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DPST-85-782-TL
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September 9, 1985

J. T. GRANAGHAN, PLANT MANAGER
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ATTENTION: W. B. BOORE

OXALIC ACID CLEANING OF TANK 24H

Attached is DPST-85-782, "Oxalic Acid Cleaning of Tank 24H." This document gives the results of the recently completed oxalic acid cleaning program which attempted to remove the approximately 10,000 gallons of zeolite which remained in Tank 24H following the completion of salt removal operations.

G. W. Wilds,
Research Manager
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Tank 24H
Zeolite Removal
Waste Tank Cleanout

TECHNICAL DIVISION
SAVANNAH RIVER LABORATORY

DPST-85-782
ACC. NO. 189389

CC: W. R. Stevens III
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SRL Records (4)
MSM File

MEMORANDUM

September 9, 1985

TO: M. A. EBRA,

FROM: M. C. H. FONG, MCHF

OXALIC ACID CLEANING OF TANK 24H

Introduction and Summary

Waste Tank 24H, which contained approximately 10,000 gallons of zeolite following the completion of salt removal in 1983, has recently undergone an oxalic acid cleaning program. The program, which consisted of two oxalic acid washes and associated water rinses, was not completely sucessful in its attempt to remove the remaining zeolite and the approximately 100,000 curies of radioactivity sorbed on the zeolite. Until a representative sample of the solids remaining in Tank 24H can pulled for analysis and testing, the chemical form the solids have taken, and consequently a definitive plan for their removal, can not be formulated with any accuracy. However, preliminary analysis of solids collected in tank dip samples indicate that the solids may have taken the form of a zeolite similar to hydroxy sodalite. The excess hydroxide ion in the silica matrix of the solid would require much more acid than originally anticipated to complete the cleaning program. Furthermore, since the majority of the solids are in a hard, immovable mass in the center of the tank, the reaction between the zeolite and the solids will take much longer than originally estimated.

Process Description

Oxalic acid cleaning of Tank 24H began on April 11, 1985 when 22,500 gallons of approximately 8 weight percent oxalic acid was added to the 11,000 gallon heel in Tank 24. Soon after completion

of the acid addition, 12,000 gallons of water were added. The oxalic acid solution was agitated continuously for 3 days, then neutralized with 2,400 gallons of 50 weight percent sodium hydroxide and transferred to Tank 38H for storage and eventual evaporation.

Tank 24 was then rinsed with 9,600 gallons of water for 2 hours, and the rinse water transferred to Tank 38. Tank 24 was rinsed a second time with 19,100 gallons of water which was slurried for one day, and this rinse water was also transferred to Tank 38.

The second oxalic acid wash began on April 26, 1985 when 23,500 gallons of approximately 8 weight percent oxalic acid was added to the 13,000 gallon heel in Tank 24. The oxalic acid solution was agitated continuously for 3 days, then neutralized with 2,400 gallons of 50 weight percent sodium hydroxide and transferred to Tank 38.

Plans call for spray washing Tank 24 at some future date. After spray washing has been completed, Waste Management Operations will attempt to pull a representative sample of the solids remaining in Tank 24, so further analyses can be conducted.

Experimental Procedure

Tank 24 was closely monitored throughout each step of the oxalic acid cleaning program. Two 100 ml dip samples were pulled from two separate tank risers (the northwest and southeast risers) during each monitoring step. Each sample received was weighed and centrifuged to obtain density and volume percent solids. The decanted supernate was sent to the Analytical Development Division (ADD), for chemical analysis.

During the second oxalic acid washing step, weight percent dissolved solids and insoluble solids were also determined. A portion of the supernate was decanted to a beaker for dissolved solids determination, and the packed solids were washed with 10 ml of dionized water. Both the washed solids and the supernate were dried overnight at 115°C, and the weight percents then calculated. Also, a small well mixed portion of each sample as received was sent to ADD for radio-chemical analysis. Results of all these procedures are given in Table 1.

