Technique of Chemical Cleaning for Removing Corrosion Products in Nuclear Reactor (PWR)

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The study of chemical cleaning technique for removing corrosion products in PWR type plant and power reactor have been carried in China Institute of Atomic Energy (CIAE), Beijing. The report summarizes the results of screening test and qualification test of chemical cleaning technique, and the results of chemical cleaning to remove corrosion products (Fe_3O_4) in primary side of PWR type power reactor which chemical cleaning process has been carried by CIAE.

The chemical cleaning agent (EDTA + assistant agent + inhibitor) is effective for removing magnetite ($Fe_3O_4 \leq 17.5g/l$).The process of chemical cleaning includes cleaning, rinse, passivation. The corrosion rate of materials is acceptable. The chemical cleaning technique is effective and safe for PWR type reactor.

1. Introduction

Transport of corrosion products to PWR core region and steam generators (SG) by the feed water and coolant of secondary and primary side leads to crud build on the fuel cladding, to sludge build on the tubes, the tube plate, tube-to-tube support plate crevices of SG. Deposit of corrosion products can lead to power generation limitation. In sludge regions, chemical impurities are concentrated which accelerates corrosion of materials under sludge. To remove corrosion products is important, chemical cleaning is one of the methods.

The study of chemical cleaning technique for removing corrosion products in PWR plant SG secondary side and primary side of PWR type reactor was carried out in CIAE since 1990.

This report summarizes the results of screening test of chemical cleaning agent component and condition of chemical cleaning process, the results of qualification test of chemical cleaning technique which are available for removing corrosion products in primary and secondary side of PWR, the results of chemical cleaning to remove corrosion products in primary side of PWR type power reactor.

2.Test equipment

Screening test and qualification test were conducted. Different test equipment were used for each type of test.

2.1 Screening test equipment

One liter (or 0.5 liter)-three neck round bottom flasks with stirring rod in middle neck was used for screening test. The corrosion specimen was inserted in the side neck of the flask. Six flaskses could be placed in a thermostat-water bath. Six stirring apparatuses were used for stirring the flasks.

2.2 Qualification test equipment

Small scale chemical cleaning test loop and medium scale chemical cleaning test loop were used for qualification test of chemical cleaning technique.

2.2.1 Small scale chemical cleaning test loop

A schematic diagram of the small scale test loop is shown in reference[1]. The test loop parameters are 30l total volume, <120±5, 0.5~2.5t/h flow rate. The test loop consists of a pump, a test section, valves, a reservoir, flow meter and heating element, which is constructed with stainless steel.

2.2.2 Medium scale chemical cleaning test loop

The parameters of medium scale chemical cleaning test loop (MSCCTL) are <200, <2.4510^{6}Pa, 0~10t/h. Total volume of the loop is 135l. The schematic diagram of MSCCTL is shown in reference[2]. The MSCCTL consists of two test section (Φ300mm, H1000mm and Φ300mm, H400mm), a main pump, valves, a flow meter, a mixer, a storage tank, a stationary pressure tank, a injection pump, outside-heater and a desk of measure meter and control. MSCCTL is constructed with stainless steel.

3. Experiments and Results

The sludge of steam generator (SG) secondary side is magnetite (Fe_3O_4). The amount of magnetite dissolved in cleaning agent that is used to evaluate effectiveness of chemical cleaning. The main materials of SG secondary side are 800 alloy (tubes of SG), S_{271} low alloy steel(tube plate and shell of SG), A_3 carbon steel, $20^{\#}$ steel, 0Cr18Ni9Ti stainless steel and 600 alloy. The main materials of primary side in PWR type power reactor is Zr-2 alloy (fuel cladding). Above materials are used to evaluate safety in chemical cleaning process.

The experiments include the screening test, the small loop test and the medium scale test to study technique of chemical cleaning for removing sludge (17.5g/l Fe_3O_4) in PWR SG secondary side, the qualification test of chemical cleaning process for removing corrosion products (1g/l Fe_3O_4) in secondary side of SG during the early period of PWR plant operation, the qualification test of chemical cleaning to remove corrosion products (5g/l Fe_3O_4) in primary side (contain core) of PWR type power reactor.

3.1 Technique of chemical cleaning for removing sludge in PWR SG secondary side.

3.1.1 Screening test of basic component and condition of chemical cleaning

The screening tests have been carried in the screening test equipment and small test loop. The component of chemical cleaning agent consists of cleaning agent (EDTA), assistant agent, inhibitor and pH adjustor. The condition of tests are 4-8 pH, 2-10% EDTA, 55-93, 0-2.0t/h, 2-48h.

The results[1] of tests show that solubility of magnetite(Fe_3O_4) increase with increase of concentration of EDTA and assistant agent, temperature, cleaning time and flow rate. The assistant agent increases solubility of Fe_3O_4 in EDTA(pH=7).

The special inhibitor (A, B_3) have been prepared by CIAE. The rate of inhibition of inhibitor (A.B_3)is 90%.

The screening tests have got that the process of chemical cleaning (10% EDTA+1% assistant agent +inhibitor A or B_3,PH=7~8, 93±5,112rpm or

1.5~2.0t/h ,8h) is effective for removing sludge (17.5g/l Fe_3O_4), the corrosion depth of A_3 caribou steel and S_{271} low alloy steel are 15.9μm and 20.8μm respectively.

3.1.2 Medium scale test for removing sludge in SG secondary side[2].

The medium scale tests have been completed in MSCCTL. The tests study effectiveness of removing sludge (17.5g/l Fe_3O_4) of SG secondary side, and safety of main materials and their weld and construction of SG (A_3 , S_{271}, 800, 600, 20#, S_{271}/S_{271}, S_{271}-800) in process of chemical cleaning.

