

《기술보고》

High Temperature Application of Iron Removal Chemical Cleaning Solvent
in the Secondary Side of Nuclear Steam Generators

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증기발생기 2차측 제철화학세정액의 고온적용

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Abstract

A qualification test was performed for the iron removal chemical cleaning of the secondary side of nuclear steam generators at the selected temperature, 125°C, higher than the standard application temperature, 93°C. The field cleaning condition for a nuclear unit was tested in a bench scale test loop including a SUS 316 stainless steel autoclave with one gallon capacity as a test vessel. The kinetics of sludge dissolution, corrosion of the secondary side materials and change of solvent chemistry were monitored. Test results indicated that more thorough cleaning was accomplished in less than half of the cleaning time required at 93°C. And the total corrosions of the secondary side materials were found to be less than the values at 93°C. While the solvent is recirculated and heated by an external chemical cleaning equipment for the conventional 93°C process, the secondary side is heated by the lateral heat of the primary coolant without the recirculation of the cleaning solution, and the solvent is mixed by vigorous boiling induced by periodic ventilation for the high temperature process. The requirement that the reactor coolant pumps should be running during the cleaning operation is the major disadvantage of the high temperature process which also should be considered when chemical cleaning is planned for steam generators under operation.

요 약

원전 증기발생기 2차측 제철 화학세정을 기존의 93°C 표준공정보다 고온인 125°C에서 검증시험을 수행하였다. 원전 증기발생기를 125°C에서 화학 세정한다는 가정아래 현장세정 조건을 결정하고 이를 다시 모사하여 3ℓ 용량의 소형 검증시험 조건을 결정하였다. 1 gallon 용량의 316 스텐레스강 압력용기를 반응용기로 사용하는 화학세정 시험장치에서 검증시험을 수행하여 슬러지 용해거동, 모재 부식률, 세정제 화학조성 변화거동 등을 측정하였다. 125°C 검증시험 결과에서 93°C 표준공정보다 세정시간을 절반이하로 단축시키고도 더 효율적인 세정효과를 얻을 수 있을 뿐만 아니라 2차측 모재의 부식률도 감소함을 확인할 수 있었다. 그러나 고온 세정공정은 아직

현장적용 경험이 없고, 별도의 외부순환 세정장치를 이용하는 93℃ 표준공정과는 달리 주냉각재의 잠열로 2차축을 가열하므로 세정이 완료될 때까지 주냉각 펌프를 계속 가동하여야 하는 단점이 있다. 가동중인 증기발생기에 대한 화학세정을 수행할 때 93℃ 표준공정과 고온공정의 장 단점을 신중히 검토하여 최적공정을 적용하여야 할 것이다.

1. Introduction

Corrosion products from the feed line system are deposited as sludge in the secondary side of nuclear steam generators. Generally, the major ingredients of the sludge are magnetite (Fe_3O_4) and metallic copper. For plants where no copper or copper-bearing alloy is used in the feed line system, the sludge is composed of mostly magnetite. The amount of sludge deposited increases with years of plant operation. The sludge can cause various types of tube corrosion and distort the eddy current signals from tubes. Effective removal of sludge is strongly recommended for achieving good maintenance of steam generators. Chemical cleaning by which the sludge is removed after being dissolved in the solvent is a very effective method.

The chemistry and temperature of the iron removal chemical cleaning solvent developed by EPRI/SGOG (Electric Power Research Institute / Steam Generator Owner's Group) are as follows [1~4],

10~20% EDTA (Ethylene Diamine Tetraacetic Acid)
 1% N_2H_4
 0.5~1.0% CCI-801 (trade name of a corrosion inhibitor manufactured and supplied by Petrolite Corp.)
 pH 7 (room temperature) by NH_4OH
 93℃

The solvent is injected into the secondary side of the steam generator and is recirculated by an

external chemical cleaning recirculation equipment. A few successful commercial applications have already been reported [5,6]. It has been suggested recently, however, that faster and more effective cleaning be achieved without the external recirculation equipment by applying the solvent at higher temperature. Concentrated solvent can be injected through the plant equipment into the secondary side of the steam generator which is filled with wet layup water heated up by lateral heat of the primary coolant. Vigorous boiling of solvent caused by periodic ventilation would bring about a thorough mixing of solvent so that the recirculation chemical cleaning equipment is not needed.

