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INFORMAL REPORT

TECHNICAL SPECIFICATIONS FOR PWR SECONDARY WATER CHEMISTRY

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AUGUST, 1977

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MASTER

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ABSTRACT

The bases for establishing Technical Specifications for PWR secondary water chemistry are reviewed. Whereas extremely stringent control of secondary water needs to be maintained to prevent denting in some units, sound bases for establishing limits that will prevent stress corrosion, wastage, and denting do not exist at the present time. This area is being examined very thoroughly by industry-sponsored research programs. Based on the evidence available to date, short term control limits are suggested; establishment of these or other limits as Technical Specifications is not recommended until the results of the research programs have been obtained and evaluated.

The subject of Technical Specifications for PWR secondary water chemistry has been under discussion for several years. At the 1976 Prairie Island Appeals Board hearings on steam generator integrity, Technical Specifications were proposed for the secondary coolant of that plant by R.R. Maccary. These are reproduced here as Appendix A. Subsequent to this hearing, all PWR licensees were requested to submit modifications to their Technical Specifications to cover this point. Our review of the licensees' responses was submitted as a letter report, which is reproduced here as Appendix B. The purpose of this report is to discuss this subject further and to suggest possible controls on secondary coolant chemistry. Our third report on denting,[1] describes in detail the recent service experience and research in progress, upon which most of this report is based.

The water chemistry controls recommended below are suggested for protection of the steam generator tubing integrity only. Whatever is present in the steam generators also has an effect on the environment within the turbines attached to them. Controls on free caustic to minimize stress corrosion of turbine rotors were discussed in a previous report to the NRC.[2]

The bases for establishing Technical Specifications for PWR secondary water are not clearly understood at the present time. Work is actively under way under the sponsorship of EPRI and the PWR manufacturers to establish these bases. Ideally, one would need access to the information being generated by these programs before any Technical Specifications that are meaningful could be written. This information could be made available to us only by formal meetings, set up at NRC request, with Westinghouse, or with EPRI.

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(1) BNL-NUREG-23219, "Third Report on Denting of Inconel Steam Generator Tubes in Pressurized Water Reactors", D. van Rooyen and J.R. Weeks, August, 1977.

(2) BNL-NUREG-22689, "Stress Corrosion Cracking in Turbine Rotors", J.R. Weeks, April, 1977

Our third report on the denting phenomena outlines what we already know regarding water chemistry history and denting reactions. Even were we to gain access to all the available information, recommending Technical Specifications from sound bases may not be possible at this time.

The history of water chemistry specifications in PWR steam generators has shown the best minds in the business to have been wrong in many instances, although much of the basic information on the problems experienced (except perhaps for phosphate wastage) was already known. At several times in recent years bases for specifications were developed, which appeared to be acceptable at the time, only to be proved wrong by subsequent operating experience. The low phosphate treatments in use prior to 1973 were perhaps sound if the utilities responsible for running the plants had followed them meticulously. Ginna and Connecticut Yankee, among others, had at least 5 years trouble-free operation each under this system. Deviations from this system tended to cause free caustic and caustic stress corrosion to develop in sludge pile areas; the use of a higher phosphate treatment after 1973 to alleviate this problem led to a more extensive generalized wastage problem, although this change did eliminate the caustic stress corrosion difficulties. The switch from phosphate to AVT around 1974, to avoid wastage problems, was followed by first a recurrence of caustic cracking in some units and later by denting in many units.

Any Technical Specifications must, therefore, be designed to prevent or minimize the occurrence of at least the following: (a), caustic stress corrosion of the Inconel, (b), wastage or pitting of the Inconel, and (c), denting or rapid corrosion of the support plates. Whereas present concerns are largely on the denting problem and its ramifications (stress corrosion of the Inconel by the primary coolant as a result of deformations caused by denting), the problems that were previously experienced must continue to be considered, including possible increased chloride pitting dangers in the absence of phosphate.

