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DEVELOPMENT OF CHEMICAL DECONTAMINATION TECHNOLOGY FOR THE FUGEN

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A study of chemical decontamination of the reactor cooling system of the Fugen has been made with KURIDECON 203, a dilute decontamination reagent. The heat exchangers of the cleanup water system and of the residual heat removal system were decontaminated with KD203. As a result, decontamination factor (DF) was about 20, and it has proved that chemical decontamination contributes to reduce the radioactive exposure.

1. INTRODUCTION

Since the start up in March, 1979, the Fugen, the boiling light water cooled, heavy water moderated, pressure tube type reactor (165MWe), has contributed the role of demonstrating technical feasibity for heavy water reactor through its over 9 years operation. The reactor cooling system of the Fugen has almost the same as BWRs'.

The corrosion products generated in the reactor cooling system are brought into the reactor core, and these radioactive corrosion products are gradually increasing the radiation of the reactor cooling system.

Decontamination studies with Fugen have been successively carried out to prevent the crud formation and to reduce the transport of crud into the reactor core. Measures to reduce the crud formation and radiation accumulation have been practiced by injecting oxygen into the feed water system, and improving the operating condition of the condensate demineralization system. But infer of unvoidable yearly increasing the dose rate of the reactor cooling system, We have engaged in the research and developmentof an effective remove the crud attached to the components and pipings since 1980. We have investigated the charactaristics of the decontamination reagents such as CAN-DECON, NS-1, KURIDECON, the adverse effects of these reagents on the materials during and after the decontamination and the disposability of the waste liquids. As a result, the KD203 which is less corrosive and can keep the component materials sound was selected as a decontamination reagent in this studies.

We have studied corrosivity of KD203 on various materials in respect of general corrosion, crevice corrosion, stress corrosion cracking etc., along with a survey on the properties of the attached crud and their decontamination conditions by KD203 using various test specimens of the pipings and components of the reactor cooling system. The refuelling machine, and then the heat exchangers of the cleanup water system (CUW) and of the residual heat removal system (RHR),were decontaminated with KD203. As a result, the decontamination operating condition such as temperature increasing method, decontamination waste lequid disposal method etc. were obtained. This paper reports mainly on the decontamination performance of KD203 and decontaminated experience.

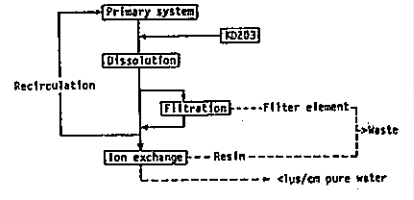
2. DECONTAMINATION PERFORMANCE OF KD203

2-1. KD203'S CHARACTER

The KD203 is a dilute solution with pH5 consisting mainly of chelating compounds, and does not need regeneration of the reagent during decontamination operation.

The solution is purified by mixed ion exchange resin bed after the decontamination process, and, as does not generate waste liquid, the KD203 acts on crud by the mechanism of

Table 1 KD203 properties and decontamination method

Main ingredient	Organic chelate compounds (pH5)
Action mechanism	Reductive dessolution and chelation
System decontaminated	BWR and ATR: the primary system components and pipings
	PWR: the primary system components and pipings multi-step with oxidation treatment
Conditions	Reagent concentration: Typical 0.1% Temperature: 100～120°C Time: Typical 24 hrs.
Method	

reductive dissolution and chelation of the dissolved metals. Table 1 shows the conditions and the method of decontamination with KD203.

2-2 CRUD PROPERTIES

The crud attached to the components and pipings of the reactor cooling system was analyzed to clarify the relationship between the crud properties and the decontamination conditions, and to estimate the amount of radioactive waste in relation to radioactive buildup.

As the test specimens, some component bolts and plates of the shield plug within the pressure tube assembly, and pieces of pipes of the CUW and the reactor cooling system (RCS) were used. Three kinds of spicements except the plates were taken from the flowing reactor water region, and the plate specimens were sampled from the stagnant water region. The results of investigation are summarized in table 2.

The crud consists of the outer soft layer (red brown) and the inner hard layer(dark grey). The outer layer contained fine particles with a 0.1 μm diameter mixed with larger one with several μm, whereas the inner layer comprised the dense particles with about 0.5μm. The crud samples from the stagnant water region consisted mostly of hard one. The amount of crud (particularly the soft crud) in the reactor cooling system differs in the position, but the average amount of crud is estimated to be 1mg/cm^2 for 20,000 operation hours.

