2024 TECHNICAL UPDATE

Hydrazine Alternatives for the Pressurized Water Reactor/Pressurized Heavy Water Reactor Secondary System

Diethylhydroxylamine (DEHA) Impact on Resin Performance

PORTIONS TRANSLATED

Hydrazine Alternatives for the Pressurized Water Reactor/Pressurized Heavy Water Reactor Secondary System

Diethylhydroxylamine (DEHA) Impact on Resin Performance

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Technical Update, October 2024

EPRI Project Manager
K. Fruzzetti

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EPRI prepared this report.

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ABSTRACT

Due to changes in environmental and occupational safety regulations as well as supply chain limitations, utilities operating Pressurized Water Reactors (PWRs) and Pressurized Heavy Water Reactors (PHWRs) have faced hydrazine use and sourcing challenges and may face larger challenges in the future. EPRI has been working on both near-term and long-term solutions. This effort is focused on testing to evaluate one of the potential long-term solutions.

One of the consensus long-term potential solutions, resulting from the EPRI 2019 global workshop on hydrazine alternatives, is the use of Diethylhydroxylamine (DEHA) for at-power oxygen scavenging and favorable impact on electrochemical potential (ECP) in the secondary system of PWRs and PHWRs. EPRI is completing work to evaluate the application of DEHA in PWRs/PHWRs, the scope of which was identified from a technical gap analysis completed in 2021 (EPRI report 3002020981). Among these gaps is the potential impact on resin performance as a result of exposure to DEHA and/or its decomposition products.

The project team performed laboratory testing to evaluate the impact of DEHA exposure, and its decomposition products, on the performance of standard condensate polishing resin.

Keywords

PWR Secondary Chemistry
Hydrazine
Diethylhydroxylamine
DEHA
Resin

CONTENTS

1 BACKGROUND

In recent years, the nuclear industry has experienced challenges with hydrazine supply and restrictions on use (e.g., discharge restrictions requiring burdensome pre-discharge treatments) [1]. Testing has shown that hydrazine is a carcinogen to animals and considered a probable human carcinogen. Hydrazine is an environmental hazard because of its known toxicity to fish and daphnia [2]. It is anticipated that there may be additional restrictions on hydrazine use in the future (e.g., hydrazine is a REACH[1]-listed chemical anticipated to be phased out of use in the European Union). To address these issues, EPRI is leading an industry effort to identify alternatives to hydrazine. Diethylhydroxylamine (DEHA) is one chemical that is under consideration for use during cycle operation in the secondary coolant system of pressurized water reactors (PWRs) and pressurized heavy water reactors (PHWRs).

Prior work identified several knowledge gaps that could be barriers to widespread use of DEHA in PWR/PHWR secondary systems [3]. Among these gaps is an understanding of the effect of DEHA and/or its decomposition products on the performance of condensate polishing resin. This work helps address this gap.

Laboratory testing was conducted to provide a quantitative determination of the effect of DEHA and its decomposition products on both the capacity and kinetics of a standard mixed bed condensate resin. In this testing, the resin bed was exposed to the test chemistry, composed of DEHA (with or without decomposition products) plus ETA, three times with regeneration of the resin between each exposure. The results were compared to a similar, baseline, exposure protocol to ETA without DEHA.

The testing program and assessments are fully described in Appendix A of this technical update.

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[1] Registration, Evaluation, Authorisation, and Restriction of Chemicals (REACH) is a European Union regulation that requires companies that import or manufacture chemicals to register those substances. Some chemicals that are considered hazardous are prohibited.

2 REFERENCES

1. *Minutes of Meeting: EPRI 2019 Hydrazine Alternatives Workshop,* from 'Keith Fruzzetti (EPRI)' to 'Participants of the EPRI 2019 Hydrazine Alternatives Workshop, Charlotte, NC, May 21-22, 2019', dated September 16, 2020. [Located on EPRI.com]
2. *Update on Hydrazine Alternatives for PWR Secondary Chemistry Control: PWR Chemistry Technical Strategy Group Report.* EPRI, Palo Alto, CA: 2018. 3002010652.
3. *Hydrazine Alternatives for the Pressurized Water Reactor/Pressurized Heavy Water Reactor Secondary System: Diethylhydroxylamine for Operational Use.* EPRI, Palo Alto, CA: 2021. 3002020981.

A IMPACT OF DEHA EXPOSURE TO NUCLEAR GRADE ION EXCHANGE RESIN

This appendix provides the letter report documenting this testing and assessment.

R&D Report

Impact of DEHA Exposure to Nuclear Grade Ion Exchange Resins

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August 2024

1. Introduction

EPRI is evaluating Diethylhydroxylamine (DEHA) for potential use as an alternative to Hydrazine, e.g., for oxygen scavenging and beneficial impact on reducing the electrochemical potential of steam generator materials. The scope of the work completed and reported herein provides testing and analysis to determine how DEHA may affect resin performance. Three different chemistries were evaluated with three cycles of exposure and regeneration of the resin.

2. Experiment Outline

A nuclear grade mixed bed comprised of 40% NRW1160 hydrogen form strong acid cation (SAC) exchange resin and 60% NRW7000 hydroxide form strong base anion (SBA) exchange resin was used for the basis of this study. The resin was analyzed prior to testing to ensure chemical functionality and integrity were to specifications (see Table 1)[1]. The resin was dry mixed by hand and 5 liters of mixed bed resin was loaded into the Resin Column (see Figures 1 and 2). To avoid separating the mixed bed resin, the 5 Liter charge was based on resin mass instead of volume by empirically measuring the apparent density of the product. If the 5 Liter charge were measured on a wet volume basis (as is typical for one component IX systems) the two components would have partially separated; therefore, the resin charge was measured via mass/density to avoid localized regions of unmixed resin throughout the column.

In this testing program, the resultant effects of multiple exposures to DEHA chemistry with ETA, with regeneration of the resin between each exposure, were assessed based upon measured resin functionality including SAC total volume capacity (TVC), SBA TVC, and Mass Transfer Coefficient (MTC) of both resin components using PSTM-6, PSTM-10 and PSTM-113, respectively[2]. This was compared to baseline chemistry of ETA only.

The mixed bed was exposed, at a flowrate of approximately 1.5 gallons (5.7 liters)/minute, to each of three separate water chemistries at ambient temperature to ensure resin exhaustion at the end of each exposure cycle. The three inlet water chemistries were: (1) 2.0 ppm Ethanolamine (ETA)—the baseline chemistry, (2) 2.0 ppm ETA and 1.0 ppm DEHA, or (3) 2.0 ppm ETA and 1.0 ppm DEHA with 20% decomposition by heat (see paragraph below). Dosing chemistries, constituted in a 50-gallon (189 L) tank, were injected into the ultra-high purity deionized (UHP DI) water inlet stream via a dosing pump to establish the target chemistry at the inlet of the resin bed (see Figures 1 and 2). Inlet

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[1] Analysis was performed on the as-is resin except for evaluation of the Mass Transfer Coefficient (MTC), which was performed on freshly regenerated resin per PSTM 113.

