-3-84	Gradual Shutdown
5-16-84	Tube Rupture Incident
11-19-84	Gradual Shutdown
3-16-85	Gradual Shutdown
9-28-85	Gradual Shutdown
7-1-86	Trip
8-1-86	Trip

Results

Data reviewed in this effort consisted of copies of daily chemistry logs for the various power reductions described above. In most cases, data were insufficient for anion-cation balances as needed for a complete description of the system. For this reason, the evaluation of chemistry as described below must be regarded as only qualitative. Pertinent data from this review are tabulated in Table 2.

The most striking observation in this chemistry review, when comparing pre-tube rupture and post-tube rupture data, is the reduction in the quantity of sodium which recovered during powerdowns or trips. While sodium had been as high as 9.6 ppm. and 12.2 ppm. in steam generators A and B, respectively, prior to the tube rupture incident, sodium recovery subsequently was in the range of 0.072 ppm. to 0.88 ppm. The values of 3.9 ppm. and 12.9 ppm. which recovered during the trip of July 1, 1986, are considered spurious in view of subsequent analyses which listed sodium concentrations of approximately 1 ppm. within hours. Furthermore, conductivity values associated with these concentrations were very low (5.45 μmhos/cm. and 5.80 μmhos/cm. in steam generators A and B respectively) suggestive of sodium concentratons only in the range of 0.5 - 1 ppm.

In contrast to the behavior of sodium, silica recovery levels since the tube rupture have declined only slightly - at best by a factor of two. In all likelihood these relatively constant silica concentrations are a consequence of very slow dissolution of silica precipitates such as $Mg_3Si_4O_{10}(OH)_2$ and various sodium silicates during shutdowns and outages. Presumably these precipitates had formed over the lifetime of plant operation prior to the tube rupture. The two and a half years of plant operation with improved chemistry control subsequent to the tube rupture event has not removed the silica from the generators. Silica, however is important as will be demonstrated below, because it, together with sodium, determines the concentration of OH^- in crevices.

Table 2

Date	3/3/84	11/19/84	3/16/85	9/28/85	7/1/86	8/1/86
Na, ppm. S/G A	9.6	0.523	0.260	0.180	3.9*	0.310
S/G B	12.2	0.539	0.270	0.165	12.9*	0.750
Cl, ppm. S/G A	0.180	0.030	0.226	0.285	-	0.070
S/G B	0.120	0.060	0.236	0.330	-	0.090
SO_4, ppm. S/G A	-	-	-	0.220	-	0.310
S/G B	-	-	-	0.215	-	0.280
SiO_2, ppm. S/G A	2.29	3.13	2.09	1.44	1.18	1.49
S/G B	4.39	3.74	2.26	1.62	1.48	1.64
k, µmhos/cm. S/G A	61.0	13.0	7.90	4.00	5.45	9.6
S/G B	72.0	13.5	8.30	4.45	5.80	10.1

* These values are considered spurious in view of the associated conductivity values as well as subsequent analyses within hours which indicated sodium concentrations approximately 1 ppm.

A major change in secondary chemistry management, which occurred at the beginning this current cycle, was the on-line neutralization effort utilizing boric acid for control of denting. Regarding other secondary chemistry parameters, boric acid has the greatest effect on pH. Very little effect, if any would be anticipated for those parameters tabulated in Table 2.

Discussion

While quantitative chemical balances (anions vs. cations) could not be perfomed due to the limited analytical data available, the trends described previously are significant. Most notable are the dramatic decline in sodium recovery and the associated decline in conductivity along with the slight decline in silica.

With regard to what is known of SCC, the most significant improvements are 1.) the reduction in sodium hideout, and 2.) the buffering effect expected from boric acid. Sodium is a direct indication of the possible presence of sodium hydroxide, caustic, in those regions where impurities concentrate. In fact, after the powerdown of 3/3/84, when such high concentrations of sodium were reported, 6.8 ppm. of free hydroxide were reported in the B steam generator. Elevated sodium along with the free hydroxide are clear indications of the presence of caustic in the hideout regions of the steam generator. Reduced concentrtations of sodium are a clear indication of a reduction and possible elimination of free hydroxide. Furthermore the presence of boric acid would buffer any residual hydroxide to pH values near neutral. Most plants operating on boric acid have experienced a reduction in SCC and IGA.[1]

When sodium concentrations are compared to prevailing silica levels, a useful inference may be made. It is assumed that silica along with hardness salts (not measured routinely at Fort Calhoun) and some sodium is present in hideout regions as insoluble silicates. As indicated above, the available data are insufficient to perform a rigorous analysis, but the following considerations may be made. If after all other anion-cation charge relationships are satisfied, the mole ratio of sodium to silica is less than 1, quartz and sodium disilicate ($Na_2Si_2O_5$) would precipitate together. In this situation, the two solid phases would buffer the system according to the following reaction.

$$2\ SiO_2 + 2\ Na^+ + 2\ OH^- = Na_2Si_2O_5 + H_2O$$

If the mole ratio of sodium to silica is between 1 and 2, sodium disilicate and sodium metasilicate (Na_2SiO_3) would precipitate together. These two solid phases would buffer the system according to the reaction.

$$Na_2Si_2O_5 + 2\ Na^+ + 2\ OH^- = 2\ Na_2SiO_3 + H_2O$$

If the mole ratio of sodium to silica exceeds 2, all the silica would precipitate as sodium metasilicate. The excess sodium would be present as unbuffered sodium hydroxide.[2] Presumably this latter case was the situation prior to the tube rupture - characterized by the impurity concentrations listed in Table 2 on 3/3/84. The more recent shutdowns show a much reduced sodium to silica ratio. From this it may be inferred that free hydroxide no longer is present in the Fort Calhoun steam generators and that the pH in any regions of concentration is buffered via the silica.

Current concentrations of impurity recoveries observed during recent trips and powerdowns are comparable to values reported for another fresh water-sited PWR.[3] In this comparison impurity recoveries at Fort Calhoun no longer appear to be excessive.

Conclusion

Combustion Engineering, Inc. has found evidence of substantial impurity removal from the Fort Calhoun steam generators subsequent to the 1984 tube rupture event, and thereby endorses Fort Calhoun's proposed action to return reactor coolant inlet temperature, Tc, to the original operating value of 545°F.

1.) Steam Generator Owners Group News, 7, December 9, 1986.

2.) Oleh Weres, "Phase Relations and Fluid Composition in Steam Generator Crevices," Unpublished Work.

3.) S. G. Sawochka, "Interpretation of PWR Steam Generator Hideout Return Data," EPRI Plant Chemists Meeting, Denver, CO, June 5-7, 1985.