In an attempt to learn the composition of the insoluble solids collected in the tank monitoring samples, further procedures were carried out on the solids obtained from samples pulled during the first oxalic acid wash, and from the second oxalic acid wash neutralization step.

The solids remaining from a sample pulled during the first oxalic

acid wash were placed in about 25 ml of 1 molar nitric acid, mixed, and centrifuged. The liquid was decanted and sent for analysis, and this step was repeated. The solids were then placed in about 25 ml of dionized water, mixed, and centrifuged. This solution was also sent for analysis. Finally, the remaining solids were placed in about 25 ml of 1 molar sodium hydroxide, all remaining insoluble solids dissolved, and this solution was sent for analysis. Results of this procedure are given in Table 2.

The solids remaining from another of the samples pulled during the first oxalic acid wash were placed in about 25 ml of 1 molar sodium hydroxide, mixed, and centrifuged. The liquid was decanted and sent for analysis. Results of this procedure are given in Table 3.

The dried solids remaining from the samples pulled during the second oxalic acid wash neutralization step were sent to ADD. A portion of these solids were dissolved in an acid bomb, and a portion in a sodium peroxide - hydrochloric acid bomb. The resulting solutions were analyzed and the results are given in Table 4.

Conclusions

Examination of Table 1 indicates that all the added oxalic acid had reacted completely during the first oxalic acid wash (the number of equivalents of sodium and aluminum almost equaled the equivalents of oxalate present). However, large amounts of unreacted zeolite still remained in the tank.

The assumed composition of the zeolite present in Tank 24 differed considerably from the composition actually found. The composition of the zeolite as it was originally placed in the tank is given as $Na_4(AlO_2)_4(SiO_2)_8 \cdot 13H_2O$. The reaction of this zeolite with oxalic acid is given below.

$$NaAlO_2(SiO_2)_2 + 2H_2C_2O_4 \rightarrow Na^+ Al(C_2O_4)_2^- + 2H_2O + 2SiO_2$$

Therefore it was originally assumed that the oxalic acid cleaning reaction would require about 1 mole of oxalic acid (135 gallons of 8 weight percent oxalic acid) for every 1043 pounds of zeolite present.

The actual composition of the zeolite contained in Tank 24 has been derived from the data obtained from the dissolution of the zeolite solids from the first oxalic acid wash step. The original zeolite is believed to have evolved into a compound similar to hydroxy sodalite, due to the long period of time it spent in the highly caustic environment of the salt tank. The composition of this solid is given roughly as $3(NaAlO_2 \cdot SiO_2) \cdot 3NaOH \cdot NaNO_3 \cdot 12H_2O$. Because of the presence of the intercalated sodium

hydroxide, larger quantities of oxalic acid (2.8 times the amount originally assumed) will be required to react with the solids remaining in Tank 24.

The compositon of these solids was obtained after careful examination of the data given in Table 2. This data indicates that for roughly every 1 mole of nitrate present in the solids, there are approximately 3 moles of aluminum, 3 moles of silica, and 7 moles of sodium. It was assumed that there were 4 waters of hydration present for every mole of aluminum. This information, along with a knowledge of zeolite structures, led to the zeolite composition just mentioned.

The oxalic acid-zeolite reaction during the second acid wash, unlike the first acid wash, did not consume all the added oxalic acid. Examination of Table 1 reveals that the total number of equivalents of sodium and aluminum was only half as much as the number of equivalents of oxalate present. Furthermore, the pH of the acid solution at the end of the second wash was 4.83 (oxalic acid enters its second buffer region at about this pH).

These results indicate that only one of the two hydrogen ions in the oxalic acid had been neutralized. Since all the oxalate did not react with as much of the zeolite as in the first oxalic acid wash, it is suspected that all the lose and easily moved solids in Tank 24 had already reacted, leaving only the densely packed immobile solids with which oxalic acid can react.