The authors, through a series of dissolution tests in the temperature range between 93 and 150℃, measured magnetite dissolution kinetics, corrosion of carbon/low alloy steel and stability of chemicals in the EPRI/SGOG iron removal solvent [4,7,8]. It was found that magnetite dissolution kinetics was accelerated significantly while corrosion was controlled still within the allowable limit when temperature was increased up to 150℃. Thermal decomposition of hydrazine in the solvent, detected to be so fast that the concentration approached to zero within a few hours at 150℃, did not ruin the effectiveness of the solvent. It was suggested that the solvent could be applied to steam generators at a temperature as high as 150℃. Qualification test would be the final step to verify the feasibility and to determine the effectiveness of high temperature iron removal process before a field cleaning is planned for a specific

plant.

This paper describes a bench scale qualification test performed in a chemical cleaning test loop which includes a SUS 316 autoclave with a capacity of one gallon. It was assumed that a specific nuclear steam generator was chemically cleaned by the EPRI/SGOG iron solvent at the selected temperature, 125°C. This temperature was chosen because the advantages of the high temperature process could be achieved while guaranteeing absence of excessive corrosion. According to the previous studies by the authors [9], a very careful on-line corrosion monitoring program would be required for the field cleaning at 150°C. It is anticipated that the steam generators in Korea Nuclear Units should be chemically cleaned by turns. If the advantages and safety of high temperature cleaning are fully verified, high temperature cleaning can be adapted as the standard chemical cleaning process for domestic nuclear units.

2. Experimental

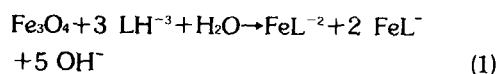
2.1. Field Cleaning Condition

The field cleaning condition designed by assuming that a specific Westinghouse model F steam generator is chemically cleaned at 125°C is shown as Table 1 [10]. The amount of sludge in the sludge pile was estimated by a simple model calculation from the sludge height data measured by eddy current on each tube. However, there is no way of precisely measuring the amount of sludge inside the operating steam generators, and any estimation of sludge inventory must be a very rough one. Conservative estimates of the amount of sludge remaining should be maintained throughout the course of the experiment since an excessive amount of chemicals is far more desirable than a shortage with a considerable amount of sludge remaining. Theoretical stoichiometric

Table 1. Field Cleaning Condition Designed for a Specific Steam Generator.

amount of sludge	sludge pile	174kg
	scale on I-600 tube	114kg
	corrosion of carbon/low alloy steel (Fe ₃ O ₄ equivalent)	31kg
	total	319kg
solvent volume :	21240 ℓ (140 inches above the secondary side of tube sheet → 23 inches above the third tube support plate)	
solvent chemistry	10% EDTA	
	1% N ₂ H ₄	
	1% CCI-801	
	pH 7 by NH ₄ OH	

dissolution capacity of 10% EDTA solvent is 26.4 g Fe₃O₄/ℓ since one EDTA molecule can react with one ferric or ferrous ion as follows,



EDTA was denoted as LH₄. In reality, the empirically determined dissolution capacity of 10% EDTA solvent is about 20 g Fe₃O₄/ℓ, a little lower than the stoichiometric one [1~4]. When total solvent volume is 21240 ℓ as given in Table 1, the total sludge dissolution capacity is about 424.8kg Fe₃O₄. It is believed that conservative estimates in the sludge inventory and in solvent volume determination can compensate for the uncertainties involved.

2.2. Bench Scale Test Loop

Figure 1 shows a schematics of the bench scale test loop used in the present experiment. A SUS 316 autoclave with one gallon capacity is used as a test vessel. Concentrated solvent can be injected directly into the test vessel which is filled with wet layup water at high temperature. The vent line

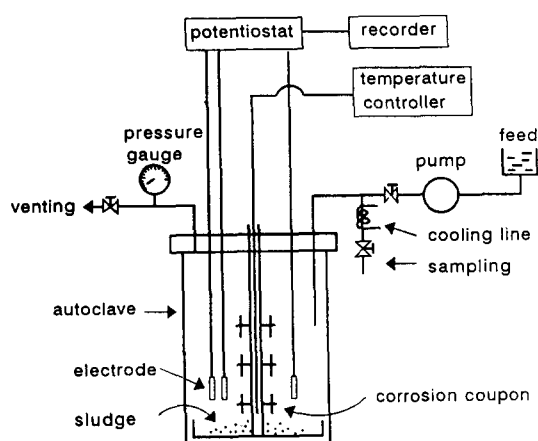


Fig. 1. A Schematics of Bench Scale Test Loop

passes through a cooling jacket so that the mixture of vapor and liquid phase forced out by a vigorous boiling during periodic ventilation is cooled to liquid phase and then collected in the outlet. The condensed solvent can be reinjected into the reactor in order to maintain the amount of solution constant. The sampling line also passes a cooling jacket so that the solvent is completely cooled down before being sampled.