[2] Purolite PSTM 6: Total Volume Capacity for Strong Acid Cations; Purolite PSTM 10: Total Volume Capacity and Salt Split Capacity for Strong Base Anions; and Purolite PSTM 113: Mass Transfer Coefficient (MTC) analysis for Cation or Anion Resin.

and outlet chemistry (ETA and DEHA), pH, and conductivity were measured once per working day. ETA concentration was measured using a Single Channel Ion Chromatograph, with DEHA measured using a HACH UV/VIS Spectrophotometer.

Decomposition of DEHA was achieved by mixing diluted DEHA on a heated stir plate. The initial concentration was analyzed before application of heat. The solution was mixed at 80°C for 60 minutes and removed from the heat for analysis to confirm 20% decomposition of DEHA. If the desired decomposition had not been achieved, additional heating at 80°C with subsequent removal from the heat and retesting of DEHA concentration was continued until 20% decomposition was achieved.

Each exposure profile consisted of 3 sequential exposures lasting 2 weeks each, totaling 6 operational weeks of exposure per exposure profile. After each 2-week exposure period, the resin was backwashed with UHP DI water in a 3-inch (7.6 cm) diameter glass column to separate the mixed bed components for individual analysis. Following analysis, resin was regenerated using a standard regeneration profile of 10lbs regenerant per cubic foot of resin (160kg regenerant per cubic meter of resin). SAC resin was regenerated with 4% sulfuric acid while SBA resin was regenerated with 4% sodium hydroxide for a standard regeneration profile of 2–4 bed volumes an hour for 1-2 hours and then rinsed with UHP DI water until conductivity was below 50 µS/cm. Components were then mixed and returned to the column for the next exposure period. This was repeated until the third and final exposure period after which the components were separated, analyzed, dewatered, and saved.

Table 1. Quality Control of New Resin Evaluated Prior to Testing

	SAC Analysis	SBA Analysis
Resin Product:	NRW1160	NRW7000
Lot#	X073S/22/7	R015Y/23/2
Volume Capacity [eq/L]	2.53 H Form	1.22 OH Form
Weight Capacity [eq/kg]	5.11 H Form	5.03 OH Form
% Strong Base	n/a	98.3
Moisture Content [%]	39.78 H Form	65.39 OH Form
% Regeneration		
% H	100	n/a
% OH	n/a	98.3
% CO3	n/a	1.6
% HCO3	n/a	0
% Cl	n/a	0
% SO4	n/a	0
% SiO2	n/a	0.1
Particle Size Distribution		
Mean Diameter [µm]	565.06	637.93
MTC [m/s]	1.91E-4	2.16E-4

Figure 1. Original Schematic with recirculation tank in circuit

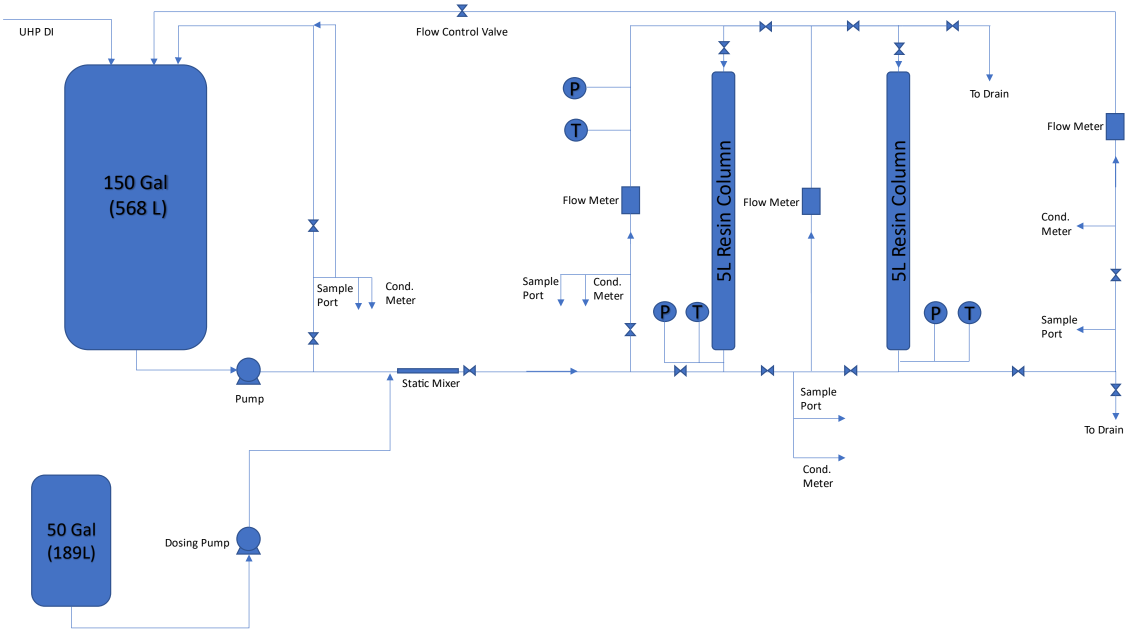
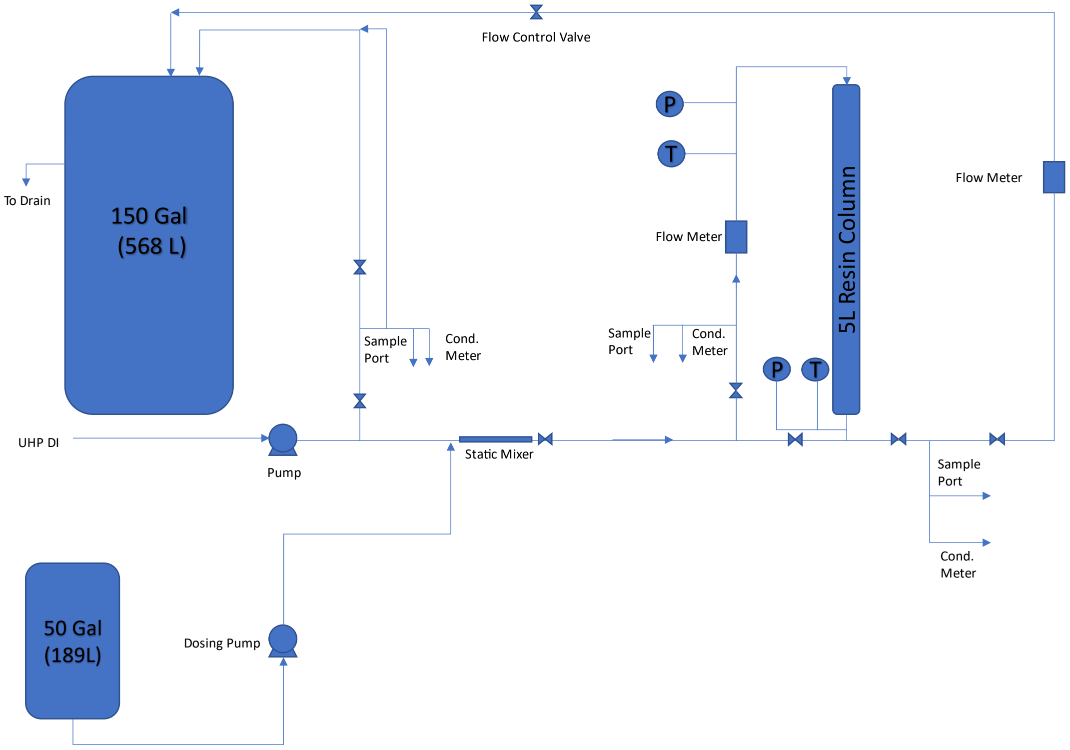


Figure 2. Modified Schematic with recirculation tank removed from circuit.



