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Development of Prototype Underwater Electric Discharge System for treating EDTA-Based Steam Generator Chemical Cleaning Waste Solutions in NPPs

Jin-Kil Kim [a], Duck-Won Kang [a], Peter Komaromy[b], and Istvan Schremmer [b]
a Korea Electric Power Research Institute, 103-16 Mungi-Dong Yuesong-Gu, Daejeon, Korea, 305-380
b G.I.C. Industrial Servicing and Trading Ltd. 118 Budapest, Tuzko u. 7. Hungary

1. Introduction

The steam generator (SG) chemical cleaning works in the secondary sides of nuclear power plants have not been proceeded in Korea since the SGs of Kori Unit 1 and 2 were cleaned in 1994 by KEPRI. There are many reasons for discontinuance of SG chemical cleaning works, but one of the most important reasons is the absence of the commercial low-level radioactive organic wastewater (LLEOW) treatment systems are not available in Korea.

It is important to achieve the technology for treating SG chemical cleaning waste solution before early year 2007 because Younggwang Unit 3 and 4 have scheduled to be cleaned in that time.

The purpose of this study is to develop the prototype system to treat the chemical cleaning waste solution more effectively and safely than available other current methods.

2. Methods and Results

The chemical cleaning waste solution used in this study was ACR chemical cleaning waste solution of 'Y' steam power plant. The compositions of chemical cleaning solvent and its chemical cleaning waste solution after chemical cleaning works are shown in Table 1 and 2, respectively. Especially an analysis of EDTA concentration was titrated by $ZrOCl_2$ [1].

Table. 1. Composition of 'Y' steam power plant ACR chemical cleaning solvents

Items	Input amount
EDTA(Purity: 40%)	< 13.5 %
N_2H_4(Purity: 35%)	<0.17 %
Corrosion Inhibitor(Purity: 100%)	< 0.3 %
Ascorbic Acid(Purity: 100%)	< 0.1%
NH_3(Purity: 26%)	<3%
H_2O_2	< 0.5%

Table. 2. Composition and analysis of 'Y' steam power plant ACR chemical cleaning waste solution

Items	Concentration	Analysis
TOC(Total Organic Carbon)	20,627mg/L	SHIMADZU,Japan Model: TOC-V (CPH/CPN)
TN(Total Nitrogen)	8,274mg/L	
EDTA	0.12mg/L	Titration method
Conductivity	10.8mS/cm	Thermo, USA Model: 250+
pH	7.07	

2.1. UED system set-up

UED (Underwater Electric Discharge) system [Fig. 1.] is one of the AOPs (Advanced Oxidation Processes) using AC power to generate plasma underwater condition [2, 3]. It is characterized by submerging electrodes in the solution, producing and maintaining a high intensity electric arc between the electrodes and the electrically conductive solution.

In a UED system, the decomposition reaction takes place in the plasma reactor. The 9 electrodes are immersed into the solution to be treated, and the plasma forms between the electrode surface and the solution. The decomposition of EDTA takes place in the high temperature of plasma and under intensive UV radiation, and the added hydrogen-peroxides intensify the oxidative environment in the plasma reactor.

(a) (b)

Fig. 1. Photographs of semi-pilot scale UED system
(a) Front view of UED system
(b) Side view of UED system

2.2. Operation strategy

The UED system consists of the following 7 parts: (1) a wastewater container, (2) a buffer tank, (3) an AC plasma reactor, (4) a condensate tank, (5) a separator, (6) a purifying tank, and (7) an electric control unit. The flow diagram of UED system is shown in Fig. 2 and Fig. 3.

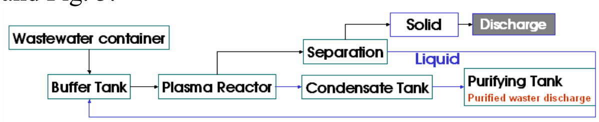


Fig. 2. A simplified w/w treatment process of UED system

A treatment cycle in the semi-pilot scale UED system consists of 4 main processes, (1) wastewater input, (2) heating wastewater, (3) decomposition of EDTA & concentration of wastewater, and (4) separate the liquid and solid with a separator. In this experiment, the UED system was operated 2 cycles with the concentration and degradation method to increase the EDTA decomposition rate in the plasma reactor [Fig. 3].