At the end of each oxalic acid wash, the sodium and aluminum oxalates were in solution and the hydrated silica was present as a solid. Upon addition of the sodium hydroxide solution added to neutralize the acid before transfer, the aluminum oxalates reacted to form soluble sodium aluminate, and the hydrated silica reacted to form soluble sodium silicate. The sodium aluminate and the sodium silicate then reacted with each other to form an alumino silicate gel. This gel has many of the properties of the original zeolite, and readily sorbs cesium. However, formation of this gel does not adversely effect the tank cleaning program, since it was easily slurried and transferred from the tank.

The composition of this alumino silicate gel has been derived from the data obtained from the dissolution of the solids contained in samples pulled following the neutralization of the second oxalic acid wash solution. Examination of this data, which is given in Table 4, shows that for every mole of aluminum present, there are about 1.3 moles of silica and 3.2 moles of sodium. Given this information, along with the assumption that there are 4 waters of hydration for every mole of aluminum in the gel structure, the gel composition can be approximated as $Na(AlO_2)\ (SiO_2)_{1.3}\ (NaOH)_{2.2}$.

TABLE 1

Sample ID	Process Step	Date Sampled	Tank Level (in)	Tank Volume (gal)	Density (g/ml)	Volume % Solids	Weight % Insoluble Solids	Weight % Dissolved Solids
T24-1-N	Oxalic Acid Addition	4/11/85	14.6	51,700	1.05	25.0	—	—
T24-1-S	Oxalic Acid Addition	1 pm	14.6	51,700	1.03	25.0	—	—
T24-2-N	Oxalic Acid Washing	4/12/85	16.3	57,700	1.03	27.0	—	—
T24-2-S	Oxalic Acid Washing	6 am	16.3	57,700	1.03	25.0	—	—
T24-3-N	Oxalic Acid Washing	4/13/85	19.4	68,600	1.01	19.8	—	—
T24-3-S	Oxalic Acid Washing	6 am	19.4	68,600	1.03	20.6	—	—
T24-4-N	Oxalic Acid Washing	4/14/85	22.0	79,900	1.02	17.5	—	—
T24-4-S	Oxalic Acid Washing	7 am	22.0	79.900	1.02	16.3	—	—
T24-5-N	Acid Neutralization	4/14/85	24.0	84,800	1.04	22.5	4.0	3.3
T24-5-S	Acid Neutralization	10 am	24.0	84,800	1.03	21.3	—	—
T24-6-S	1st Water Wash	4/17/85 7 am	6.4	22,600	1.01	12.5	—	—
T24-8-N	2nd Water Wash	4/24/85	13.0	46,000	1.0	7.85	.92	.83
T24-8-S	2nd Water Wash	morning	13.0	46,000	1.0	8.43	.88	.79
T24-10-N	Oxalic Acid Washing	4/28/85	15.2	53,800	1.03	24.19	1.67	4.10
T24-10-S	Oxalic Acid Washing	6 am	15.2	53,800	1.02	11.82	.52	4.61
T24-11-N	Oxalic Acid Washing	4/29/85	19.5	69,000	1.01	33.8	2.31	3.3
T24-11-S	Oxalic Acid Washing	7 am	19.5	69,000	1.03	33.1	2.39	3.1
T24-12-N	Acid Neutralization	4/29/85	21.2	75,000	1.05	32.5	4.55	2.91
T24-12-S	Acid Neutralization	3 pm	21.2	75,000	1.06	33.0	3.79	3.58

1) ND = None Detected

2) NA = Not Applicable

TABLE 1
(Continued)