Table 2 Crud characperistics

Item \ Sample	Primary coolant system piping	Pressure tube bottom (water stagnant part)
Formation	Outer layer and inner layer	Almost inner layer
	Metal	Metal
Crystalline structure	αFe_2O_3, Fe_3O_4	αFe_2O_3, Fe_3O_4
Composition Outer	Fe:(Ni+Cr)≒90:10	90 : 10
Inner	Fe:(Ni+Cr)≒85:15	80 : 20
Crud amount	∿1mg/cm^2	∿1mg/cm^2
Radioactivity	1∿2μCi/cm^2	∿1.5μCi/cm^2
Specific Radioactivity	∿3x10^{-3}μCi/μg	∿2x10^{-3}μCi/μg

2-3 DECONTAMINATION PERFORMANCE

The effects of temperature, reagent concentration, and treatment time on the decontamination of KD203 were studied.

The CUW and RCS piping pieces were used as the specimens in the decontamination tests. Tests were carried out by the immersion method using 500ml Erlenmeyer flasks equipped with reflux tube for the temperature below 100℃ , and using a 1000ml glass autoclave for the temperature at 100 ℃ or above. The tests to investigate the effect of dissolved oxygen (DO), were conducted in N gas environment.

1) TEMPERATURE ;

The effect of temperature on the decontamination was studied within a range of 80 ～ 120 ℃. The infuluence of temperature on the removal of radioactivity was obviously shown Fig. 1. There existed the reaction initiation temperature for the decontamination (i.e. for the crud dissolution reaction to advance), and the reaction rate rapidly increased beyond this temperature. The reaction initiation temperature was 80 ～90℃ for the test specimens collected from the flowing water region and 100 ℃ or higher for those from the stagnant region. Figure 2 shows the Arrhenius plotting of the initial reaction rate constants obtained by crud dissolution tests with the bolt specimens. The activation energy for KD203 was calculated to be apporximately 22 Kcal/mol. The activation energy

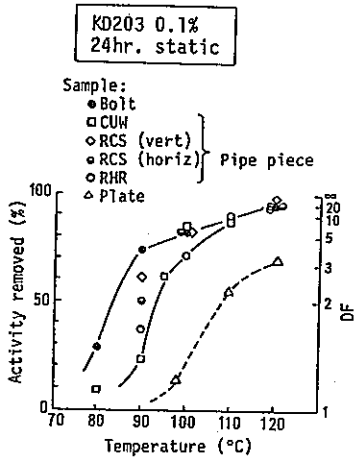


Fig. 1 Effect of temperature on decontamination

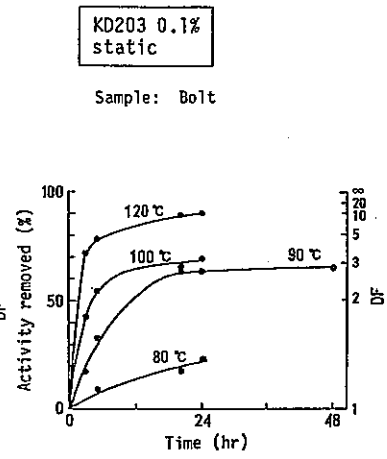
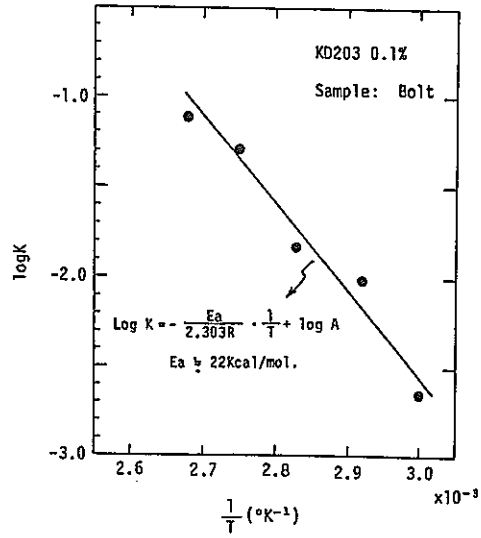


Fig. 3 Effect of temperature of crud dissolution



Feg.2 Arrhenius plot of crud dissolution reaction.

indicates the rate determining factor of the crud dissolution is temperature rather than the diffusion of KD203.