3. Results & Discussion

The original schematic for the testing process (Figure 1) utilized the 150 gallon (568 liters) recirculation tank as part of the dosing system. As the testing progressed and ionic breakthrough began from the resin column, ETA eventually recirculated back into the inlet stream creating an increase in dosing chemistry concentration as the mixed bed began to exhaust, as seen in Table 2, beginning about 4/17/23.

Using ETA as a control, dosing chemistry effectively loaded onto the SAC portion of the mixed bed until eventual exhaustion and ionic breakthrough. Increased ionic breakthrough at the end of the 2-week exposure coincided with the severity of cation exhaustion. The increase in cation exhaustion can be seen as the reduction of %H sites between each cycle in Table 5. ETA appeared to have had minor ionic exchange interaction with the SBA resin component as the majority of the OH groups were still intact following the three sequential ETA exposures (with the exception of run 5C that had just 47.5% of the OH sites remaining at exhaustion).

It was determined that the configuration of the test loop required alteration after the completion of the ETA exposure cycle to maintain a steady inlet concentration of DEHA. Initial testing of the ETA and DEHA exposure system in its original configuration (i.e., Figure 1) showed a steady and gradual increase of DEHA in the inlet concentration over the two-week period. This was followed by a sharp increase in DEHA concentration of the recirculated system, coinciding with possibly minor ETA leakage, as shown by the data in Table 8 and the leakage curve in Figure 7. An attempt was made to clear the accumulated DEHA from the recirculated solution as is noted in Table 8, but upon restart with fresh DI water the accumulation was observed to continue. Analysis of the ion exchange resin that had been subject to the increased levels of DEHA with use of the recirculation tank (Figure 1) can be seen in Table 9. The cation exchange resin had a notable 11% reduction in TVC and minor reduction (3%) in MTC, while the anion exchange resin had a minor reduction (3%) in TVC and a notable 41% reduction in MTC. This may suggest potential negative impacts when exposed to large quantities of DEHA.

The primary alteration to accommodate the observed irregularities with DEHA concentration was to reconfigure the test loop from a recirculated column to a single pass column. This was achieved by removing the 150-gal (568L) recirculation tank from the circuit (as shown in Figure 2). Due to the location of the flow control valve and its role in maintaining a system flow, the tank was then used as a drain to the waste vessel.

It is worth noting that even after the changes described above, it was observed that outlet DEHA concentration increased above the inlet concentration near the end of the exposure period (see

7/05/23 (Table 3 Dosing Exposure 1), 8/11/23 (Table 3 Dosing Exposure 3), 9/05/23 (Table 4 Dosing Exposure 1), 10/03/23 (Table 4 Dosing Exposure 2), and 10/23/23 (Table 4 Dosing Exposure 3)). This may suggest a selective preference in SAC resin for ETA over DEHA and/or may reflect the degree of DEHA ionization in the conditions of the experiment (e.g., an effect of pH). However, information from the literature indicates that the dissociation constant for DEHA can appear to be widely different, reporting the calculated pKa value as low as 5.7 or as high as 14.2—making the determination of DEHA ionization highly uncertain. Additionally, there may be some contribution of analytical uncertainty of the colorimetric analysis via the HACH spectrophotometer.

There are a few instances where the ETA outlet concentration exceeds its inlet concentration (see 7/26/23 (Table 3 Dosing Exposure 2), 8/14/23 through 8/18/23 (Table 3 Dosing Exposure 3)). These observed behaviors are not uncommon as resin approaches exhaustion and unloads bound ions. Further, EPRI technical report 1003599[3] discusses how cation exchange resins appear to absorb an additional 16-20% ETA above their theoretical ion-exchange capacity limit. This may have contributed to the increased outlet ETA concentration above equilibrium.

It should be noted that on the third chemistry exposure of ETA and DEHA with decomposition products (see Table 4 Dosing Exposure 3), the inlet UHP DI experienced a drop in quality that occurred for some period between 10/20/23 and 10/23/23. It is not known how long this period of compromised water quality lasted during that period. Operators on site reported water conductivity reaching upwards of 2500 µS/cm. This event likely contributed to early exhaustion of the resin but would not have impacted the amine chemistry exposure.

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[3] *Investigation of ETA Interactions in Mixed Bed Ion Exchange Systems—Phase 1,* EPRI, Palo Alto, CA: 2002. 1003599. See Section 4.

Table 2. ETA Dosing using schematic from Figure 1.

Begin ETA Dosing Exposure 1

Date [mm/dd/yy]	Inlet Chemistry			Outlet Chemistry		
	ETA [ppm]	pH	Conductivity [µS/cm]	ETA [ppm]	pH	Conductivity [µS/cm]
3/22/23	2.76	8.11	5.45	0	5.83	0.85
3/23/23	2.03	9.35	4.14	0	8.44	0.62
3/24/23	1.90	8.90	3.75	0	8.45	0.66
3/27/23	2.30	9.02	4.39	0	7.28	0.72
3/28/23	1.88	9.01	3.92	0	8.36	0.37
3/29/23	1.98	8.00	3.83	0	7.20	0.56
3/30/23	1.93	9.10	3.91	0.01	5.50	0.47
3/31/23	1.94	9.14	3.83	0.01	5.91	0.50

End of ETA Dosing Exposure 1, See Resin Analysis 5A.

Begin ETA Dosing Exposure 2

Date [mm/dd/yy]	Inlet Chemistry			Outlet Chemistry		
	ETA [ppm]	pH	Conductivity [µS/cm]	ETA [ppm]	pH	Conductivity [µS/cm]
4/07/23	2.61	9.27	5.04	0	6.05	0.49
4/11/23	1.83	9.06	3.78	0	5.97	0.51
4/12/23	2.05	8.98	4.20	0	5.93	0.59
4/13/23	1.81	9.14	3.84	0	5.89	0.54
4/14/23	2.05	9.30	3.91	0.02	5.80	0.59
4/17/23	2.57	9.19	5.11	0.12	7.49	1.11
4/18/23	2.61	9.10	5.00	1.12	8.74	2.60
4/19/23	8.50	9.56	12.11	8.26	9.57	12.09
4/20/23	25.48	9.71	24.24	25.58	9.59	24.30
4/21/23	43.56	9.86	32.67	43.36	9.78	32.79

End of ETA Dosing Exposure 2, See Resin Analysis 5B.