2.3. Corrosion Coupon and Sludge

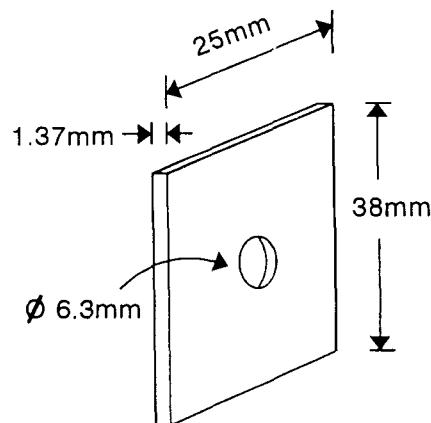
Figure 2 shows corrosion coupon and electrode used in the present experiment. Materials tested and their usage in the Westinghouse Model F steam generator are listed in Table 2. Corrosion electrodes and coupons were polished with #400 and #600 emery papers and cleaned ultrasonically in acetone and then in ethanol. The specimens were completely dried before being weighed. Corrosion was estimated from weight loss of the corrosion coupon by the following formula,

$$\text{corrosion penetration} = \Delta W / (A d) \quad (2)$$

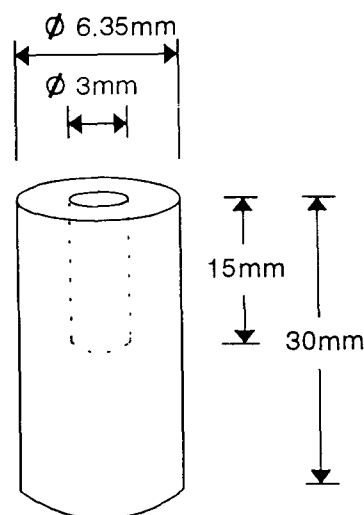
where ΔW : weight loss

A : surface area of coupon

d : density



(corrosion coupon)



(corrosion electrode)

Fig. 2. Corrosion Coupon and Electrode

Corrosion electrodes are installed in the high temperature and high pressure electrode holder which had been shown elsewhere [9]. Corrosion coupons are put in Teflon hangers so that the coupons are insulated electrically from the autoclave body. Some coupons were put on the bot-

Table 2. List of Materials Tested

materials ID	remarks
SA 508 Cl.3	tube plate (substitute for SA 508 Cl.2)
SA 285 Gr.C	wrapper
SA 516	wrapper position block, shear lug
ductile cast iron	stay rod (simulating SA 396 Gr.C)
SUS 405	tube support plate, flow distribution baffle (identical to A-240 Type 405)
Inconel-600	tube, blowdown system pipe and liner
weld (E9018M)	primary boundary weld, Shielded Metal Arc Welding

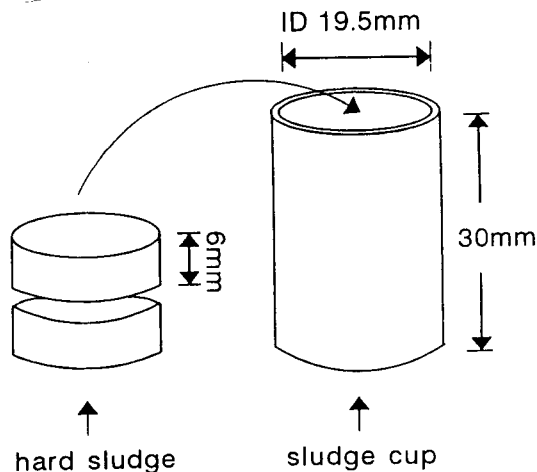
tom of the pan onto which sludge was piled.

Instantaneous corrosion rate was monitored with the corrosion electrodes using linear polarization corrosion monitoring method. Details of on-line corrosion monitoring method are found elsewhere [7].

