I 1. Clinch River Breeder Reactor Plant Steam Generator Water Quality

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The recent problems experienced by some LWR Steam Generators have drawn attention to the importance of system water quality and water/steam side corrosion. Several of these reactor plants have encountered steam generator failures due to accelerated tube corrosion caused, in part, by poor water quality and corrosion control. The CRBRP management is aware of these problems, and the implications that they have for the Clinch River Breeder Reactor Plant (CRBRP) Steam Generator System (SGS). Consequently, programs are being implemented which will: 1) investigate the corrosion mechanisms which may be present in the CRBRP SGS; 2) assure steam generator integrity under design and anticipated off-normal water quality conditions; and 3) assure that the design water quality levels are maintained at all times. However, in order to understand the approach being used to examine this potential problem, it is first necessary to look at the CRBRP SGS and the corrosion mechanisms which may be present.

Steam Generator System

The SGS provides the necessary facilities to produce superheated steam for use in a conventional turbine generator. The SGS is composed of four major subsystems located in each of three identical loops: the main sodium heat transport subsystem; the sodium drain subsystem; the water/steam subsystem; and the vent relief subsystem. Each Steam Generator System receives 325 MW_t of 936°F sodium directly from the intermediate heat transport loop. The sodium flows through the shell side of the superheater and the evaporators before being returned to the intermediate heat exchanger by the pump. A loop configuration of one superheater in series with two evaporators operated in parellel results in essentially identical component designs (AI hockey stick) for the evaporators and superheaters.

The water/steam subsystem, a recirculating concept, has been selected to provide a comparatively simple plant control system and to minimize primary plant thermal transients induced by steam side malfunctions. Water is recirculated from the steam drum to the evaporators where a 50% steam/water mixture (a 2:1 recirculation ratio) is formed and returned to the steam drum. Following separation of steam and water in the drum, saturated steam is superheated on its way to the turbine. Steam conditions at the turbine are 1450 psig and 900°F. The feedwater is returned from the turbine condensor to the steam drum using full flow demineralization for water quality control. Volatiles, ammonia and hydrazine, are added to control pH and O_2 concentrations respectively. To maintain required water quality levels in the steam drum, a 2½%-5% water blowdown is used as required to prevent the buildup of contaminants.

Steam Generator System Corrosion

The conclusions of the ASME sponsored laboratory research program on internal boiler corrosion (1) were that deposit buildup plus the presence of an active corrodent were required to induce tube failure from corrosion. A field study by the ASME (2) indicated that the main source of deposit buildup was from the ingress of oxidation products from the pre-boiler system. A typical source in the CRBRP is the feedwater heater which has a large surface area. The same study concluded that the major sources of corrodents are salts which enter the system because of in-leakage of condensor cooling water, and from chemicals, such as phosphates, added as boiler water treatments.

These corrosion conditions are applicable to all boiler systems, and can generally be accommodated by proper design. The concern about corrosion problems in the CRBRP Steam Generators has arisen because of the possibility of corrodent concentration due to operation with Departure from Nucleate Boiling (DNB), steam drum, and recirculation. These mechanisms concentrate corrodents in the system water because of the corrodent's higher solubility in water as compared to steam. Since this type of system is fairly unique, no actual data on the degree of corrodent concentrations in such a system is available. However, indications are that concentrations will be somewhere above those attained in once through systems, but below concentrations considered to be dangerously corrosive. Depositable material is also expected in significant quantities, but should not be a problem in itself. The major potential steam generator problem exists in the interaction of deposits and concentrated corrodents in the film dry-out region of the evaporator.

CRBRP Approach

In order to eliminate the uncertainties raised with regard to the steam generator's integrity, the project is implementing a number of investigative programs. These programs are aimed at areas such as: 1) System Material Selection; 2) System Concentration Potential; 3) Thermal/Hydraulic Studies of DNB; 4) DNB and water quality effects; and 5) other tests which will provide water quality/corrosion information as a sidelight to their major purpose. It is felt that information obtained from these programs will answer present uncertainties, and ensure that the SGS will operate successfully.