pH	Free Acid	Total OH (molar)	Free OH (molar)	C_2O_4 (molar)	NO_2 (molar)	NO_3 (molar)	Al (molar)	Fe (molar)	Ca (molar)
4.54	[1]ND	[2]NA	NA	.475	<.002	.043	.20	.008	.008
4.56	ND	NA	NA	.519	<.002	.041	.20	.008	.008
5.50	ND	NA	NA	.455	<.002	.075	.136	.005	.002
5.53	ND	NA	NA	.440	<.002	.072	.136	.005	.002
5.71	ND	NA	NA	.362	<.002	.070	.103	.004	.0006
5.73	ND	NA	NA	.355	<.002	.069	.104	.004	.0006
6.04	ND	NA	NA	.296	<.002	.059	.084	.004	.0003
6.06	ND	NA	NA	.291	<.002	.058	.083	.004	.0003
12.72	NA	.193	.15	.217	<.002	.056	.074	4.7×10^{-5}	.0002
12.76	NA	.174	.157	.221	<.002	.056	.072	.0002	.0004
—	NA	.032	.025	.107	<.002	.021	.022	9×10^{-6}	$<2 \times 10^{-7}$
9.95	NA	.007	ND	.132	<.002	.013	.002	3.9×10^{-5}	ND
9.74	NA	.007	ND	.132	<.002	.012	.002	5.4×10^{-5}	1×10^{-5}
4.33	ND	NA	NA	.905	<.002	.040	.190	.011	.011
4.38	ND	NA	NA	1.015	<.002	.043	.189	.011	.011
4.86	ND	NA	NA	.721	<.002	.039	.133	.008	.007
4.83	ND	NA	NA	.884	<.002	.045	.135	.008	.007
--	NA	.167	.093	.603	<.002	.034	.050	.0001	5.5×10^{-5}
—	NA	.166	.084	.537	<.002	.034	.052	.0002	.0005

TABLE 1
(Continued)

Na (molar)	Si (molar)	K (molar)	SR-90 (d/m/ml)	Decanted Supernate: Gross Beta/Gamma (d/m/ml)	Decanted Supernate: Gamma Scan CS-137 (d/m/ml)	Decanted Supernate: Gamma Scan CS-134 (d/m/ml)
.39	—	—	—	1.46×10^7	2.17×10^7	7.74×10^4
.38	—	—	4.85×10^5	1.04×10^7	2.21×10^7	8.42×10^4
.425	—	—	2.76×10^5	6.58×10^6	1.16×10^7	4.20×10^4
.424	—	—	2.76×10^5	7.1×10^6	1.23×10^7	4.45×10^4
.354	.002	—	1.57×10^5	5.42×10^6	7.23×10^6	—
.354	.002	—	1.68×10^5	5.64×10^6	1.00×10^7	3.60×10^4
.309	.002	—	1.64×10^5	4.56×10^6	6.79×10^6	—
.302	.002	—	9.29×10^4	4.54×10^6	6.7×10^6	—
.687	.002	—	5.55×10^3	5.04×10^6	1.04×10^7	4.27×10^4
.675	.002	—	1.32×10^4	5.24×10^6	1.03×10^8	4.00×10^4
.237	.0004	—	1.35×10^3	2.02×10^6	4.15×10^6	1.33×10^4
.137	1.2×10^{-4}	—	—	1.36×10^6	—	—
.128	1.4×10^{-4}	—	—	1.34×10^6	—	—
.287	.004	—	3.37×10^5	1.17×10^7	2.66×10^7	8.40×10^4
.287	.004	—	4.18×10^5	1.26×10^7	3.06×10^7	1.20×10^5
.264	.003	.0004	2.38×10^5	7.44×10^6	1.73×10^7	6.54×10^4
.264	.003	.0004	2.28×10^5	7.86×10^6	1.67×10^7	5.94×10^4
.605	.002	.0003	2.50×10^3	7.68×10^6	2.0×10^7	4.36×10^4
.604	.004	.0003	2.14×10^3	7.85×10^6	1.97×10^7	3.98×10^4

TABLE 1
(Continued)

Slurried Supernate and Solids		
Gross Beta/Gamma (d/m/ml)	Gamma Scan CS-137 (d/m/ml)	Gamma Scan CS-134 (d/m/ml)
—	—	—
—	—	—
—	—	—
—	—	—
—	—	—
—	—	—
—	—	—
—	—	—
—	—	—
4.41×10^7	1.16×10^8	5.86×10^5
2.60×10^7	5.64×10^7	2.93×10^5
1.29×10^7	3.06×10^7	1.18×10^5
1.68×10^7	3.84×10^7	1.65×10^5
2.91×10^7	7.19×10^7	3.00×10^5
2.10×10^7	4.35×10^7	1.54×10^5
3.34×10^7	9.67×10^7	3.89×10^5
3.74×10^7	9.49×10^7	3.67×10^5
2.47×10^7	5.21×10^7	2.20×10^5
6.28×10^7	1.1×10^8	4.13×10^5

