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Evaluation of Boiler and Heat Recovery Steam Generator Chemical Cleaning Waste Treatment Options

Lab-Scale Feasibility Testing of a Vapor Compression Thermal Evaporation Technique

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ABSTRACT

Boiler and heat recovery steam generator chemical cleaning is conducted to remove internal tube deposits to minimize the potential for underdeposit corrosion and overheating. Due to changes in environmental regulations, an increasing number of conventional fossil and combined cycle plants need an alternative method for managing the waste generated from these chemical cleanings. This report presents laboratory-scale feasibility testing data from a vapor recompression thermal evaporation process conducted on a tetra-ammonium ethylene di-amine tetra-acetic acid (EDTA) waste solvent from a conventional fossil boiler cleaning. The waste solvent consisted of the initial spent solvent drain with no rinse water co-mingled. The 0.2 gallons per minute (0.9 liters per minute) test unit is not an exact process replica of the larger-scale, commercially available field unit but simulates the conditions and has been used for feasibility testing of other waste streams. Approximately 140 gallons (530 liters) of boiler chemical cleaning waste was treated, resulting in approximately 105 gallons (397 liters) of distillate and 35 gallons (132 liters) of brine concentrate, thus demonstrating a 75% waste reduction. The distillate was of sufficient quality to be considered for re-use as feed supply to a boiler makeup water treatment plant or potentially discharged, depending on plant-specific environmental permitting and regulations. The final brine concentrate contained levels of dissolved solids and metals that were approximately four times the levels of the initial waste feedstock. Approximately 60% of the ammonia remained in the brine concentrate, with the balance either being vented with non-condensable gases or condensing in the distillate stream. No scaling and solids handling issues were encountered as metals and dissolved solids concentrated in the test unit. Information from this testing is presented for evaluation by utilities as a potential on-site treatment option for managing their specific boiler chemical cleaning waste streams. Scaled-up testing and/or a field trial is the next step in evaluating this process to ensure that solids handling is not a limiting factor.

Keywords

Boiler chemical cleaning waste
EDTA chemical cleaning waste
Heat recovery steam generator chemical cleaning waste
Vapor recompression thermal evaporation treatment
Wastewater treatment

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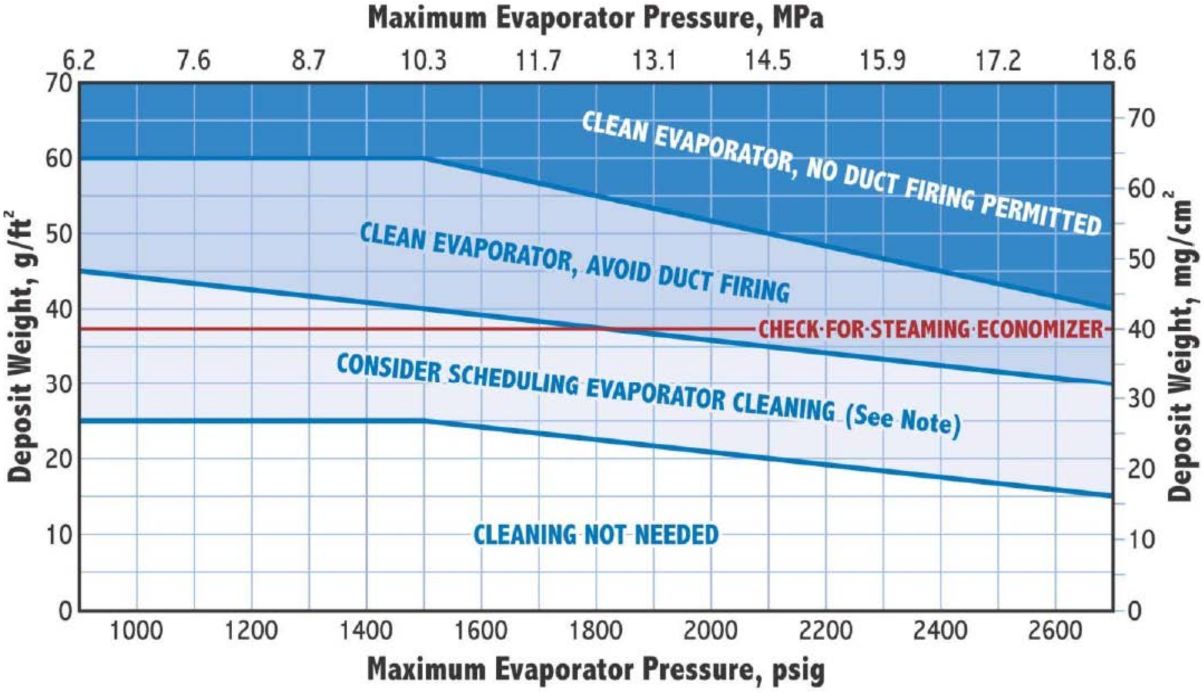
INTRODUCTION