To prevent the caustic stress corrosion problems, AVT Technical Specifications of the type recommended for Prairie Island by R.R. Maccary at the 1976 Appeals Board hearing (Appendix A) are probably satisfactory for inland plants. To prevent wastage of the Inconel, elimination of the phosphates is probably satisfactory. To prevent denting reactions, however, a much more complex set of controls will be necessary. In-service denting reactions seem to require the presence in a crevice of an acid chloride environment plus perhaps the presence of copper and/or nickel ions. Recent laboratory work at Westinghouse suggests that removal of the copper ions tends to stop the denting reaction in these specific tests. The nickel ions are probably present as a result of wastage reactions in those steam generators that previously operated with a phosphate chemistry for an extended period of time (greater than 6 months). Chloride ions are present in all steam generators to some extent, primarily from in-leakage of cooling waters in the condenser. The acid environment could be produced naturally in the crevices by hydrolysis of seawater or brackish water, of chlorides of iron, copper, or nickel, or of previously precipitated phosphates. The primary source of the copper ions is corrosion of condenser tubes and feedwater heaters, both of which are frequently made of copper alloys. On a coastal plant with copper alloy condenser tubes and feedwater heaters it may be impossible to reduce chloride ions to a safe level without demineralizers. Experience at Maine Yankee and Millstone 2 suggests that the speed with which the utility reacts to a condenser leak and the diligence with which it maintains chlorides below 0.1 ppm will have an effect on how long it takes for denting reactions to develop in a given unit. But it may still not be sufficient to prevent the denting over the lifetime of the plant. Demineralizers, if they are used in conjunction with diligent monitoring of condenser leakage rather than used as a cushion to reduce the impact of condenser leaks, may increase the time for denting to develop substantially. Maintaining chloride levels as low as .05 ppm, however, may be necessary. Such controls may not be practicable in an operating unit without demineralizers.

Where copper alloys are not used in condenser or feedwater heaters, allowable chloride levels, however, may be somewhat greater since the copper ions will not be present. Allowable chloride levels in an inland plant that has not previously used phosphates may also be somewhat higher since the acid environment is less likely to develop. On such units, controls of condenser inleakage aimed at minimizing the formation of caustic in the sludge or crevice areas will probably also result in a sufficient reduction of other impurities to minimize denting problems.

From all of this we draw the following conclusions:

1. Technical Specifications for PWR secondary coolant cannot be developed at the present time that are based on firm experimental evidence and service experience. Any specifications, such as those suggested below, are at best an educated guess, and may be subject to change as a result of programs currently underway.
2. The absence of any corrosion-caused problems to date in the straight-tubed once-through steam generators suggests that the Technical Specifications proposed by Duke Power Company, SMUD, and Metropolitan Edison for Occonee, Rancho Seco, and Three Mile Island are satisfactory, as discussed in our memorandum of March 29, 1977 (Appendix B).
3. For inland plants with U-tubed steam generators, and no copper alloys in their secondary system, Technical Specifications of the type proposed for Prairie Island are probably satisfactory. Those plants that have had long histories of phosphate,

however, should consider chemical cleaning to remove the residual phosphate sludge at the earliest possible convenience.

4. For plants with copper alloys in their condensers and/or feedwater heaters, especially on coastal sites, stringent controls should be obtained on chloride ion levels. We would suggest a steady state limit of .05 ppm chloride in the blowdown with transient limits of 0.5 ppm for a maximum of 24 hours. These numbers are, at best, semi-educated guesses at the present time because the research needed to provide a sound basis for their selection is not yet complete. They may also not be tight enough to prevent denting, nor may they be achievable in a practical sense in some units without demineralizers.

5. For plants without copper alloys the chloride levels could probably be increased by a factor of 2 to 3.

6. Those plants still on phosphate should not be forced to change their water chemistry to AVT at this time. It is highly possible that a small amount of wastage progressing at a known rate will, in the long run, be less serious than the consequences of the denting reactions almost certain to be exaggerated by a change to AVT unless a chemical cleaning is performed using a proven technique.

7. The basis for water chemistry controls on these units that are already moderately to severely dented are even less clear. Experience at Point Beach suggests that stringent controls on chlorides may have arrested or slowed the progress

of denting, whereas experience at Surry and Turkey Point have suggested this is not true. Using the numbers given above in "3" and "4" may, therefore, be helpful only in some cases. Controls in these units should, therefore, be considered individually.

8. Putting these numbers into Technical Specifications serves the positive purpose of ensuring that a utility pays proper attention to its water chemistry.

9. In the absence of a sounder basis for selecting chloride levels, however, putting these numbers into a Technical Specification may not be wise simply because they may be wrong. They should, therefore, be considered short term control items, rather than long term Technical Specification limits, in our opinion.

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APPENDIX A

Testimony of R.R. Maccary
January, 1976 Appeals Board Hearings

Prairie Island Nuclear Power Station
Units 1 and 2
Docket Nos. 50-282 and 50-306

TECHNICAL SPECIFICATIONS

LIMITING CONDITIONS FOR OPERATION

3.12 Secondary Water Monitoring Requirements

APPLICABILITY:

Applies to the secondary water monitoring of the condensate and steam generator blowdown during power operation and hot standby conditions.