TABLE 2

Analysis	Sample T24-3N As Received	1st Acid Decant	2nd Acid Decant	Water Decant	1st Caustic Decant
Solids Volume	7.9 ml	4.5 ml	7.5 ml	6.5 ml	<.5 ml
Total Volume	40 ml	30 ml	30 ml	29.5 ml	30 ml
Free Acid	ND	.1598 M	.7312 M	--	NA
pH	5.71	3	1.15	--	--
Total OH	NA	NA	NA	ND	.7250 M
Free OH	NA	NA	NA	ND	.5873 M
C_2O_4	.362	.143 M	.048 M	.002 M	<.001 M
NO_2	<.002 M	<.002 M	<.002 M	<.002 M	<.002 M
NO_3	.0698 M	1.23 M	1.04 M	.189 M	.043 M
Al	.103 M	.133 M	.032 M	.0065 M	.0023 M
Fe	.004 M	.003 M	.002 M	.0007 M	.0001 M
Ca	.0006 M	.014 M	.009 M	.0022 M	.0001 M
Na	.354 M	.122 M	.027 M	.0059 M	.7334 M
Si	.002 M	.047 M	.008 M	.0017 M	.1773 M
B/Gamma	5.42×10^6 d/m/ml	5.78×10^7 d/m/ml	1.72×10^7 d/m/ml	3.51×10^6 d/m/ml	8.74×10^5
Sr-90	1.57×10^5 d/m/ml	3.96×10^5 d/m/ml	--	--	--

TABLE 3

Analysis	Sample T24-3S As Received	1st Caustic Decant
Solids Volume	8.25 ml	--
Total Volume	40 ml	30 ml
Free Acid	ND	--
pH	5.73	--
Total OH	--	.491 M
Free OH	--	.4465 M
C_2O_4	.355 M	.136 M
NO_2	<.002 M	<.002 M
NO_3	.069 M	.022 M
Al	.104 M	.022 M
Fe	.004 M	4.66×10^{-5} M
Ca	.0006 M	$<2 \times 10^{-7}$ M
Na	.354	.784 M
Si	.002	.013 M
B/Gamma	5.64×10^{6} d/m/ml	7.46×10^{6} d/m/ml

TABLE 4

Analysis	Acid Bomb	Na_2O_2 - HCl Bomb
K(AA)	1.08 ppm	—
HG(AA)	.142 ppm	—
C_2O_4(IC)	<.01 μg/ml	<.01 M
NO_3(IC)	<.01 μg/ml	<.01 M
Ag(ICP)	<.01 wt%	28.1 wt%
Al(ICP)	6.36 wt%	6.53 wt%
Ca(ICP)	.932 wt%	1.24 wt%
Fe(ICP)	3.33 wt%	1.92 wt%
Na(ICP)	17.3 wt%	—
Ni(ICP)	—	—
Si(ICP)	—	8.82 wt%
Zn(ICP)	.106 wt%	—
Pd(ICP)	<.01 wt%	<.01 wt%
Rh(ICP)	<.01 wt%	<.01 wt%
U	.4 ppm	.829 ppm
SR-90	1.25×10^4 d/m/ml	1.26×10^5 d/m/ml
SE-79	<100 d/m/ml	<100 d/m/ml
TC-99	2.10×10^2 d/m/ml	3.55×10^2 d/m/ml
Pu(TTA)	1.18×10^3 d/m/ml	1.40×10^3 d/m/ml
B/Gamma	1.16×10^6 d/m/ml	1.94×10^5 d/m/ml
G/SCAN:		
CS-137	7.05×10^5 d/m/ml	5.06×10^6 d/m/ml