The Need for Boiler and Heat Recovery Steam Generator Chemical Cleaning

Corrosion in the condensate, feedwater, and preheater sections of conventional fossil and combined cycle heat recovery steam generator (HRSG) units results in deposition in the steam generator tubing. These internal deposits have been the direct cause of several types of boiler and HRSG tube failures. The protective magnetite (Fe_3O_4) layer formed during normal service increases resistance to heat transfer relative to the base metal. Impedance to heat transfer in boiler tubes has been determined to be a function of scale density (or thickness) and composition [1]. Long-term exposure to elevated temperatures caused by internal tube deposits can lead to overheat failures in drum and supercritical waterwalls. Underdeposit corrosion (UDC) risk also increases exponentially with deposit weight due to the propensity for corrosive contaminants like chloride, sulfate, sodium, or phosphate to concentrate underneath the protective magnetite layer, particularly in drum units. Mitigating these risks includes managing boiler contaminant levels within EPRI limits and chemically cleaning the heat transfer surfaces to remove internal deposits on a periodic basis when levels exceed EPRI limits for deposit weight. Figure 1-1 provides guidance on determining the need to chemically clean a HRSG based on evaporator pressure and deposit weight. Similar guidance is available for conventional fossil boilers in the same reference [2].



NOTE: Consider Scheduling Evaporator Cleaning if Duct Firing or if Experiencing Hideout, Chemistry Upsets, or Deposition of Silica, Hardness, Carbon or Aluminum (See Discussion)

Figure 1-1
EPRI chemical cleaning requirements at evaporator pressures and deposit weight [2]

Tube sampling and analysis for deposit weight and composition is normally performed at some frequency to determine when a boiler needs to be chemically cleaned. With an optimized feedwater chemistry in place to reduce corrosion product transport to the boiler, plants have successfully extended the period of time between chemical cleanings. Other factors such as cycling, layup practices, feedwater metallurgy, and heat flux rates also impact accumulation of internal scale deposits. Depending on the specific unit design, cycle chemistry control, and operational practices, conventional fossil boilers are typically cleaned on a 4–10 year frequency, while HRSG high-pressure evaporators can extend this frequency to >15 years in many cases.

Lastly, new units often require a pre-operational chemical cleaning to remove mill scale and any oil residue. Performing a pre-operational cleaning may reduce the deposition rate when the unit is placed in service and has also been shown to help meet steam purity requirements sooner.

Boiler and HRSG Chemical Cleaning Waste Volume and Characterization

Conventional fossil boiler and combined cycle HRSG cleaning processes generate waste equal to the approximate volume of the economizer and boiler or evaporator section being cleaned. If rinse water is co-mingled with the waste, additional waste volume is added in proportion to the number of rinses. In small HRSG units, this volume can be in the 10,000–20,000-gallon (45–90 m^3) range, while in large once-through, supercritical fossil boilers it can be as high as 500,000 gallons (2,273 m^3).