Actual plant sludge was used for the experiment. Sludge removed by water lancing of a specific steam generator was dried in a vacuum to fine dry powder. Half of the sludge loaded in the test vessel was the powder as it was, and the other half was small disks consolidated by pressing and baking. Part of the disks were put into a sludge cup made of I-600 tube as shown in Figure 3, in order to simulate hard sludge consolidated to pile inside the dense tube forest, where access of fresh solvent is hindered. Chemistry of the sludge, analyzed by inductively coupled plasma (ICP) spectroscopy after being dissolved in boiling Aqua Regia, showed that 97.75% was magnetite with various minor elements such as nickel, boron and others [8].

2.4. Test Procedure

The field cleaning condition was downsized into a bench scale test with 2840ml solvent and 42.65g sludge. The test procedure was as follows,

**Fig. 3. Hard Sludge Disk and Sludge Cup**

- The reactor was filled with 2060ml of lay up water after corrosion coupons, electrodes and sludge were loaded. The chemistry of the wet layup water was as follows [11],
200 ppm N_2H_4
pH 10.2 with NH_4OH
- The reactor was heated up to $130^\circ C$, $5^\circ C$ higher than the cleaning temperature to compensate for the temperature drop which occurred as cold concentrated solvent was injected.
- 750ml of concentrated solvent (47.9% EDTA) was injected.
- Sampling and then one-minute ventilation were repeated every hour until the reaction was stopped. pH and concentrations of free EDTA, hydrazine and iron in the solvent were analyzed. Details of the chemistry analysis method are found elsewhere [10]. Ventilation at the first hour was omitted since vigorous reaction could have resulted in too much back flow of the mixture of sludge and solvent.

3. Results

3.1. Dissolution of Sludge

Visual inspection after uncovering the test vessel revealed that most of the sludge loaded had been dissolved. Disks in the sludge cups were also found to be dissolved almost completely. Figure 4 shows how the concentration of iron in the solvent varied after concentrated solvent was injected. Excessively high concentration of iron in the two-hour sample was due to incomplete mixing of solvent. It is believed that complete mixing was achieved during the first ventilation done just after the two-hour sampling. Free EDTA and hydrazine concentration profiles to be shown later indicated the same trend.

80% of total sludge loaded was dissolved within three hours and 96.5% was dissolved when the reaction was completed in 11 hours. Table 3 is the material balance indicating the sludge removal efficiency. Figures 5~7 show free EDTA and hydrazine concentrations and pH trends during the

Table 3. Sludge Removal Efficiency

	Fe (g)	sludge(Fe_3O_4 , g)
sludge loaded	30.369	42.653
soft sludge	15.232	21.393
hard sludge	15.137	21.260
dissolved amount	31.231	43.144
corrosion effect	-1.929	-2.665
net dissolved amount	29.302	40.479
removal efficiency	96.5 %	-

reaction. High concentration of hydrazine and free EDTA for the two-hour sample indicates incomplete mixing before the first ventilation, as mentioned previously.

3.2. Corrosion

Table 4 summarizes corrosion coupon test results. All the corrosion coupons tested showed far less corrosion than EPRI/SGOG guideline [2]. Visual inspection indicated no traces of localized

