HYDROGEN PEROXIDE AS A LIQUID RADWASTE PRETREATMENT ON THE DUKE POWER SYSTEM

Brian Cauthen, Lance Loucks and Mary Maner
Duke Power Company

ABSTRACT

Duke Power has initiated laboratory testing on the effects of hydrogen peroxide additions to various radioactive waste streams from its three nuclear facilities. New lab techniques were utilized that provided data to prescribe a hydrogen peroxide dosage that would inhibit microbiological growth which inhibits effective radwaste processing.

Current operational data shows the effectiveness of the peroxide in the reduction of biomass in the waste system at McGuire Nuclear Station.

INTRODUCTION

Last year, changes were made to improve the processing of radioactive waste at Duke Power's Catawba Nuclear Station (1). As a follow-up to the changes made, a new study was undertaken to minimize microbiological growth in the waste feed tanks and the associated system. The most available and economical option considered was treatment with hydrogen peroxide (2).

Laboratory tests were conducted on the effect of peroxide on biological life in radioactive waste streams. The tests on waste water from each of Duke Power's nuclear facilities provided data that resulted in recommendations to reduce microbiological growth and provide for a clean system. Two stations began adding maintenance doses of peroxide on a regular basis. At the McGuire station, tests were conducted to determine the effectiveness of peroxide in cleaning the system and the effect on radionuclide removal.

The overall study goals were as follows:

1. Define the necessary dosage to effectively eliminate microbiological organisms in liquid radwaste systems while enhancing system performance.
2. Evaluate lab methods to determine actual reduction of microbiological life in liquid radwaste systems.
3. Evaluate peroxide dosage effectiveness with respect to microorganisms throughout an entire liquid radwaste processing system.

LABORATORY TEST

The first tests were conducted on samples from each of Duke's nuclear plant's waste systems. These samples were from Oconee (Miscellaneous Waste Hold-up Tank), McGuire (Spent Resin Storage Tank) and Catawba (Floor Drain Tank). Various concentrations (50, 100, 500 and 1000 PPM) of hydrogen peroxide (H2O2) were added to each of these samples. The total living biomass (bacteria included) was determined before addition and at various time intervals (1, 4, 16.5 and 21 hours) after the additions.

Total living biomass in the liquid was determined by measuring the adenosine triphosphate (ATP) levels. ATP is a substance found in all living cells. When a cell dies the ATP leaves and is destroyed by a phosphatase enzyme that is also released from the cell. At Duke, both ATP and Epiflourescence have been proven to be effective methods to determine total bacteria counts. However, ATP was selected as the preferred method to determine a total bacteria count because it takes only 30 minutes to complete as compared to Epiflourescence which requires 24 hours. The ATP sample extraction consist of the addition of dimethyl sulfoxide (DMSO) while the addition of a HEPES water buffer solution is for stabilization. By measuring the amount of ATP in the waste samples before and after addition, the biocide effectiveness can be determined.

The stock H2O2 was assayed to be 35% H2O2 by titration with permanganate and then diluted to a 0.35% concentration using demineralized water. The diluted biocide was then added to 100 mL aliqouts of the three samples of waste water to achieve the desired concentrations. The ATP measurements were then taken. The results of these samples are shown in Tables I, II and III.

The H2O2 concentrations were measured utilizing a Chemetrics test kit which is based on a color comparison. The test kit proved to be efficient and accurate in this application. Accuracy was verified by comparing the kit results with that of permanganate titration. However, during further analytical testing, it was observed that the presence of nitrites, from closed loop cooling system leakage, in the waste stream caused a positive interference in the H2O2 determination. The nitrite analysis was also errant due to H2O2 in the sample. The analysis of H2O2 is based on the oxidation of ferrous iron to ferric iron while the sodium nitrite also oxidizes ferrous to ferric. Therefore, these analyses are suspect when both nitrite and peroxide are present.

Since the samples studied for this investigation were free of any nitrites, the H2O2 concentrations are valid. Although the H2O2 did provide effective treatment of biomass, it was not depleted during the test. The concentrations were found to be depleted by only 15% on the Catawba and Oconee samples after 21 hours. The McGuire sample showed no depletion, possibly due to the smaller amount of biomass in that sample that required destruction.