2) TREATMENT TIME ;

When the temperature was below the reaction initiation temperature, the decontamination rate remanined low, but when it was raised to 120℃ , the rate increased rapidly and then levelled off, as shown in Figure 3. At the temperature between 90℃ to 100 ℃ , the rate increased as the time passed, but became constant after 24 hours from the start of reaction though some radioactivity still remained on the test specimens. Thus the rate was found to be almost saturated within 24 hours. Further it was apparent that the achieved decontamination rate was more strongly governed by the solution temperature rather than the reaction time.

3) CONCENTRATION ;

Figure 4 shows the effect of the KD203 concentration (0.025 ～0.1%) on decontamination. A nearly uniform decontamination effect is obtainable if the reagent's dissolution capacity(about 190 ppm Fe at 0.1%) is secured. The minimum amount of reagent necessary can be calculated from the amount of crud to be decontaminated, the liquid volume and the reagent's crud dissolution capacity, the proper concentration can be selected by adding an appropriate margine to it.

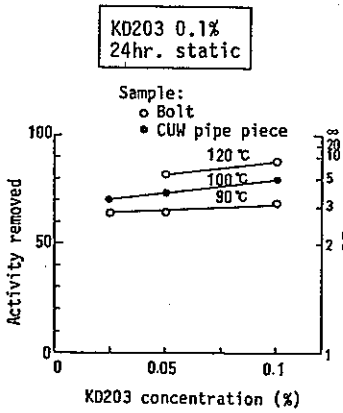


Fig. 4 Effect of KD203 concentration on crud dissolution

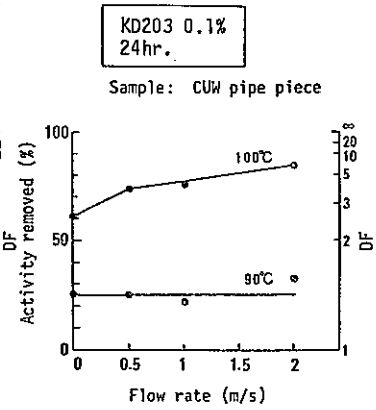


Fig. 5 Effect of flow rate on crud dissolution

4) FLOW RATE ;

Figure 5 shows the effect of flow rate (0 ～2 m/s) on the decontamination. The effect of flow rate was almost negligible at 90 ℃, but was remarkable at 100 ℃. Since the reaction initiation temperature for the CUW pipe test speciment was about 95℃,little crud dissolution reaction occurred at 90 ℃, and flow rate had no effect on the chemical reaction and mechanical removal of the contaminated surfaces.But at 100 ℃ the crud became porous through the dissolution,and the flow rate contributed to mechanical separation and dissolution of crud.

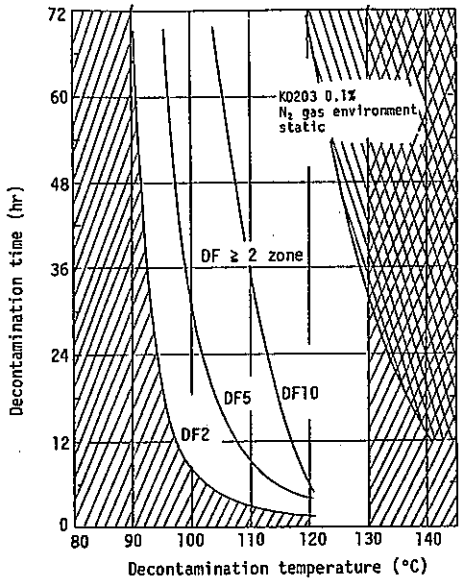


Fig. 6 Temperature and time required to achieve DF2, 5 and 10.

Figure 6 shows the relationship between solution temperature and treatment time at 0.1% KD203 concentration, which indicates the temperature/time conditions to attain required decontamination factor.

2-4 CORROSION OF MATERIALS

2-4-1 CORROSION DURING DECONTAMINATION

The corrosion of materials during decontamination was studied using a 0.1% solution. The corrosion study included the test on general corrosion, galvanic corrosion, and stress corrosion cracking (SCC). Decontamination conditions were varied as follows : temperature 90-130℃, time 24 ～48hr., flow rate 0～4m/s.