Begin ETA Dosing Exposure 3

Date [mm/dd/yy]	Inlet Chemistry			Outlet Chemistry		
	ETA [ppm]	pH	Conductivity [µS/cm]	ETA [ppm]	pH	Conductivity [µS/cm]
4/28/23	2.87	9.07	4.90	0	7.0	0.57
5/02/23	1.77	8.80	3.56	0	5.85	0.49
5/03/23	2.08	8.93	4.12	0	6.58	0.55
5/04/23	1.85	9.03	3.68	0	6.35	0.44
5/05/23	2.14	8.94	3.80	0	5.67	0.60
5/09/23	41.96	9.90	31.39	41.87	9.90	31.59
5/10/23	64.38	9.85	40.34	63.87	9.93	40.20
5/11/23	97.68	10.10	50.40	96.50	10.13	50.30
5/12/23	100.71	10.01	51.05	101.53	10.05	51.03

End of Dosing Exposure 3, See Resin Analysis 5C.

Table 3. ETA and DEHA Dosing using schematic from Figure 2. Begin ETA and DEHA Dosing Exposure 1								
Date [mm/dd/yy]	Inlet Chemistry				Outlet Chemistry			
	ETA [ppm]	DEHA [ppm]	pH	Conductivity [µS/cm]	ETA [ppm]	DEHA [ppm]	pH	Conductivity [µS/cm]
6/27/23	2.44	0.96	9.12	4.75	0	0.142	6.61	0.62
6/28/23	2.39	0.748	9.14	4.45	0	0.375	6.08	0.81
6/29/23	2.15	0.900	9.14	4.52	0	0.557	6.42	0.78
7/03/23	2.24	0.922	9.02	4.52	0	0.870	6.54	0.54
7/05/23	2.21	0.964	8.83	4.52	0.09	1.328	6.07	0.45
7/06/23	1.75	0.766	8.77	3.45	0.24	1.620	7.27	0.45
End of ETA and DEHA Dosing Exposure 1, See Resin Analysis 6A. **Begin ETA and DEHA Dosing Exposure 2**								
Date [mm/dd/yy]	Inlet Chemistry				Outlet Chemistry			
	ETA [ppm]	DEHA [ppm]	pH	Conductivity [µS/cm]	ETA [ppm]	DEHA [ppm]	pH	Conductivity [µS/cm]
7/13/23	2.22	0.779	8.96	4.32	0	0.072	6.20	0.35
7/14/23	2.25	0.960	8.96	4.64	0	0.169	5.81	0.54
7/17/23	2.58	1.090	8.97	6.43	0.03	0.400	6.84	0.73
7/18/23	1.85	0.724	8.76	3.86	0.04	0.470	6.75	0.51
7/19/23	1.84	0.726	8.99	5.13	0.02	0.752	7.17	0.96
7/20/23	1.97	0.808	8.98	4.31	0	0.464	6.88	0.66
7/24/23	2.67	1.148	9.13	5.16	2.56	1.036	9.16	5.26
7/26/23	2.31	1.035	9.01	4.80	2.67	0.964	9.01	5.30
End of ETA and DEHA Dosing Exposure 2, See Resin Analysis 6B. **Begin ETA and DEHA Dosing Exposure 3**								
Date [mm/dd/yy]	Inlet Chemistry				Outlet Chemistry			
	ETA [ppm]	DEHA [ppm]	pH	Conductivity [µS/cm]	ETA [ppm]	DEHA [ppm]	pH	Conductivity [µS/cm]
8/08/23	2.07	0.78	9.07	4.51	0.06	0.588	6.01	0.48
8/09/23	2.21	0.966	9.24	5.08	0	0.640	6.64	0.31
8/10/23	2.14	0.926	9.13	4.36	0.03	0.956	6.57	0.38
8/11/23	1.57	0.704	8.40	3.28	0.17	1.032	6.61	0.55
8/14/23	1.77	0.812	8.92	3.69	2.24	0.808	9.14	4.82
8/15/23	2.20	1.188	9.02	4.52	2.53	1.020	9.14	5.36
8/16/23	2.05	0.956	8.48	4.45	2.24	0.912	8.86	5.26
8/17/23	1.88	0.825	8.91	3.64	2.42	0.908	9.01	4.96
8/18/23	2.31	1.022	9.04	4.44	2.43	0.864	9.08	5.04
End of ETA and DEHA Dosing Exposure 3, See Resin Analysis 6C.								

Table 4. ETA and DEHA + Decomposition Products Dosing using schematic from Figure 2. **Begin ETA and DEHA + Decomposition Products Dosing Exposure 1**								
Date [mm/dd/yy]	**Inlet Chemistry**				**Outlet Chemistry**			
	ETA [ppm]	**DEHA [ppm]**	**pH**	**Conductivity [µS/cm]**	**ETA [ppm]**	**DEHA [ppm]**	**pH**	**Conductivity [µS/cm]**
8/28/23	2.82	0.886	9.11	5.62	0	0.276	6.02	0.46
8/30/23	1.86	0.792	9.0	4.55	0	0.440	5.99	0.41
8/31/23	2.35	0.946	9.15	4.77	0	0.544	5.93	0.50
9/01/23	2.32	0.980	9.06	4.63	0	0.628	5.89	0.51
9/05/23	1.97	0.814	8.89	4.24	0.04	1.056	6.04	0.35
9/06/23	1.87	0.704	8.88	3.47	0.15	1.352	6.18	0.51
9/07/23	1.90	0.800	9.02	4.05	0.55	1.772	8.30	1.31
9/08/23	1.65	0.588	9.08	3.18	0.74	1.552	8.57	1.77
End of ETA and DEHA + Decomposition Products Dosing Exposure 1, See Resin Analysis 7A **Begin ETA and DEHA + Decomposition Products Dosing Exposure 2**								
Date [mm/dd/yy]	**Inlet Chemistry**				**Outlet Chemistry**			
	ETA [ppm]	**DEHA [ppm]**	**pH**	**Conductivity [µS/cm]**	**ETA [ppm]**	**DEHA [ppm]**	**pH**	**Conductivity [µS/cm]**
9/25/23	2.69	0.858	9.18	5.50	0	0.160	5.82	0.54
9/26/23	1.63	0.574	8.32	3.05	0	0.120	5.58	0.43
9/27/23	1.67	0.681	8.89	3.58	0	0.188	5.23	0.63
9/28/23	1.76	0.718	9.08	4.06	0	0.260	5.74	0.54
9/29/23	1.78	0.740	8.98	3.74	0	0.384	5.96	0.67
10/02/23	1.73	0.664	8.99	3.71	0.03	0.636	6.14	0.39
10/03/23	1.61	0.610	8.97	3.76	0.04	0.848	6.18	0.42
10/04/23	2.27	0.858	9.08	4.37	0	0.512	5.57	0.43
10/05/23	2.25	0.916	9.04	4.39	0.40	0.890	8.35	0.68
10/06/23	1.79	0.68	8.90	3.80	1.40	0.956	9.04	3.30
End of ETA and DEHA + Decomposition Products Dosing Exposure 2, See Resin Analysis 7B **Begin ETA and DEHA + Decomposition Products Dosing Exposure 3**								
Date [mm/dd/yy]	**Inlet Chemistry**				**Outlet Chemistry**			
	ETA [ppm]	**DEHA [ppm]**	**pH**	**Conductivity [µS/cm]**	**ETA [ppm]**	**DEHA [ppm]**	**pH**	**Conductivity [µS/cm]**
10/18/23	2.45	0.668	9.20	4.36	0	0.156	5.59	0.43
10/19/23	2.60	0.696	9.19	5.30	0	0.340	5.44	0.41
10/20/23	1.98	0.492	8.96	3.93	0	0.370	6.10	0.49
10/23/23	1.86	0.348	9.09	3.74	1.39	0.832	8.94	3.15
10/24/23	1.73	0.456	9.11	3.67	1.82	0.760	9.16	3.92
10/25/23	2.45	0.289	9.30	4.70	2.27	0.712	9.28	4.70
10/26/23	1.79	0.392	8.99	4.28	1.83	0.608	8.87	5.15
10/27/23	2.22	‡	9.05	5.10	2.05	‡	9.00	4.25
10/31/23	1.90	0.690	9.05	4.35	1.80	1.328	9.18	4.25
11/01/23	1.87	0.538	9.02	4.25	1.34	0.816	9.10	4.65
End of ETA and DEHA + Decomposition Products Dosing Exposure 3, See Resin Analysis 7C.								