The biocide was considered effective if the number of organisms were reduced by greater than 90%. Table IV

TABLE I

Oconee Nuclear Station Misc. Waste Hold-Up Tank

ELAPSED TIME (HR)		H202 CONCENTRATION (PPM) 50	100	500	1000
0	ATP	2.5E-09	2.5E-09	2.5E-09	2.5E-09
	BACTERIA	4.9E+06	4.9E+06	4.9E+06	4.9E+06
1	ATP	4.1E-10	6.4E-10	1.3E-09	1.0E-09
	BACTERIA	8.2E+05	1.3E+06	2.6E+06	2.0E+06
4	ATP	2.0E-10	3.2E-10	2.0E-10	4.1E-10
	BACTERIA	4.1E+05	6.5E+05	4.0E+05	8.2E+05
16.5	ATP		6.4E-11		
	BACTERIA		1.3E+05		
21	ATP	0.0E+00	0.0E+00	0.0E+00	0.0E+00
	BACTERIA	0.0E+00	0.0E+00	0.0E+00	0.0E+00

TABLE II

Catawba Nuclear Station Floor Drain Tank

ELAPSED TIME (HR)		H202 CONCENTRATION (PPM) 50	100	500	1000
0	ATP	1.4E-09	1.4E-09	1.4E-09	1.4E-09
	BACTERIA	2.8E+06	2.8E+06	2.8E+06	2.8E+06
1	ATP	6.6E-10	3.0E-10	2.1E-10	1.8E-10
	BACTERIA	1.3E+06	6.0E+05	4.2E+05	3.6E+05
4	ATP	3.1E-10	1.8E-10	1.9E-10	2.3E-10
	BACTERIA	6.3E+05	3.6E+05	3.8E+05	4.5E+05
21	ATP	0.0E+00	0.0E+00	0.0E+00	0.0E+00
	BACTERIA	0.0E+00	0.0E+00	0.0E+00	0.0E+00

The units for ATP are grams/50ml and #/ml for bacteria.

TABLE III

McGuire Nuclear Station Spent Resin Storage Tank

ELAPSED TIME (HR)		H2O2 CONCENTRATION (PPM) 50	100	500	1000
0	ATP	3.7E-11	3.7E-11	3.7E-11	3.7E-11
	BACTERIA	4.9E+06	4.9E+06	4.9E+06	4.9E+06
1,4	ATP	0.0E+00	0.0E+00	0.0E+00	0.0E+00
21	BACTERIA	0.0E+00	0.0E+00	0.0E+00	0.0E+00

The units for ATP are grams/50 ml and #/ml for bacteria.

shows a 90-100% reduction in all samples at all concentrations. Table V lists the specific bacteria in each sample.

These tests proved that the methods utilized to determine ATP and H2O2 gave an accurate estimate of living biomass. Also, the lab tests indicate that only low concentrations of H2O2 are needed to provide an effective kill of the assorted bacteria in liquid radwaste, in approximately 12 hours. These results are based on lab tests and did not account for biofilm existing in tanks and continual waste additions to the system as opposed to a given volume in the lab.

Results of the tests on the ONS samples are shown in Fig. 1. The targeted "kill rate" was typically achieved between four and sixteen hours. The results from the other two stations were very similar, although the addition to the McGuire sample provided acceptable results immediately.

FULL SCALE IMPLEMENTATION

The use of peroxide at Catawba (CNS) provided results in the attempt to maintain a "clean" system. Prior to the addition of H2O2 (10 PPM) to the system, filter media exhibited a very sour or septic odor at changeout due to microbiological growth. After the additions had been made for a period of two to three weeks, the odor associated with a radwaste filter change was eliminated. With this observation, it has been determined that the additions have cleaned and continue to maintain a clean waste treatment system.