1) GENERAL CORROSION ;

The result of the corrosion test, 10 kinds of materials constituting the reactor cooling system summarized in table 3. Two kinds of materials (carbon steel STPT42 and maltensite stainless steel SUS440C) showed a corrosion tendency, but the others were almost free from corrosion in the immersion test. Five kinds of alloys including Type 304 stainless steel (SUS304), Zircaloy 2 were studied at a flow rate up to 4m/s, but none of them showed any acceleration of corrosion. The corrosion of STPT42 and SUS440C rapidly increased at a temperature above 120℃,and 130℃ respectively. The corrosion of every material during decontamination is judged to be within the design value (less than 10 μm for carbon steel and less than 1 μ m for stainless steel),because decontamination condition are temperature 90 ～ 120 ℃ and time 24 hours.

2) GALVANIC CORROSION ;

A rolled joint of the pressure tube

Table 3 Corrosion test results for KD203

(μm/48hr)

	Materials	Corrosion		Materials	Corrosion
General Corrosion	SUS304	0.01	Weld Corrosion	SUS304/SUS304	0.01
	Sen. SUS304	0.04		SUS304/STPT42	-/3.39
	SUS403 Mod.	0.15	Galvanic Corrosion	SUS403 Mod.	0.26
	SUS440C	1.18		SUS440C	1.18
	SUS630	0.02		SUS403 Mod.	0.22
	SCS13	0.03		Zr-2.5Nb	0.00
	INCONEL 718	0.01		SUS630	0.05
	Zr-2.5Nb	0.00		Zr-2.5Nb	0.00
	ZIRCALLOY 2	0.00			
	Ti-6Al-4V	0.01	Test condition		
	STELLITE No6	0.00	KD203 0.1%		
	STPT42	3.42	130°C, N_2 gas environment		

(Zr-2.5%Nb) and the extension tube (SUS403Mod.) the contact part between the pressure extension tube (SUS403Mod.) and the seal plug (SUS630) were used to investigate the galvanic corrosion by the contact of different kinds of materials. The test results proved no difference from the results of the general corrosion test and no occurence of any uneven corrosion.

3) STRESS CORROSION CRACKING (SCC) ;

To investigate the SCC sensitivity of the heat affected weld part to KD203, SCC test by the single U-bend, slow strain rate test (SSRT) and the uniaxial constant load test (UCLT) were made on the sensitized SUS304. There was no such uneven corrosion as intergranular corrosion and pitting, no effects by KD203 have been observed. From all these test results KD203 was confirmed to be a low corrosive decontamination reagent.

4) ANODE POLARIZATION CURVE ;

The anode polarization of the materials in a 0.1% KD203 solution at 120°C were obtained, te ndency of each material has been confirmed to agree well with corrosion. The results are shown in Figure 7, which indicates that all the alloys except the carbon steel consistently remained at the passive state in the KD203 solution, proving that KD203 is a generally low corrosive reagent. Further more, the correlation between the current density levels and anticorrosion test results.

2-4-2 CORROSSION DECONTAMINATION LIQUID REMAINED

Corrosive effect of a residual decontamination liquid was investigated assuming that the plant was operated with the liquid remaining in the systems after the decontamination. Table 4 summarizes the results with a KD203 solution diluted 100 times the standard concentration (0.1%) and with dearated demineralized water at 285 °C for 600 hours. There was no corrosive effect on general corrosion, galvanic corrosion and SCC. The KD203 is a weak acid reagent with pH5,and when thermally decomposed in a high temperature water, it produces some amine compounds and increases pH, which may provide a more anticorrosive environment than

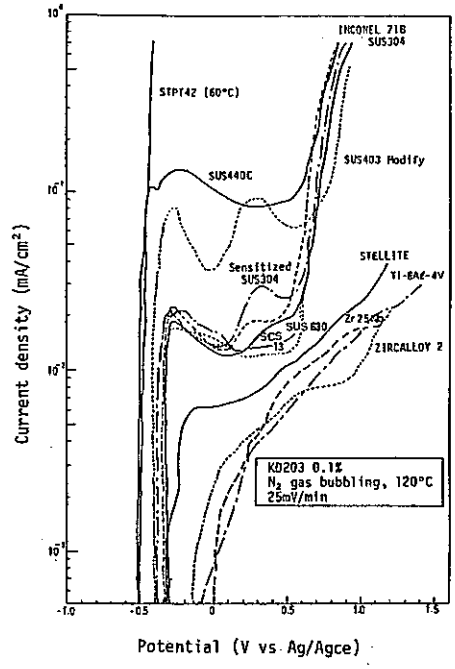


Fig. 7 Anode polarization curve of various materials in KD203

the demineralized water does. It is improvable that any decontamination liquid is no remain within the systems after the decontamination, but even if it should remained, it would not damage the component materials.