The part of sludge were prepared on tube to tube plate construction by equipment of similar condition of SG.

The process of chemical cleaning includes cleaning, rinse, passivation. The technique and the corrosion rate of materials in cleaning process have been shown in Table 1.

Table 1 Results of medium scale chemical cleaning test for PWR SG secondary side: the corrosion depth of materials

Materials	Area /cm^2	Crossion depth /μm			
		large section	small section	large section	small section
S_{271}	58.9 10.8	7.2 28.0	4. 3 14.3	4.6	7. 2 28.9
S_{271}-800	10.8	30.0		37.2	
S_{271}/S_{271} weld		10.0		12.9	
A_3	36.4	8.7	7.8	6.4	2.8
A_3	11.8	21.0	6.9	5.9	26.4
20#	48.2	9.25	9.3	8.5	4.5
800	C type sample	no SCC		no SCC	
0Cr18Ni9Ti		no SCC		no SCC	
600		no SCC		no SCC	
Technique	Total time :20h chemical cleaning: 10% EDTA+1% assistant agent+0.25% inhibitor A (pH=7), 93±5,5±0.5t/h,8h. rinse:600ppm rinse agent, pH=9.5-10.0,20-30,5±0.5t/h,1.5h. passivation::600ppm passivation agent, pH=9.5-10.0,60±5,5±0.5t/h,8h.			Expect for inhibitor is B, technique is same.	

The medium scale chemical cleaning test have proven the cleaning on Table 1 process which is effective for removing magnetite (17.5g/l Fe_3O_4) and safe for materials. 800 alloy,600 alloy and 0Cr18Ni9Ti is no stress corrosion cracking, The corrosion depth of A_3 carbon steel ,S_{271} low alloy steel and S_{271}/S_{271} weld 20# steel are less than 30μm.

3.1.3 Qualification test of chemical cleaning for removing corrosion products in secondary side of SG during the early period of PWR plant operation[3].

There are about 1g/l Fe_3O_4 in secondary side of PWR plant SG during the early period of operation. The chemical cleaning process will be carried during shut down.

A low concentration cleaning agent has been chosen. The condition of process of chemical cleaning are ambient temperature, static.

The inhibitor 1# and 2# have been prepared by CIAE, which used for low concentration cleaning process. Reference[3] shown date in detail.

The results of the qualification test indicate that the process of low concentration cleaning (2% EDTA+1% assistant agent + inhibitor 1# or 2#, pH~7, 20~30, 48h, static) is effective for removing corrosion products (1 g/l Fe_3O_4) in SG, the corrosion rate of main materials of SG secondary side is acceptable. The corrosion depth of A_3 carbon steel and S_{271} low alloy steel are 1-3μm only. The chemical cleaning process consists of cleaning, rinse, passivation.

3.2 Technique of chemical cleaning in primary side (contain core) of PWR type power reactor.

In primary side of PWR the corrosion products consists of Fe_3O_4(2g/l) and a little of CrNi oxide, the material of cladding is Zr-2 alloy. The qualification test had been completed in the small test loop.

The technique of chemical cleaning for removing magnetite in primary side of PWR have been quilified. The cleaning agent components of the technique of chemical cleaning are 5% EDTA +0.5% assistant agent (pH=7). The condition of cleaning are 93±5, 1.5-1.8t/h, 8h.

The results of study of qualification indicate that the technique is effective for removing magnetite (~5g/l Fe_3O_4),and is safe for Zr-2 alloy

(fuel cladding of PWR).

Above chemical cleaning technique was used in primary side of PWR type power reactor for removing corrosion products. Total 25Kg magnetite were removed in 24h, fuel cladding is integral.

4. Conclusions

The chemical cleaning agent (EDTA + assistant + inhibitor + pH adjuster) is effective for removing corrosion products (magnetite) in PWR secondary and primary side, and is safe for materials of PWR.

Four varieties of inhibitor (A, B_3, $1^{\#}$ and $2^{\#}$) have been prepared by CIAE.

Three type chemical cleaning technique have been obtained, which could be used to remove magnetite in primary and secondary side of PWR during early, medium, older period of PWR type reactor operation:

(1) The cleaning technique (10% EDTA + 1% assistant agent +inhibitor A or B_3,93±5,pH=7~8,5t/h) removes 17.5g/l magnetite (Fe_3O_4).

(2) The cleaning technique (2% EDTA +1% assistant agent , pH=7,20-30,>48h, static) removes 1g/l Fe_3O_4.

(3) The cleaning technique (1.5% EDTA + 0.5% assistant agent, pH=7,93±5, 1.8-2.0t/h) removes ~5g/l Fe_3O_4. This technique have been used in primary side of PWR type power reactor. The total 25kg magnetite (Fe_3O_4) were removed, fuel cladding (Zr-2 alloy) is integral.

Reference

[1] Zhang Mengqin et al study of chemical cleaning Technique for Removing Sludge in Secondary side of PWR SG,China Nuclear Science & Technology Report, CNIC-00806, IAE-0129, 1993.12.

[2] Zhang Mengqin et al.Medium Scale Test Study For Chemical Cleaning of Secondary Side of PWR SG. China Nuclear Science & Technology Report, CNIC-01171,IAE-0166,1997.8.

[3] Zhang Mengqin et al.Qualification Test of Chemical Cleaning For Secondary Side of Steam Generator In Qinshan Nuclear Power Plant;

China Nuclear Science & Technology Report, CNIC-01172, IAE-0167,1997.7.