Hydrogen peroxide additions were also made at Oconee Nuclear Station. These additions were made to the waste storage tanks as a weekly maintenance dose. The typical dosage was 20 PPM. The elimination of microorganisms was also observed at ONS utilizing a simple count which grossly measured the number of colonies of organ-

TABLE IV

Biocide Effectiveness

		1 HOUR	4 HOURS	16.5 HOURS	21 HOURS
ONS	50 PPM	83 %	92 %	-	100 %
	100 PPM	73 %	87 %	97 %	100 %
	500 PPM	47 %	92 %		100 %
	1000 PPM	59 %	83 %		100 %
MNS	50 PPM	100 %	100 %	-	100 %
	100 PPM	100 %	100 %	100 %	100 %
	1000 PPM	100 %	100 %		100 %
CNS	50 PPM	54 %	92 %	-	99 %
	100 PPM	79 %	87 %	100 %	100 %
	500 PPM	85 %	86 %		100 %
	1000 PPM	87 %	84 %		100 %

TABLE V

Culture Reports/Bacteria Identified

SLIME BACTERIA	OCONEE	CATAWBA	McGUIRE
KLEBSIELLA PNEUMONIAE	XX	XX	--
CITROBACTER FREUDII	XX	XX	--
ENTEROBACTER CLOACAE	XX	XX	--
PSEUDOMONAS TESTOSERONI	XX	--	--
AEROMONAS SPECIES	--	XX	--
PSEUDOMONAS ACIDOVORANS	--	XX	--
IRON-OXIDIZING BACTERIA			
SPHAEROTILUS SPP	XX	--	--
SULFATE REDUCING BACTERIA			
10^4 DESULFOVIBRIO/ML	--	XX	--

isms on a before and after sample as opposed to the ATP method of measurement.

The results of the lab test discussed above provided a starting point for the full scale use of H2O2 in each batch of liquid processed through the radwaste systems. At McGuire Nuclear Station (MNS), baseline samples were taken from the floor and equipment drain tank to provide a reference of as-found bacteria levels. After one month of processing with intermittent 25 PPM doses of H2O2, a reduction of approximately 85% was realized in the waste processing samples.

The addition of H2O2 was implemented in conjunction with the installation and operation of two new ion exchange vessels. Data collected to date indicate that the H2O2 additions are slowly sanitizing the waste treatment system upstream of the new vessels. The targeted concentration of

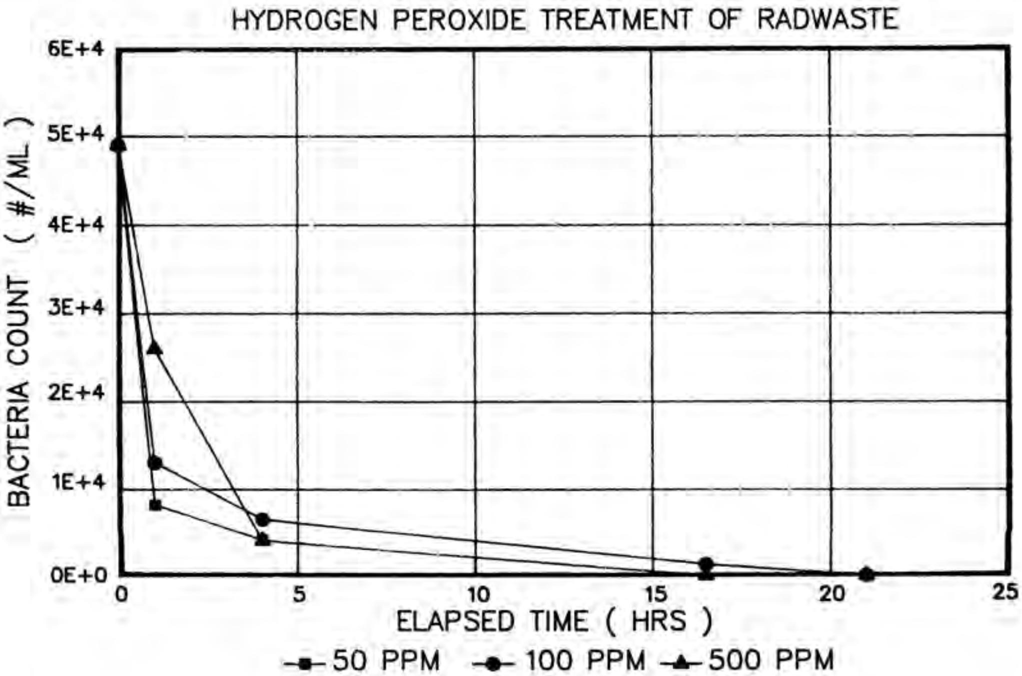

Fig. 1. Oconee Nuclear Station.