‡ HACH UV/VIS Spectrophotometer down for maintenance. Samples not saved.

Table 5. Resin Analysis, ETA Dosing from Figure 1 Configuration

NRW1160 Cation Exchange Resin Analysis

	Table 1 Value	5A. ETA Exposure 1		5B. ETA Exposure 2		5C. ETA Exposure 3	
		Exhausted	Regenerated	Exhausted	Regenerated	Exhausted	Regenerated
TVC (H+) [meq/mL]	2.53	2.41	2.43	2.52	2.28	2.28	2.50
% H Sites	100	25.28	75.0	0.90	86.1	2.67	83.9
MTC [m/s]	1.91E-4	-	1.98E-4	-	1.92E-4	-	1.76E-4

NRW7000 Anion Exchange Resin Analysis

	Table 1 Value	5A. ETA Exposure 1		5B. ETA Exposure 2		5C. ETA Exposure 3	
		Exhausted	Regenerated	Exhausted	Regenerated	Exhausted	Regenerated
TVC (OH-) [meq/mL]	1.22	1.12	1.17	1.16	1.16	1.16	1.19
% OH Sites	98.3	82.6	94.5	78.1	82.5	47.5	74.5
MTC [m/s]	2.16E-4	-	1.94E-4	-	1.81E-4	-	1.82E-4

Table 6. Resin Analysis, ETA and DEHA Dosing from Figure 2 Configuration

NRW1160 Cation Exchange Resin Analysis

	Table 1 Value	6A. ETA and DEHA Exposure 1		6B. ETA and DEHA Exposure 2		6C. ETA and DEHA Exposure 3	
		Exhausted	Regenerated	Exhausted	Regenerated	Exhausted	Regenerated
TVC (H+) [meq/mL]	2.53	2.32	2.31	2.32	2.38	2.36	2.41
% H Sites	100	5.26	81.8	3.3	79.5	2.1	78.7
MTC [m/s]	1.91E-4	-	2.23E-4	-	1.95E-4	-	1.82E-4

NRW7000 Anion Exchange Resin Analysis

	Table 1 Value	6A. ETA and DEHA Exposure 1		6B. ETA and DEHA Exposure 2		6C. ETA and DEHA Exposure 3	
		Exhausted	Regenerated	Exhausted	Regenerated	Exhausted	Regenerated
TVC (OH-) [meq/mL]	1.22	1.21	1.14	1.16	1.20	1.16	1.19
% OH Sites	98.3	80.3	94.56	83.6	91.9	75.2	92.0
MTC [m/s]	2.16E-4	-	1.94E-4	-	1.82E-4	-	1.85E-4

Table 7. Resin Analysis, ETA and DEHA + Decomposition Products Dosing from Figure 2 Configuration

NRW1160 Cation Exchange Resin Analysis

	Table 1 Value	7A. ETA and DEHA + Decomposition Products Exposure 1		7B. ETA and DEHA + Decomposition Products Exposure 2		7C. ETA and DEHA + Decomposition Products Exposure 3	
		Exhausted	Regenerated	Exhausted	Regenerated	Exhausted	Regenerated
TVC (H+) [meq/mL]	2.53	2.40	2.44	2.42	2.44	2.34	2.21
% H Sites	100	3.7	77.67	2.4	83.4	3.7	96.4
MTC [m/s]	1.91E-4	-	1.96E-4	-	2.04E-4	-	1.74E-4

NRW7000 Anion Exchange Resin Analysis

	Table 1 Value	7A. ETA and DEHA + Decomposition Products Exposure 1		7B. ETA and DEHA + Decomposition Products Exposure 2		7C. ETA and DEHA + Decomposition Products Exposure 3	
		Exhausted	Regenerated	Exhausted	Regenerated	Exhausted	Regenerated
TVC (OH-) [meq/mL]	1.22	1.15	1.20	1.21	1.20	1.20	1.11
% OH Sites	98.3	78.02	91.06	82.25	95.31	78.0	94.4
MTC [m/s]	2.16E-4	-	1.74E-4	-	1.70E-4	-	1.88E-4

Table 8. ETA and DEHA Dosing using schematic from Figure 1.
Begin ETA and DEHA Dosing Exposure 1

Date [mm/dd/yy]	Inlet Chemistry				Outlet Chemistry			
	ETA [ppm]	DEHA [ppm]	pH	Conductivity [µS/cm]	ETA [ppm]	DEHA [ppm]	pH	Conductivity [µS/cm]
5/17/23	2.57	1.045	8.82	4.18	0.05	0.017	5.88	0.68
5/18/23	2.07	1.168	9.12	4.29	0.02	0.189	5.79	0.40
5/19/23	2.05	1.328	9.06	4.45	0.00	0.623	5.82	0.46
Recirculation tank dumped to clear accumulated DEHA								
5/23/23	2.14	1.392	9.02	4.37	0.00	0.5880	5.88	0.55
5/24/23	1.76	2.220	8.93	3.45	0.00	2.060	5.54	0.51
5/25/23	1.74	4.110	8.78	3.50	0.02	3.770	5.54	0.51
5/26/23	2.36	5.410	9.05	4.24	0.01	5.180	6.05	0.50
5/30/23	2.21	16.250	8.85	4.38	0.03	15.700	6.45	0.58
5/31/23	2.15	34.500	9.06	4.38	0.08	38.300	7.90	0.45
End of ETA and DEHA Dosing Exposure 1, Dosing using schematic from Figure 1.								