Table 4 Corrosion test results for residual KD203

(μm/600hr)

	Materials	Corrosion		Materials	Corrosion
General Corrosion	SUS304	0.31 (0.35)	Weld Corrosion	SUS304/SUS304	0.13
	SUS403 Mod.	0.90 (0.80)		SUS304/STPT42	0.13/ 0.69
	SUS440C	0.84 (1.31)	Galvanic Corrosion	SUS403 Mod.	1.20
	SUS630	0.58 (0.72)		SUS440C	1.08
	SCS13	0.49 (0.77)		SUS403 Mod.	1.29
	Zr-2.5Nb	0.18 (0.13)		Zr-2.5Nb	0.27
				SUS630	0.43
				Zr-2.5Nb	0.27
	ZIRCALLOY 2	0.10 (0.04)	Test condition KD203 10ppm. 285°C		
	STPT42	0.56 (1.08)			

( ): Demineralized water

3 DECONTAMINATION EXPERIENCE

In the Fugen, the components shown in Table 5 have been chemically decontaminated to reduce the radioactive exposure during their overhaul and inspection work. The decontamination experience of the heat exchangers of the cleanup water system (CUW-HX) and of the residual heat removal system (RHR-HX) is discussed below.

Table 5 Decontamination experience of "Fugen"

Component	Decontamination condition				DF
	Reagent	Conc. (%)	Temp. (°C)	Time (hr)	
Shield plug for pressure tube	KD101 KD201	10 5	80 80	2 6	2∿5
Recirculation pump internal	KD101 KD202	10 5	80 60	2 6	3∿5
Refueling machine	KD203	0.1	110	24	2∿15
CUW-HX	KD203	0.2	120	22	2∿60
RHR-HX	KD203	0.2	120	18	1.5∿6

3-1 DECONTAMINATION PROGRAM

1) OBJECTS ;

In the periodical inspection, the heat exchangers are opened and checked to inspect the leakage from their heat transfer tubes. The surface dose rate of CUW-HX and RHR-HX becomes as high as 100～300 mR/h because of crud accumulation and increases worker's dose rate during the inspection work, so their chemical decontamination was carried out.

2) CONDITIONS AND METHOD ;

The form, quantity and radioactivity of the crud attached to the CUW-HX and RHR-HX components were estimated based on the crud property study described in the previous section and the radioactivity measurement and analysis of the crud attached to these components. Based on these results, the decontamination conditions for attaining the target value of DF 5 were decided as follows,

Temperature : 120 ℃
Time : 24 hours
Concentration :
0.2% (the value was selected because of the large amount of crud relative to that of liquid)

To satisfy these conditions, a potable unit with the functions of raising temperature, injecting and circulating chemical liquid and disposing of waste liquid was used. A closed liquid circulation loop was formed including the heat exchanger for its decontamination. During the circulation, the liquid was sampled at an interval to measure the gross gamma radiation, ferrous ion and KD203 concentrations. Figure 8 shows these values with time in decontamination of CUW-HX. The corrosion during the process were evaluated by test specimens within the loop.

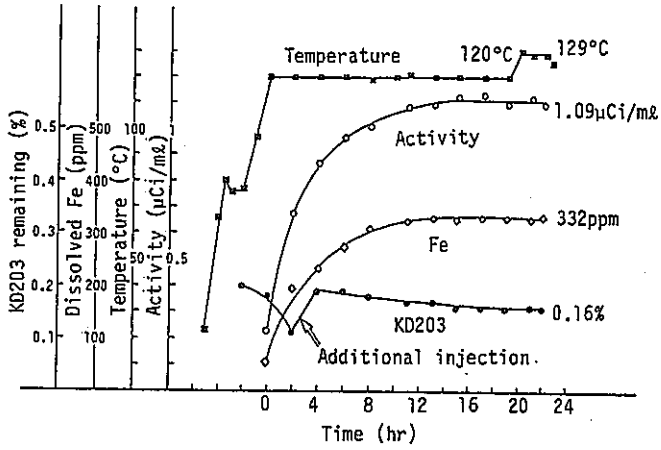


Fig. 8 Change of major items during decontamination operation (Decontamination of CUW-HX)

3-2 DECONTAMINATION RESULTS

Table 6 summarized shows the decontamination results for RHR-HX and CUW-HX.