25 PPM has been achieved in the waste feed tank; however, only 10 PPM has been observed in the influent of the ion exchange vessels. The section of piping that is being used to transport this waste to the new vessels has been stagnant for several years and has an average total bacteria count of approximately 2E6 per ml. The total count after peroxide dosages has decreased to 3E5 per ml, which does meet the goal of a 90% "kill rate".

There was no significant increase in radionuclide removal from the waste stream as a result of the H2O2 addition. Conversely, there was no detrimental affect.

The floor and equipment drain tank was not in a "clean" condition at the beginning of the current evaluation. The tank has not been physically cleaned since initial plant operation. The addition of peroxide was never intended to replace the need to perform a desludging of the tank. After the tank is cleaned, it is anticipated that the addition of peroxide in conjunction with the installation of mechanical mixers will decrease the likelihood of frequent tank cleaning in the future.

The elimination of biological organisms in the McGuire radwaste system has shown success through late January. As shown by Fig. 2, the initial addition of peroxide on December 12 shocked the system; thus, providing the most effective "kill rate" to date. The December 12, January 14 and January 23 samples were taken 1-2 hours after peroxide additions. The January 22 samples, collected 16 hours after addition, indicate that biological growth reestablishes itself over a relatively short period of time. The other data shows that the peroxide additions are providing the effective results on the piping downstream of the feed tank.

The consistent "kill rate" of 80-90% at the new ion exchange vessel sample points indicate that the desired 90% rate is achievable with continued H2O2 additions.

SUMMARY

As a direct result of the testing of hydrogen peroxide, the existence and growth of microorganisms in the liquid radwaste treatment systems at Duke Power have been curtailed. This success was achieved by:

1. Utilizing lab methods which required neither extensive labor nor capital expenditures.
2. Defining a hydrogen peroxide dosage of 10 to 25 PPM which eliminates the organisms while not affecting radionuclide removal.
3. Assuring a 90% elimination of microorganisms throughout the entire system with the use of various concentrations of hydrogen peroxide.

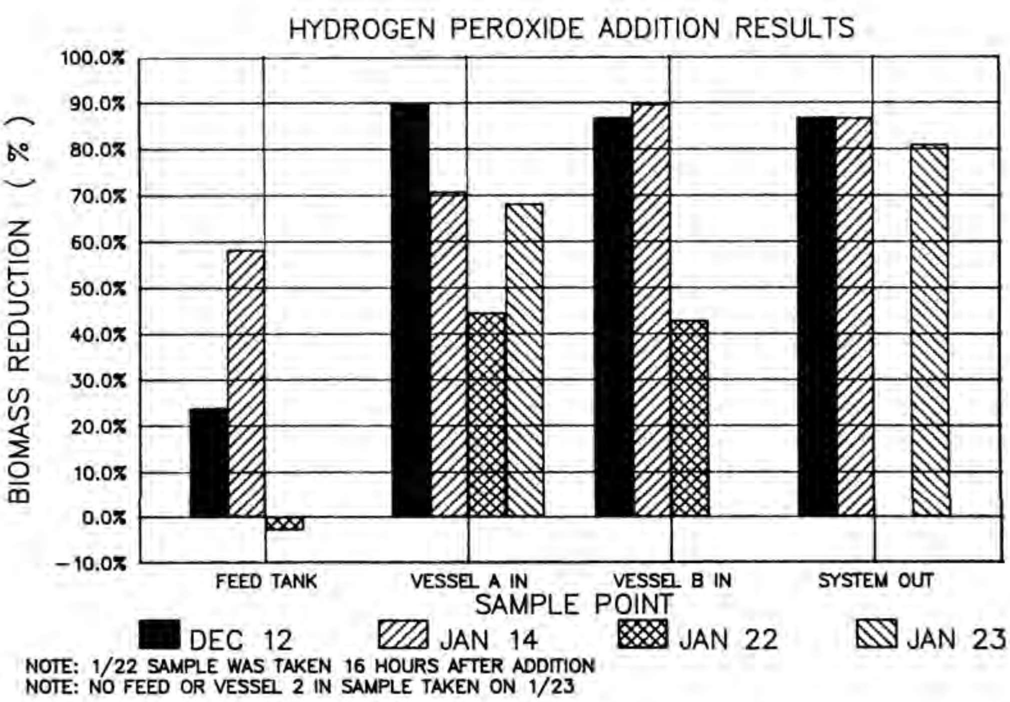

Fig. 2. McGuire Nuclear Station.

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