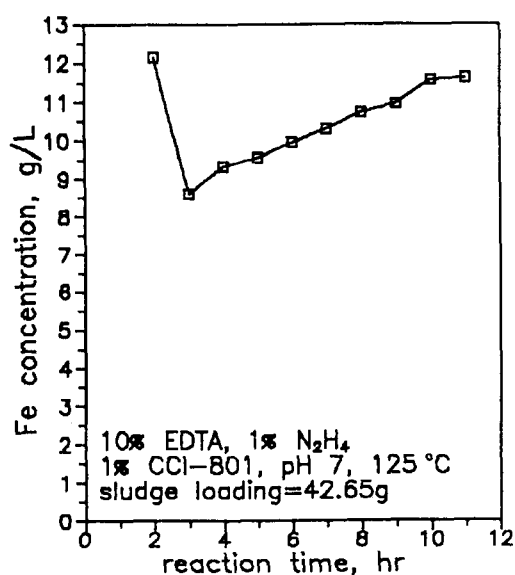


Fig. 4. Fe Concentration vs. Reaction Time

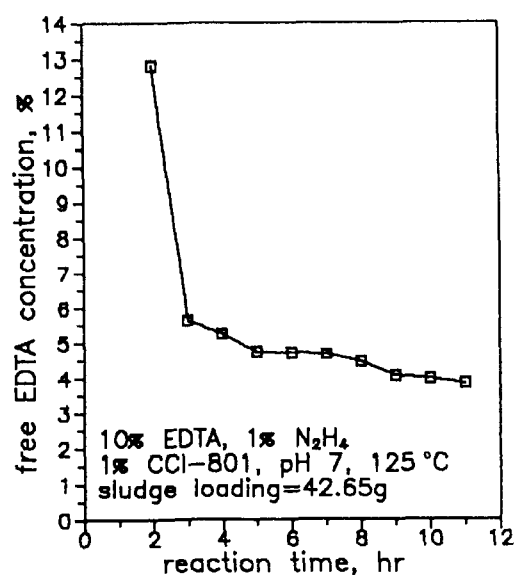


Fig. 5. Free EDTA vs. Reaction Time

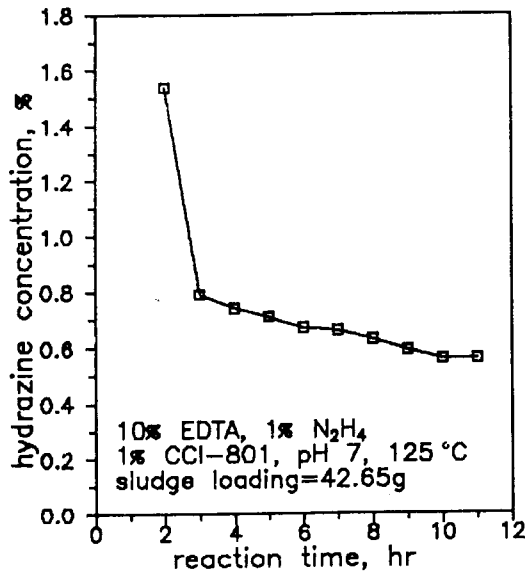


Fig. 6. Hydrazine Concentration vs. Reaction Time

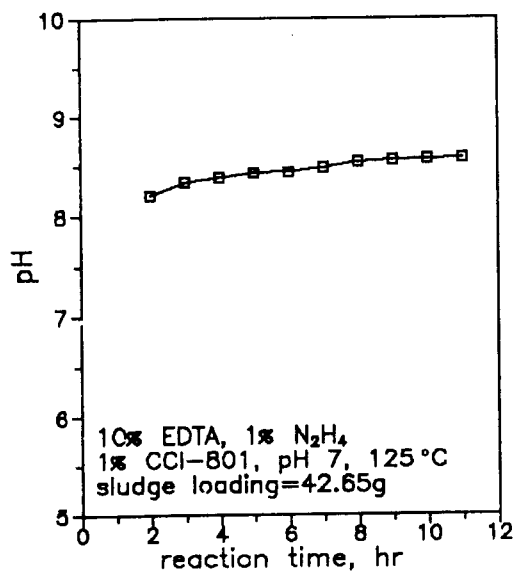


Fig. 7. pH vs. Reaction Time

attack on the surface of the corroded coupons. Figure 8 shows corrosion rate monitored by linear polarization. A consistently steady corrosion rate is

Table 4. Corrosion of Coupons Calculated from Weight Loss

material ID	corrosion penetration(mils)		EPRI/SGOG guideline (mils)
	insulated	on the pan	
SA 508 Cl.3	0.0822	0.173	10
SA 516	0.150	—	10
SA 285 Gr.C	0.169	0.468	10
weld (E9018M)	0.101	—	10
SUS 405	0.0064	—	3
ductile cast iron	0.126	—	10
Inconel-600	<0.001	—	0.25

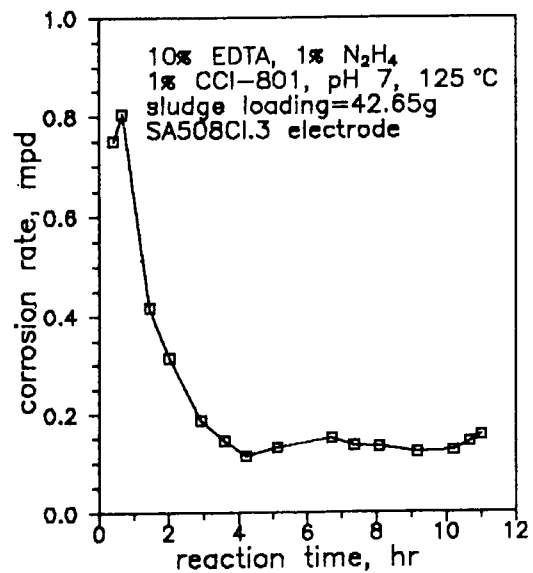


Fig. 8. Corrosion Rate vs. Reaction Time

observed after the high corrosion rate in the initial period of reaction.