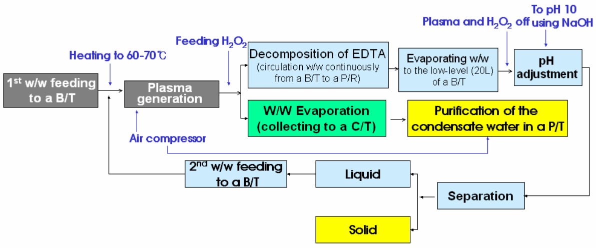
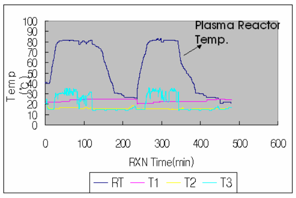


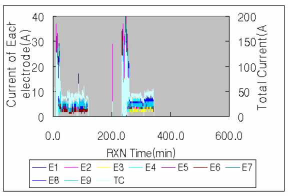
Fig. 3. An Operation method of UED system to treat SG chemical cleaning waste solution

2.4. On-line monitoring UED system

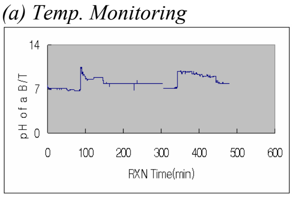
The AC plasma reactor of the UED system was monitored by on-line computer program LUDWIG (G.I.C, HU) during the experiment. The temperature of a plasma reactor was maintained 80 ℃ and total carrying current of 9 electrodes was about 42A 380V. [Fig. 4. (a), (b)]. To increase separation efficiency, pH was increased during separation time [Fig. 4. (c)].



(a) Temp. Monitoring



(b) current monitoring



(c) pH change monitoring

Fig. 4. Monitoring UED system with LUDWIG program

2. 5. Experiment results

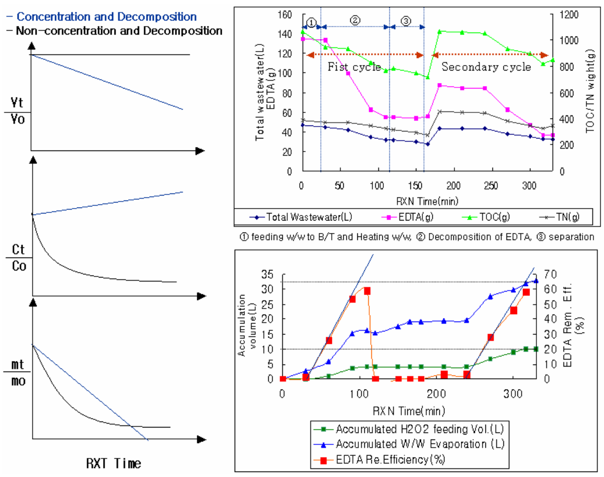


Fig. 5. An Operation method of UEDS to treat steam generator chemical cleaning waste solution

The chemical cleaning waste solution treatment capacity of the UED system was about 14L/hr. In this experiment, we fed 25 v/v% of H_2O_2 (40%), and treated about 30L waste solution during the 2 cycles. The main experiment results in this study are shown in Fig. 5. The result that the more the volume of wastewater becomes concentrated, the better EDTA decomposition rate becomes was noticeable with left 3 graphs in Fig. 5.

2.5. Heavy metal analysis for purified condensate water

Concentration of heavy metals in purified waste solution is presented at Table 3. Although the concentration of heavy metals in the raw waste solution was very high, their concentrations in purified water collected in a purifying tank were very low. For discharging safely to environment, an ion exchange resin tower should be installed at the final part in this system.

Table. 3. Raw wastewater contents of chemical

	RXN Time (min)	Heavy Metal								
		Fe	Cu	Ni	Zn	Ca	Cr	Al	※ Co (ppb)	※Cs (ppb)
Raw w/w(ppm)		8000	41	4.95	306	9.6	3.93	2.82	204.8	385.4
1st W/W Feeding	0	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.045	0.018
	60	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.124	0.026	0.011
	90	N.D.	0.15	N.D.	N.D.	N.D.	N.D.	0.106	0.05	0.046
	100	0.554	0.27	N.D.	0.015	N.D.	N.D.	0.129	0.047	0.05
2nd W/W Feeding	0	N.D.	N.D.	N.D.	0.015	N.D.	N.D.	0.151	0.055	0.059
	60	0.802	N.D.	N.D.	0.027	N.D.	N.D.	0.135	0.05	0.76
	90	N.D.	0.15	0.029	0.102	N.D.	N.D.	0.154	0.104	0.122
	137	0.118	N.D.	0.29	0.117	N.D.	N.D.	0.168	0.128	0.243

※ 1) Raw wastewater is derived from an ACR chemical cleaning process of Y power plant.
2) Cs and Co are put artificially into raw wastewater.

3. Conclusions

The aim of the work was to develop the treatment system of the SG chemical cleaning waste solution. The developed semi-pilot scale UED system was very useful and safe for treating LLEOW containing EDTA. Moreover, the concentration and decomposition method adopted in this system was effective.

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