Table 9. Resin Analysis, ETA and DEHA Dosing from Figure 1 Configuration

NRW1160 Cation Exchange Resin Analysis

	Table 1 Value	5A. ETA Exposure 1	
		Exhausted	Regenerated
TVC (H+) [meq/mL]	2.53	2.25	2.36
% H Sites	100	13.6	84.9
MTC [m/s]	1.91E-4	-	1.85E-4

NRW7000 Anion Exchange Resin Analysis

	Table 1 Value	5A. ETA Exposure 1	
		Exhausted	Regenerated
TVC (OH-) [meq/mL]	1.22	1.18	1.20
% OH Sites	98.3	84.24	80.54
MTC [m/s]	2.16E-4	-	1.27E-4

Figure 3. Cation Volume Capacity

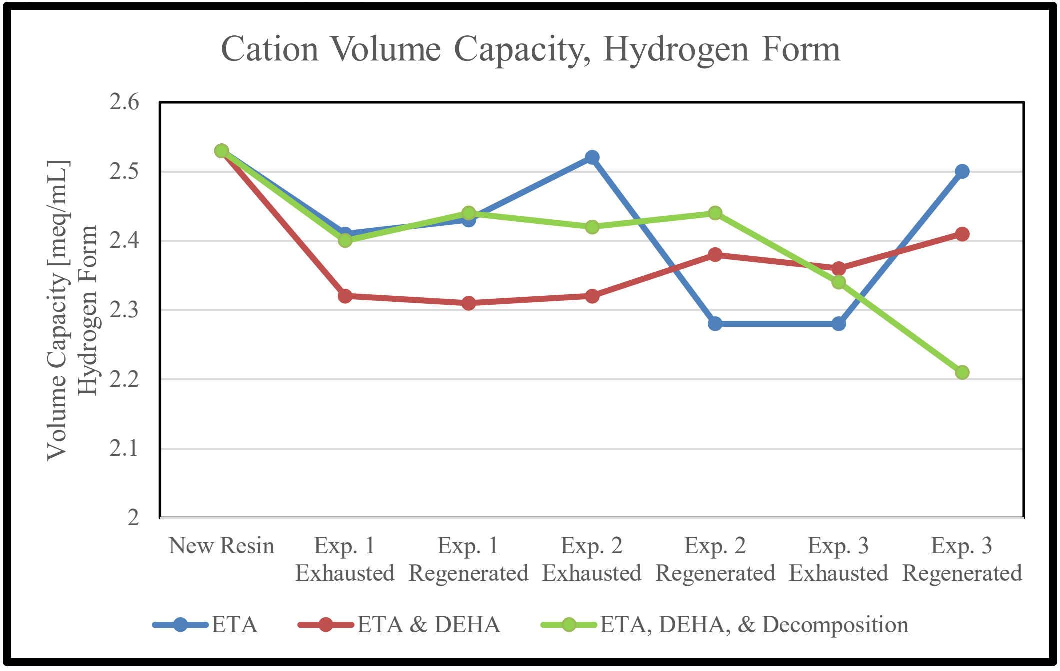


Figure 4. Anion Volume Capacity

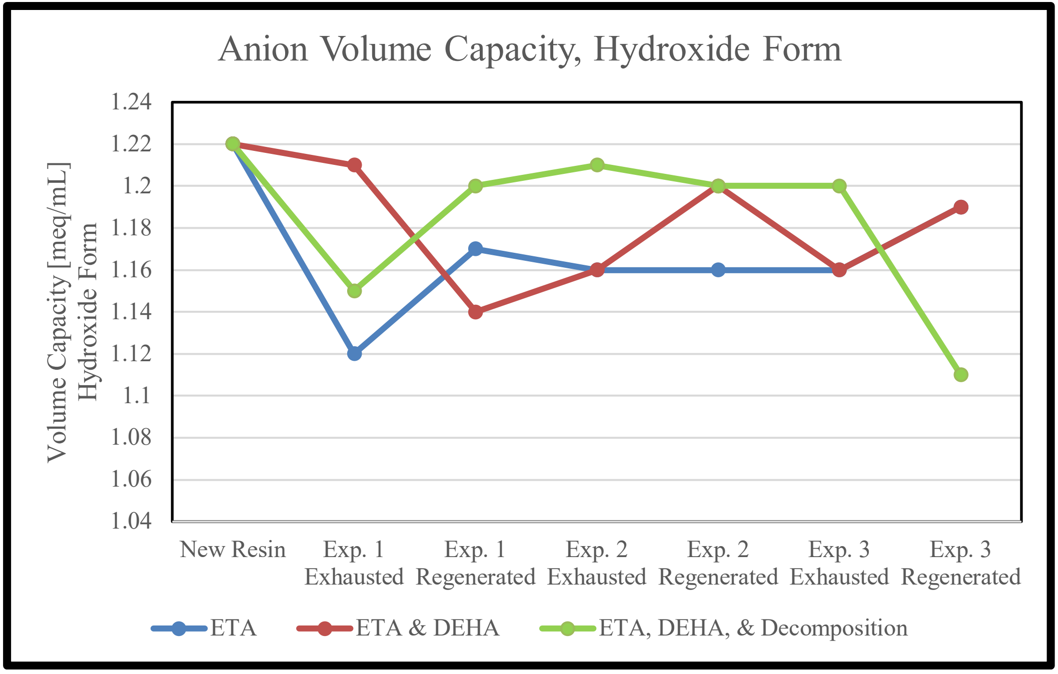


Figure 5. Cation Mass Transfer Coefficient

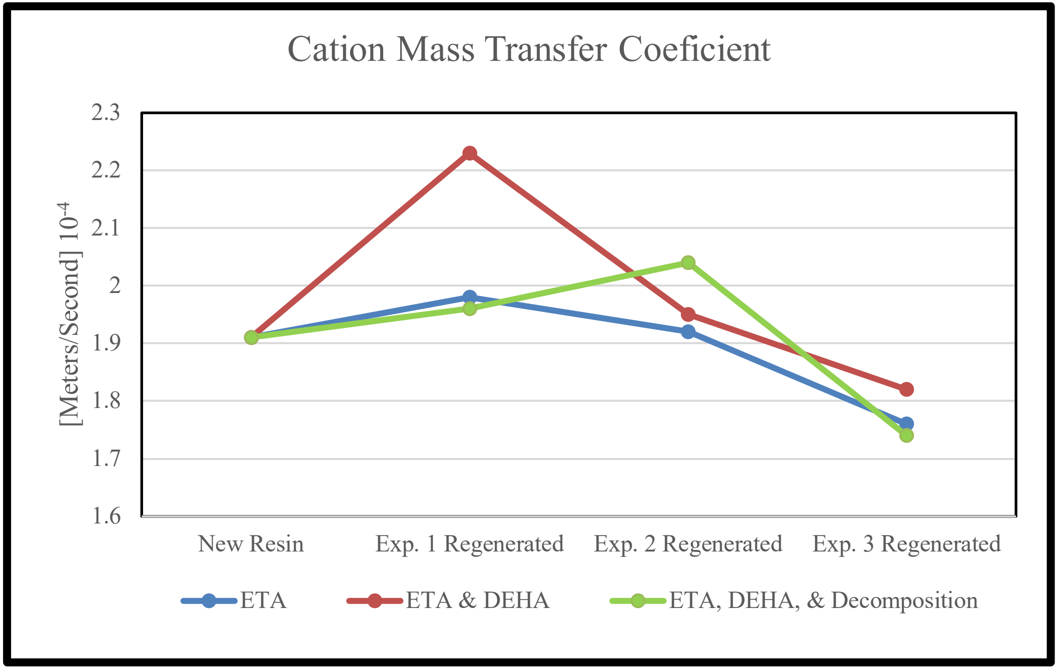


Figure 6. Anion Mass Transfer Coefficient

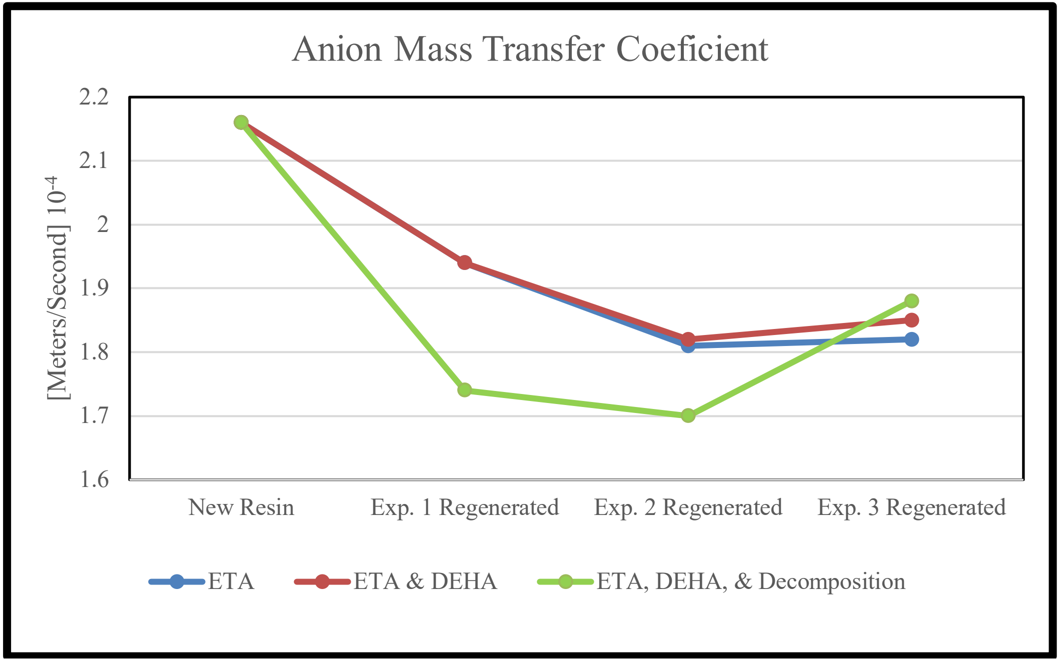
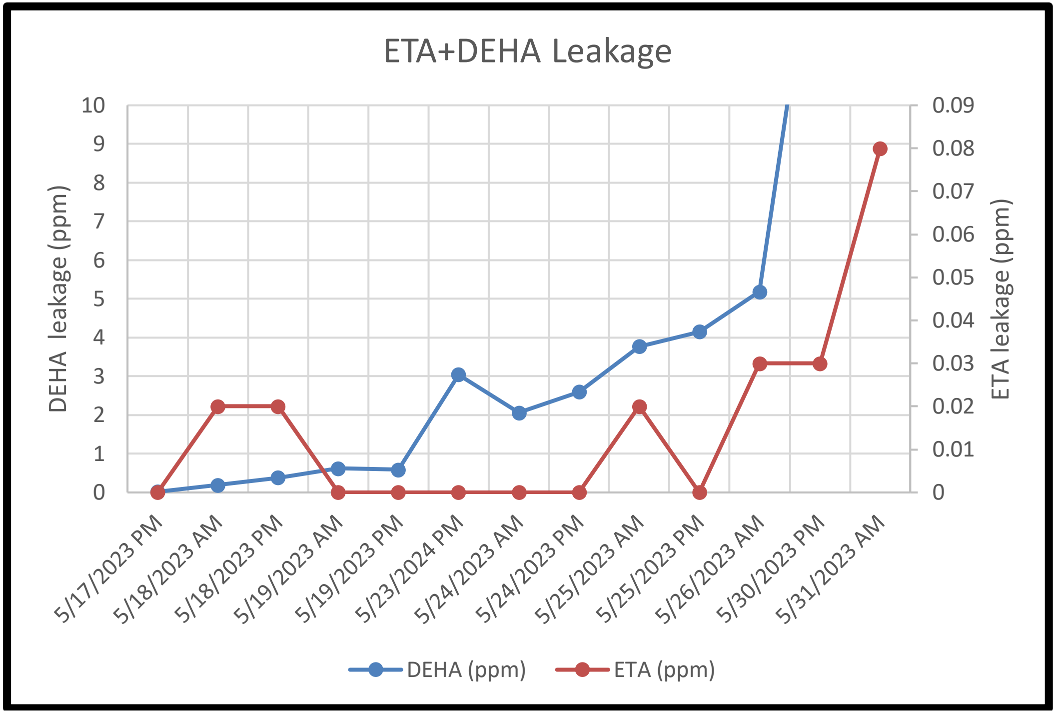


Figure 7. Exhaustion/Leakage of initial ETA+DEHA exposure in column configuration 1 (Figure 1)



4. Conclusions

When comparing resin TVC throughout each exposure cycle, we must consider the naturally occurring variations in the measurement process. Although the third exposure of the ETA and DEHA + Decomposition Products appears to have a reduction in TVC for both cation and anion samples, this is considered to be within the range of variation associated with the method. Reduction in resin capacity also may have been affected by compromised UHP DI water loss previously noted between dates of 10/20/23 and 10/23/23 during the third exposure period.

Negligible loss in volume capacity in SAC and SBA resins was observed throughout the three sequential ETA exposure cycles as well as three sequential ETA and DEHA exposure cycles. Minor loss of capacity through three sequential ETA and DEHA + Decomposition Products with both SAC and SBA resins, a reduction of 12.6% and 9.0% respectively.