1) REMOVAL OF CRUD AND RADIOACTIVITY :

The RHR-HX had crud 2 times as much as CUW-HX per surface area. The crud in RHR-HX was mostly iron, but one in CUW-HX contained about 2% of Cr and Ni respectively. On the other hand, the specific radioactivity in CUW-HX was about 10 times greater than in RHR-HX, and CUW-HX was characterized by a large content of Cr-51. These differences are considered due to materials used in RHR-HX and CRW-HX, i.e. The components and piping of RHR are made of carbon steel except for the heat transfer tube, and operated at a low temperature of less than 120℃ whereas CUW is made of austenite stainless steel and operated at a high temperature of 100～ 280℃.

These results agree well with the estimation from the previous studies.

Table 6 Decontamination results

	RHR-HX	CUW-HX
Crud removed (g)		
Fe	1,729	930
Cr	1.8	22.7
Ni	3.4	17.1
Co	0.8	0.6
Total	1,735	970
(equivalent oxide)	(2,480)	(1,386)
Radionuclide removed (mCi)		
Co-60	330	1,196
Mn-54	126	524
Fe-59	6.8	255
Cr-51	-	1,033
Co-58	-	57
Total	460	3,060
Specific radioactivity (μCi/mg)	0.18	2.21
DF with shield probe	18.0	20.6

2) DECONTAMINATION FACTOR AND EXPOSURE REDUCTION EFFECTS:

The decontamination factor (DF) achieved for RHR-HX alone was about 18. But the contribution to its dose rate from the other heat exchanger (not decontaminated) was so great that the atmospheric dose rate could only be reduced to about 1/2 or 1/3. The decontamination programs should include the ambient components to reduce the atmospheric dose rate. The DF achieved for CUW-HX was about 15 and the target value of DF 5 could be secured.
The dose rate decreased from 13.8 to 6 man-rem for RHR-HX maintenance and from 15.5 to 7.5 man-rem for CUW-HX maintenance.

3) CORROSION :

The suspended test specimens and the heat exchanger materials surfaces were investigated to survey the corrosion during the decontamination. The CUW-HX components were found not to have any corrosion at all as they were made of SUS304, and SUS316. In RHR-HX, no corrosion was observed on SUS304, but a slight corrosion was the carbon steel SB49, STPT42.

4) PURIFICATION AND WASTE VOLUME ;

In both heat exchangers, the conductivity of KD203 solvent after decontamination was a 1,900 μs/cm. After the completion of decontamination,the liquid was cooled to 60℃ and passed through a mixed bed ion exchange resin column.As a result, it was reduced to less than 1 μs/cm in conductivity and 1 μCi/ml in gross gamma radiation. The decontamination waste such as the waste ion exchange resin and filters were sealed in the lead shield drums. A total of 9 drums were required to accommodate the waste materials produced from the decontamination process.

4 CONCLUSION

1) The crud attached to pipings of the reactor cooling system consisted of an outer soft layer (mainly α Fe_2O_3) and an inner hard layer(mainly Fe_3O_4). Their amount of crud was about 1 mg/cm^2 and the radioactive concentration was about 2 μCi/cm^2.

2) The decontamination tests clarified the effects of temperature, operating time, reagent concentration, flow rate, dissolved oxygen and other factors on the decontamination performance of KD203. The optimum decontamination conditions for attaining the DF 2, 5 and 10 were found to be 90℃, 100 ℃, 120 ℃ , respectively for 24 hours.

3) In the corrosion tests on the component materials, no effects from KD203 was recognized even under such severe conditions as 130℃, the maximum allowable temperature for KD203.
Thus, it was confirmed that the materials can be decontaminated without any adverse effects with in the temperature range of 90～120 ℃.

4) The decontamination experience of RHR-HX and CUW-HX of the reactor cooling system has proved that KD203 is not corrosive to the component materials and chemical decontamination is effective to reduce the radioactive exposure. These test results and experience obtained from decontamination of the heat exchangers will be contributed in the decontamination programs for the reactor cooling system of Fugen.

ACKNOWLEDGEMENT

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