OBJECTIVE:

To minimize potential steam generator tube degradation caused by contamination of the secondary coolant.

SPECIFICATION:

Monitoring of the condensate and steam generator blowdown shall be performed to operate within the limits specified in Table 3.12.1.

CORRECTIVE ACTIONS

Operating conditions exceeding control parameters in Table 3.12-1 shall require the following corrective actions:

A. Whenever the cation conductivity limit is exceeded in the condenser condensate for a period of 24 hours, the steam generator blowdown shall be increased to the maximum flow allowed by Technical Specification 3.9 Radioactive Effluents until corrective action is completed which restores the conductivity to a value less than the limit.

B. Whenever the cation conductivity of the steam generator blowdown exceeds 3 μmhos/cm, an analysis for pH and free hydroxide in the blowdown shall be performed daily until corrective action is completed which restores the conductivity to a value less than the limit. If the pH or the free hydroxide limits are exceeded for a period of 72 hours, the steam generator shall be brought to and held in the hot shutdown condition within 36 hours until further corrective action is completed which restores the cation conductivity to a value less than the limit.

C. Whenever the cation conductivity of the steam generator blowdown exceeds 10 μmhos/cm for a period of 72 hours, the steam generator shall be brought to and held in the hot shutdown condition within 36 hours until corrective action is completed which restores the cation conductivity to a value less than the limit; unless it can be demonstrated by chemical analysis of the blowdown that such high conductivity readings are not conductive to corrosion or stress corrosion of steam generator tubes.

Among the corrective actions required in A, B, and C above, a sampling analysis

TABLE 3.12-1

SECONDARY WATER MONITORING CONTROL PARAMETERS

Water Sample	Total cation conductivity µmhos/cm @ 25°C		pH @ 25°C	Free Hydroxide ppm $CaCo_3$
	Frequency	Limits	Limits	Limit
Condenser Condensate	Continuous* On-line Monitor	0.2	-	-
Steam Generator Blowdown	Continuous* On-line Monitor	3.0-10.0	8.5-10.0	1.0

* If inoperable, daily grad samples and analysis required until monitor is returned to service.

of the condenser condensate may be required to confirm condenser tube inleakage followed by plugging of leaking condenser tubes.

BASIS

3.12 Secondary Water Monitoring

Contamination of the steam generator secondary coolant can cause potential tube degradation and impair tube integrity. Generally, the most severe contamination results from condenser inleakage of caustic-forming impurities that may accumulate on the secondary side of the steam generator. High concentrations of free caustic deposited in the steam generator, or on the high heat flux surfaces of the Inconel-600 tubes can lead to the potential for intergranular stress corrosion cracking.

Monitoring of the condenser condensate by cation conductivity is an effective means of detecting condenser tube inleakage. The leakage rate can then be determined by comparing the cation concentration in the condensate with the cation concentration in the condenser cooling water. The cation conductivity of the steam generator blowdown will indicate when blowdown is required to remove the accumulation of caustic-forming impurities and the scale forming solids in the steam generator. Monitoring the pH and free hydroxide level in the blowdown provides a means to initiate balance of corrective actions needed to restore the operating secondary coolant.

Monitoring the secondary water within the Technical Specification limits will control the potential accumulation of corrosive impurities in the steam generator and minimize tube degradation. This monitoring provides reasonable assurance that the conditions in the steam generator minimize the potential for tube degradation during all conditions of operation, and postulated accidents, as a measure of protection of the steam generator tubing which is an essential part of the reactor coolant pressure boundary.

BROOKHAVEN NATIONAL LABORATORY

MEMORANDUM

DATE: March 29, 1977

TO: F.M. Almeter

FROM: J.R. Weeks

SUBJECT: Technical Specifications For PWR Secondary Water Chemistry

By Mr. Shao's letter of February 15, 1977, our Corrosion Group was asked to provide written comments on the proposed Technical Specifications received from several licensees. Our comments are given below.

The proposed Technical Specifications from the licensees with once-through steam generators, i.e. Duke Power Company (Oconee Units 1, 2 and 3), SMUD (Rancho Seco Unit 1), and Metropolitan Edison (Three-Mile Unit #1), are essentially identical in that cation conductivity limits are established for the feedwater. The proposed limits are tight, and seem reasonable for this particular type of steam generator. I think we should be careful, however, to make these Technical Specifications sufficiently flexible that operation of the plant will not be curtailed by unnecessary paperwork. These steam generator materials are quite tolerant to temporary water chemistry excursions. With a once-through steam generator, control of stress corrosion in the turbines may require tighter limits on the water chemistry than are needed to control corrosion of the steam generator tubing. Metropolitan Edison, in addition, added a pH limit. pH controls, I think, represent good practice, but I wonder if they need to have a Technical Specification for pH.