Minor reduction of both SAC as well as SBA ion kinetics was observed in each of the three exposure profiles. Addition of DEHA or DEHA + Decomposition Products did not significantly affect the mass transfer kinetics when compared to the control ETA exposure.

Neither of the three exposure profiles were observed to limit standard regeneration efficacy of either SAC or SBA resins.

While not the intention of this study, the observations from the unintended exposure to higher concentrations of ETA and DEHA may help inform direction of future studies. Extended exposure periods may also yield valuable information as this may resemble in field resin usage over the long term. Additionally, selectivity studies of ETA vs. DEHA may provide further insight on ionic loading of mixed bed resins as well as any additional non-ionic interactions.

5. Formulation / Raw Materials

Ethanolamine	
Lot# R131007	Expiration Date: n/a
Lot# A0377482	Expiration Date: n/a
Diethylhydroxylamine	
Lot# RW64F-TR	Expiration Date: n/a

6. References

Purolite PSTM 20B; Bulk Density
Purolite PSTM 6; Total Volume Capacity For Strong Acid Cations
Purolite PSTM 10; Total Volume Capacity and Salt Split Capacity for Strong Base Anions
Purolite PSTM 113; Mass Transfer Coefficient (MTC) analysis for Cation or Anion Resin

HACH DR6000 UV-VIS Spectrophotometer
- Method 8140 for Oxygen Scavengers

Metrohm 930 Compact Ion Chromatograph
- Application C-126 For methylamines and Ethanolamines
- Metrosep C6 Analytical Column
- Eluent for Metrosep C 6 (1.7mM Nitric Acid, 1.7 mM Dipicolinic Acid

B TRANSLATED TABLE OF CONTENTS

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EPRI PREPARED THIS REPORT.

用于压水反应堆/加压重水反应堆二回路系统的联氨替代品

二乙基羟胺 (DEHA) 对树脂性能的影响

3002029320

技术更新，2024 年 10 月

EPRI 项目经理
K. Fruzzetti

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摘要

由于环境和职业安全法规的变化以及供应链限制，运营压水反应堆 (PWR) 和加压重水反应堆 (PHWR) 的电厂面临联氨的使用和采购挑战，未来可能面临更大的挑战。EPRI 致力于短期和长期解决方案的研究。本项工作侧重于测试，以评估一项可能实现的长期解决方案。

在 EPRI 2019 年全球联氨替代品研讨会上产生的可能实现的长期解决方案之一，是使用二乙基羟胺 (DEHA) 进行功率除氧，并对 PWR 和 PHWR 二回路系统中的电化学电位 (ECP) 产生有利影响。EPRI 正在评估 DEHA 在 PWR/PHWR 中的应用并且该工作即将完成，其范围是从 2021 年完成的技术差距分析中确定的（EPRI 报告 3002020981）。其中一个差距是 DEHA 和/或其分解产物暴露对树脂性能的潜在影响。

项目团队进行了实验室测试，以评估 DEHA 及其分解产物暴露对标准冷凝抛光树脂性能的影响。

关键词

PWR 二回路化学
联氨
二乙基羟胺
DEHA
树脂

目录

加圧水型原子炉/加圧重水型原子炉二次系のヒドラジン代替物質

ジエチルヒドロキシルアミン(DEHA)が樹脂性能に与える影響

3002029320

技術情報更新、2024 年 10 月

EPRI プロジェクトマネージャー
K. Fruzzetti

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概要

環境や、労働安全規制の変化や、サプライチェーンの制約により、加圧水型原子炉(PWR)や加圧水型重水型原子炉(PHWR)を運転する公益事業者は、ヒドラジンの使用と調達という課題に直面しており、この問題は将来より大きくなる可能性があります。EPRIは、短期的および長期的な解決策の両方に取り組んでいます。この取り組みは、長期的な解決策の1つとなり得るものの評価テストに焦点を当てたものです。

ヒドラジン代替案に関するEPRI 2019グローバルワークショップから得られた長期的な解決策として挙げられたものの一つには、電力での酸素除去にジエチルヒドロキシルアミン(DEHA)の使用があり、それはPWRとPHWRの二次系における電気化学ポテンシャル(ECP)に好ましい影響を与えます。EPRIはPWR/PHWRへのDEHAの適用を評価する作業を完了しており、その範囲は2021年に完了した技術的ギャップ分析(EPRIレポート3002020981)で特定されています。このギャップの中には、DEHAやその分解生成物への曝露による樹脂性能への潜在的な影響があります。

DEHA曝露とその分解生成物が標準的な凝縮系研磨樹脂の性能に及ぼす影響を評価するために、実験室で試験を行いました。

キーワード

PWR 二次化学
ヒドラジン
ジエチルヒドロキシルアミン
DEHA
樹脂

目次

Alternativas a la hidracina para el sistema secundario de los reactores de agua a presión/reactores de agua pesada a presión

Impacto de la dietilhidroxilamina (DEHA) en el rendimiento de la resina

3002029320

Actualización técnica, octubre de 2024

Gestor de proyectos de EPRI
K. Fruzzetti

A este producto le son aplicables, total o parcialmente, los requisitos del Programa de Garantía de Calidad Nuclear de EPRI. YES [✓ NO]

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RESUMEN

Debido a los cambios en la normativa medioambiental y de seguridad laboral, así como a las limitaciones de la cadena de suministro, las compañías eléctricas que explotan reactores de agua a presión (PWR) y reactores de agua pesada a presión (PHWR) han sufrido problemas con el uso y el abastecimiento de hidracina, que podrían agravarse en el futuro. EPRI ha estado trabajando en soluciones a corto y largo plazo. Este proyecto se centra en las pruebas para evaluar una de las posibles soluciones a largo plazo.

Una de las soluciones consensuadas a largo plazo, surgida del taller global de EPRI 2019 sobre alternativas a la hidracina, es el uso de dietilhidroxilamina (DEHA) para la eliminación de oxígeno y el impacto favorable sobre el potencial electroquímico (ECP) en el sistema secundario de los PWR y PHWR. EPRI está completando la evaluación de la aplicación de DEHA en reactores PWR/PHWR, cuyo alcance se identificó a partir de un análisis de las deficiencias técnicas completado en 2021 (informe de EPRI 3002020981). Entre estas deficiencias se encuentra el posible impacto sobre el rendimiento de la resina como resultado de la exposición a la DEHA y/o a sus productos de descomposición.

El equipo del proyecto realizó pruebas de laboratorio para evaluar el impacto de la exposición a la DEHA y sus productos de descomposición en el rendimiento de la resina de pulido de condensado estándar.

Palabras clave

Química secundaria de PWR
Hidracina
Dietilhidroxilamina
DEHA
Resina

ÍNDICE

About EPRI

Program:

Chemistry and Radiation Safety, P41.09.04

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