Materials

Material selection for the Steam Generators has proceeded with the goal of using metals which are resistant to the corrosive conditions which may occur in the CRBRP. The material which will be used is a 2¼ Cr - 1 Mo steel. This material has been used successfully for boiler tubes for a number of years, and a large amount of data on its performance is available. This information indicates that 2¼ CR - 1 Mo has good high temperature properties, resistance to general corrosion, and is almost immune to stress corrosion cracking. In support of the large amount of industrial data on this material, a program to test 2¼ Cr - 1 Mo in caustic environments at CRBRP temperatures and pressures was developed at ORNL. The results from this program indicate that 2¼ Cr - 1 Mo performance and corrosion resistance under CRBR conditions is excellent (3).

Material selection to reduce possible steam generator corrosion is also being practiced in the feedwater delivery system. The main goal is to use materials in the feedwater heater which will introduce as little oxidation product material as possible into the feedwater. This should inhibit corrosion by reducing the amount of deposit buildup on the steam generator tubes. Attention is also being given to the material choice for the condensor tubes. The thrust here is to use materials which will resist failure, since condensor tube leaks will be the major source of corrodents in the SGS. Any reduction in condensor leaks will lower the amount of steam generator and feedwater train corrosion.

DNB - Recirculation - Steam Drum System

Because the combination of DNB with a steam drum and recirculation is so unique, some uncertainty exists as to the impurity concentration levels which will be attained by the system. However, based on once through feedwater quality and 2½% steam drum blowdown, specifications for SGS water quality have been developed.

Feed Water Quality Specification

Total Solids	50 ppb (max)
Dissolved Oxygen	7 ppb (max)
Silica	20 ppb (max)
Iron	10 ppb (max)
Copper	2 ppb (max)
pH @ 25°c	9.3 to 9.6
Hydrazine (Residual)	5 ppb (max)
Conductivity (cation) @ 25°c	0.3 micro-mho/cm
Sodium	2 ppb

Water Quality Steam Drum

Total Dissolved Solids	2 ppb (max)
ph @ 25°c	9.0 to 9.5
Conductivity (cation) @ 25°c	3 micro-mho/cm
Sodium	80 ppb (max)

In order to clarify the effects on impurity levels that system interactions might have, a study is currently being done on a fossil fuel plant in Corpus Christi Texas, which was found to have a DNB - Recirculation - Steam Drum System. The plant will also operate using volatile treatment during the study, and the plant has experienced some condensor leakage in the past. The results of this study should give information on the impurity concentrating effects of this type of system.

DNB - Water Quality effects

Little information is presently available on the effects of DNB and water quality interaction on corrosion rates. A major effort is directed at addressing this uncertainty. One series of tests is planned at Argonne National Lab which will primarily investigate the thermal/hydraulic aspects of DNB operation. However, design level thermal conditions will be used in the test. This will allow separation of the corrosion rates produced by DNB-operation (i.e., corrosion induced by thermal strain fatigue) when the corrosion data are compared to the results of the DNB Effects Test.

The major investigation of DNB-water quality effects on steam generator corrosion rates will be in the DNB Effects Test, to be run at General Electric. The scope of this program includes: a survey of U.S. and Foreign experience with DNB operation in boiler tubes: a Phase I series of tests to establish the absence of accelerated corrosion effects, qualify operation with design water quality levels, and determine upper limits of corrosion under DNB conditions; and a Phase II series of extended endurance testing to confirm 30 year thermal fatigue/corrosion design margins, and to qualify upset (operation with condensor leakage) CRBRP water chemistry operating conditions.

Related Tests

In addition to these tests, which are primarily directed at DNB and water quality aspects, other tests are planned which, although directed at other targets, will still provide very useful information on steam generator corrosion. A good example of this is the Few Tube Test, also to be run at CE. The primary purpose of this program is to examine thermal expansion and wear aspects of the reference steam generator design. The test will consist of a 7 tube evaporator and 3 tube superheater run at prototypical heat transfer and water quality condition. The test is planned to run for 3-4 years, which should provide valuable information on long term corrosion effects on the steam generators.