4. Discussion

Quantitative data for the sludge dissolution kinetics and corrosion of secondary side materials were produced under the assumption that a speci-

fic steam generator was chemically cleaned at 125°C. Rapid sludge dissolution kinetics indicating 80% dissolution in three hours and 96.5% in eleven hours is a very attractive feature of high temperature process. It ordinarily took about 20 hours to reach over 80% dissolution for the conventional process at 93°C. Thorough dissolution of hard sludge in sludge cup is also promising since consolidated sludge pile inside the dense tube bundle is the last part to be dissolved in the 93°C process. It is believed that periodic ventilation is a very effective way of supplying fresh solvent inside the area where supply of fresh solvent is limited otherwise. Bench scale qualification test for the same steam generators with conventional 93°C process indicated that 70% of sludge was dissolved in 6 hours and 20 minutes, and 87% in 24 hours [10]. Corrosion penetrations of low alloy / carbon steels were in the range 0.19~0.25 mils, higher than those shown in Table 4. Lower corrosion penetration at higher temperature was surprising initially. It could be explained, however, by the differences in reaction time and in flow condition. A 125°C test lasted for eleven hours while 24 hours was required for the 93°C test. 125°C process was applied as fill,soak and drain while 93°C process as recirculation. It is a very general trend that flow of the solution accelerates corrosion [12].

Free corrosion was shown to be well within the allowable limits. Galvanic effect may be a concern. Galvanic corrosion cannot be estimated accurately through the bench scale test since the galvanic corrosion in the real steam generator depends on the geometrical factor significantly [13]. The authors have performed a series of electrochemical experiments to estimate galvanic corrosion of carbon/low alloy steel coupled to Inconel-600 in the chemical cleaning solvent at temperatures between 93 and 150°C [9]. It was concluded that galvanic corrosion of carbon/low alloy steels coupled to Inconel-600 could be con-

trolled in the allowable limit at temperatures not exceeding 150°C.

Incomplete mixing of solvent until the first ventilation was surprising to the authors. For the field cleaning in real steam generators, ventilation should be done while injecting the concentrated solvent into the steam generators so that the concentrated solvent and lay up water are mixed thoroughly from the beginning of reaction. For the bench scale test, ventilation in the initial period of reaction where rapid reaction was occurring with gas evolution, would have caused too much back flow of solvent. However, for real steam generators vigorous boiling will not cause back flow since there is plenty of space between the solvent surface and steam outlet.

It is conclusively determined that field application of the 125°C cleaning process is feasible, and that faster and more thorough cleaning is achievable than that for the conventional process at 93°C. High temperature process does not require external recirculation chemical cleaning equipment. Instead, the secondary side is heated by the lateral heat of the primary coolant, and therefore the reactor coolant pumps should be running during the cleaning process. This would be the major disadvantage of the high temperature process since the scheduled maintenance procedure can be started only after the reactor coolant pumps are stopped. The lack of field experience presents another disadvantage. Nevertheless, combination of faster, more thorough cleaning and less corrosion is a very attractive feature of 125°C process. It is recommended that application of 125°C process be considered when chemical cleaning of specific steam generators under operation is planned.

5. Conclusions

Quantitative data for sludge dissolution kinetics and corrosion, produced during a bench scale

qualification test simulating an assumed field cleaning condition of steam generators of a nuclear unit at 125°C, indicated a very attractive feature that is the combination of faster, more thorough cleaning and less corrosion was achievable than that by the conventional process at 93°C. Feasibility of 125°C cleaning process was verified conclusively. The requirement that the reactor coolant pumps must be running during the cleaning operation, and the fact that there is no field experience available yet are disadvantages of the high temperature process which also should be considered when chemical cleaning is planned for steam generators under operation. However, it is recommended that the 125°C process be applied in the future.

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