The responses from the Westinghouse units all reflect the Westinghouse position that Technical Specifications should not be placed on the secondary coolant. The Westinghouse position paper stated, "deviations from secondary water quality guidelines are not a safety problem". Westinghouse also states that in their judgement, "it would not be appropriate to legally limit potential causes of degradation of the reactor coolant pressure boundary". With these two statements I disagree. Their acceptance by the NRC would mean that no Technical Specification limits need be placed on primary coolant chemistry in any LWR. By the time degradation is detected by inservice eddy current inspections or leakage, a sufficient number of serious defects may have already formed to constitute a safety consideration.

At the same time, however, recent experience has shown that deterioration of steam generator tubing has occurred under water chemistry conditions previously believed adequate to protect the material. Any Technical Specifications, therefore, on the secondary coolant of these units should be, in my opinion, very flexible and allow for transients over and above the limits. However, as stated in our memo of September 13, 1976, these specifications should also limit the permissable time allowed above the steady state limit to something like four weeks per year.

The submittals from Wisconsin Electric Power Company (Point Beach Units 1 and 2), Indiana and Michigan Power Company (Donald C. Cook) and Rochester Gas and Electric (R.E. Ginna) all propose Technical Specifications on monitoring, with the acceptable limits being placed in the plant procedures or to be proposed at a later date. It seems to me that some limits need to be placed in a Specification if it is to have any value.

The responses from Florida Power and Light (Turkey Point Units 3 and 4), and from Virginia Electric and Power Company (Surry Units 1 and 2), offer no Technical Specifications whatsoever. The NRC should determine what action will be taken in these matters.

The responses from Carolina Power and Light (Robinson Unit #2) and Southern California Edison (San Onofre Unit #1) reflect units still on phosphate treatment. Robinson has had secondary water Technical Specifications for several years, so their only change is to specify the frequency of monitoring the secondary water coolant. San Onofre again references plant operating procedures. I think the NRC should be very cautious in attempting to force either of these units to change their water chemistry at the present time.

The need for Technical Specifications on the secondary coolant arises from a situation several years back, in which several units ran into stress corrosion difficulties while operating under a low phosphate treatment because they did not, in my opinion, put sufficient emphasis on maintaining good secondary water quality in their steam generators. This situation was reviewed by me in the spring of 1973, in a report in which I recommended Technical Specifications be placed on secondary coolant in order to ensure that the licensees paid proper attention to this item. The subsequent experiences with phosphate wastage, denting, and possible fatigue in the various units, however, have not per se arisen because of poor control of water chemistry compared to what were then acceptable standards. We still do not have available sufficient information to determine exactly what limits will be required to be effective in controlling steam generator corrosion. Such information can only be obtained by several years' experience with the individual or similar units. Until that time, any Technical Specifications should be flexible.

I think that Technical Specifications on secondary water chemistry covering at least the feedwater and/or blowdown conductivity may still be a good idea to encourage proper attention in this area, but that they should be written as loosely as possible, so as not to provide undue hardship and paperwork to the licensee. But Specifications that merely state surveillance without indicating some limits at which actions should be taken are meaningless. In a recent review for D.S.S. of stress corrosion in turbines, I concluded that secondary water chemistry requirements to prevent stress corrosion in the turbines may in the long term be more stringent than those to prevent stress corrosion or wastage of the steam generator tubing.

This leaves the question, what should the NRC require as a Technical Specification, and what should the licensee consider for its own requirements for good practice? If the NRC is primarily interested in requiring some control to ensure that the licensee is paying proper attention to their steam generator water chemistry, then a Technical Specification on feedwater and blowdown cation conductivity may be sufficient. If the NRC is interested in applying controls to ensure that deterioration of the reactor coolant pressure boundary will not occur or will be minimized in an operating unit, then I think they may be asking for the impossible at this time. When long term (∿ 5 years or more) experience with AVT or ZST units with a given condenser coolant have been successfully demonstrated, detailed Technical Specifications may be reasonably considered. The Maine-Yankee and Prairie Island experiences, if subsequent inspections bear out their good records to date, may be able to serve as guidelines for future Technical Specifications, but not, in my opinion, at this early date. The licensees, however, should be taking advantage of this experience to date in order to establish their own operating procedures.

Distribution:

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