Feedwater Quality

Besides initiating programs which should demonstrate design life steam generator integrity at the expected water quality levels, the project is also investigating ways to assure that the desired water quality levels are supplied reliably throughout the CRBRP lifetime. In the case of the condensor, this involves assuring that the condensor is designed to be as reliable and leak free as possible; using the best materials (corrosion resistant) for construction; assuring adequate Quality Assurance during fabrication and installation; and lowering impurity levels in the cooling tower water (condensor cooling water) as much as possible. As mentioned previously, attention is also being focused on material selection for the feedwater system to reduce the production of depositable materials.

Other important aspects in maintaining desired feedwater quality levels are the use of volatile chemicals and full flow condensate polishing. LWR experience has shown that solids, such as phosphates, used to control pH levels in the system, can be important sources of corrodents. Since pH and O_2 control is required, volatile ammonia and hydrazine will be employed. In addition, mixed bed demineralizers will treat the full condensate flow to remove any impurities. This will act as the primary barrier to any impurities, entering the system due to condensor leaks, form reaching the steam drum.

In conclusion, the project has developed specific programs to address the uncertainties involved with water quality, DNB, and corrosion in the SGS for the CRBRP. This approach will assure the use of the most corrosion resistant materials for the system while at the same time keeping the level of corrodents as low as possible. The development programs will also provide basic information on the concentrating mechanisms which may be present in the system, as well as demonstrating that steam generator integrity under design and anticipated off-normal conditions is assured. The project is confident that this approach will lead to a successful demonstration of the Liquid Metal Fast Breeder Reactor concept in the CRBRP.

References

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I.2. Experimental Investigations on Waterside Corrosion Problems of Sodium-Heated Steam Generators

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Abstract

Based on experimental results, it is shown that the formation of a protective magnetite layer in sodium-heated steam generators - operated with neutral demineralized water - proceeds very fast. The stability of the magnetite layer is excellent even at sudden load changes and at the start-up or shut-down operation.

1. Introduction

Since 1964 steam generators for the KNK Reactor Project and for the SNR-300 Fast Breeder Project have been tested in the 5MW Test Facility of INTERATOM. Under the experimental programme mainly thermohydraulic investigations have been carried out, but investigations on waterside corrosion phenomena have also been included from the beginning.

The characteristic data of the tested steam generators and the KNK steam generator are shown in Fig. 1. Technical details of the test units, the 5MW Test Facility and the KNK Reactor have been published in literature /¯1 - 4_7; therefore, only the design characteristics are given in the following:

The KNK steam generator is of the concentric tube-in-tube design; a helically coiled steam generator has been investigated for the SNR Project. The reaction-protected, integrated steam generator (IDA) permits the operation of a sodium-cooled reactor without secondary sodium system.

2. Boiler water treatment

Nearly all experiments have been carried out using neutral, demineralized water in accordance with the values recommended by the VGB for the feedwater of once-through boilers being operated with neutral water (without addition of alkalizing agents) /¯5_7 (Fig. 2). We see the following advantages if operating steam generators with neutral water:

- Due to the correlations between electrical conductivity, pH value and iron-dissolution rate in neutral water, the presence of dissolved iron (II) hydroxide (i.e. due to higher corrosion rates) can be detected simply and specifically by measuring the pH value and the electrical conductivity.

- In-leakage of impurities (e.g. chlorides) as a consequence of a small condenser leakage can be detected by measuring the electrical conductivity what is not possible in case of alkalized and thus salt-bearing water.

- Informations on the build-up and the integrity of the protective magnetite layer can be obtained by continuous measurement of the hydrogen being released due to the following reactions:

$$3\ Fe + 4\ H_2O \rightleftharpoons Fe_3O_4 + 4\ H_2 \qquad (t > 250^\circ C)$$

or

$$Fe + 2\ H_2O \longrightarrow Fe(OH)_2 + H_2 \qquad (t < 250^\circ C)$$
$$3\ Fe(OH)_2 + 1/2\ O_2 \longrightarrow Fe_3O_4 + 3\ H_2O$$

In case of neutral water systems, this hydrogen formation is not disturbed e.g. by the decomposition of hydrazine or ammonia.

- Neutral demineralized water must not be degassed to the