Boiler and HRSG evaporator waste is high in iron and may contain substantial levels of copper, nickel, calcium, and magnesium, depending on the condensate and feedwater metallurgy and contaminant exposure. Trace amounts of other metals like chromium, lead, zinc, and aluminum are often present in chemical cleaning waste, and some of these constituents may have an environmental impact, depending on regulations and plant-specific discharge limits. Depending on the chemical cleaning solvent used, significant levels of ammonia may be present. With some solvents, pH can be a concern. For example, if mineral acids, such as hydrochloric acid or hydrofluoric acid, are utilized, waste solution pH will be low and neutralization is normally employed at some phase of the process. Preoperational cleaning solvent waste is lower in iron and other dissolved solids and may contain a surfactant and an alkalizing agent. Additional information on boiler and HRSG evaporator chemical cleaning processes and waste characterization is available in the EPRI report *Chemical Cleaning Guidelines for Fossil-Fuel-Fired Power Plants* [2].

Previous EPRI Research on Boiler and HRSG Chemical Cleaning Waste Management Alternatives

A comprehensive summary of previously utilized and available boiler cleaning waste treatment technologies is available in the report *Boiler Chemical Cleaning Waste Management Manual*, which was released in 2013 [3]. Additional options were investigated in 2016 and are available in the technical update *Evaluation of Boiler and Heat Recovery Steam Generator Chemical Cleaning Waste Treatment Options* [4].

This technical update carries the investigation of alternative chemical cleaning waste further by evaluating thermal evaporation vapor recompression, which has been looked at previously as a potential means for treating other plant waste streams such as flue gas desulfurization blowdown and cooling tower blowdown.

2

THERMAL EVAPORATION VAPOR RECOMPRESSION TECHNOLOGY OVERVIEW

Technology Evaluated

The AVARA Thermal Evaporation Wastewater Treatment System is a patented submerged-core mechanical vapor recompression wastewater treatment system developed and commercialized by Purestream, Inc. The AVARA mobile or engineered unit was originally designed for the removal of chlorides and heavy metals from wastewater for reuse or discharge. Typical water results with the AVARA are total suspended solids (TSS) removal below 20 ppm and total dissolved solids (TDS) reduction below 100 ppm [5]. Water recovery rates are based on feed or input TDS levels. The AVARA technology includes a monitoring system that allows remote support and operation of the equipment. Discussions with the manufacturer indicated the technology might be applicable for treating waste solutions generated from a boiler chemical cleaning.

AVARA Technical and Operational Overview

The AVARA system is a low-pressure wastewater purification and brine concentration system characterized by:

- Modular construction, with effective scale-up capacity from 4,200 gpd (19 m^3/day) to 420,000 gpd (1,900 m^3/day)
- Higher-volume projects above 420,000 gpd (1,900 m^3/day) may include custom plant engineering and construction
- Proprietary software controls optimizing feed water flow and pre-heating
- Proprietary heat transfer surface design that aims to improve boiling and condensation heat transfer with minimal scaling
- Low-pressure operation resulting in reduced energy cost
- Proprietary level control optimizes water-handling capacity across a wide TDS range
- Adaptable to on-site power possibilities: grid or generator (natural gas or diesel)
- Can be designed for electrical immersion heaters or steam immersion heaters
- No open combustion sources, for improved safety and reduced fire risk
- Wireless transmission of operating parameters, diagnostics, and control inputs

Influent to the unit can be pretreated with scale inhibitor, pH adjustment, and/or defoamer, depending on the chemical constituent concentrations, scaling index, and propensity to generate foam. Immersion heaters are used to bring the solution to the target temperature and once the process reaches steady state are only used to balance heat in the tank from losses. At steady state, the influent stream is preheated for optimal efficiency by pumping through heat exchangers where energy from hot distillate and brine concentrate is used to transfer heat. As shown in Figure 2-1, the AVARA core is made up of two separate containment chambers: (1) an outer evaporative chamber, and (2) a higher pressure-condensing inner chamber with associated reservoir. As feed water flows into the evaporation chamber across heat transfer surfaces, it is heated to the evaporation temperature. The heat transfer surfaces, in turn, serve as containment for hot distillate on the opposite side of the AVARA core. These surfaces are a part of the proprietary AVARA core design and are key to very high thermal efficiency. An ultrasonic clean-in-place method is utilized to prevent and eliminate scale and mineral build-up on core.

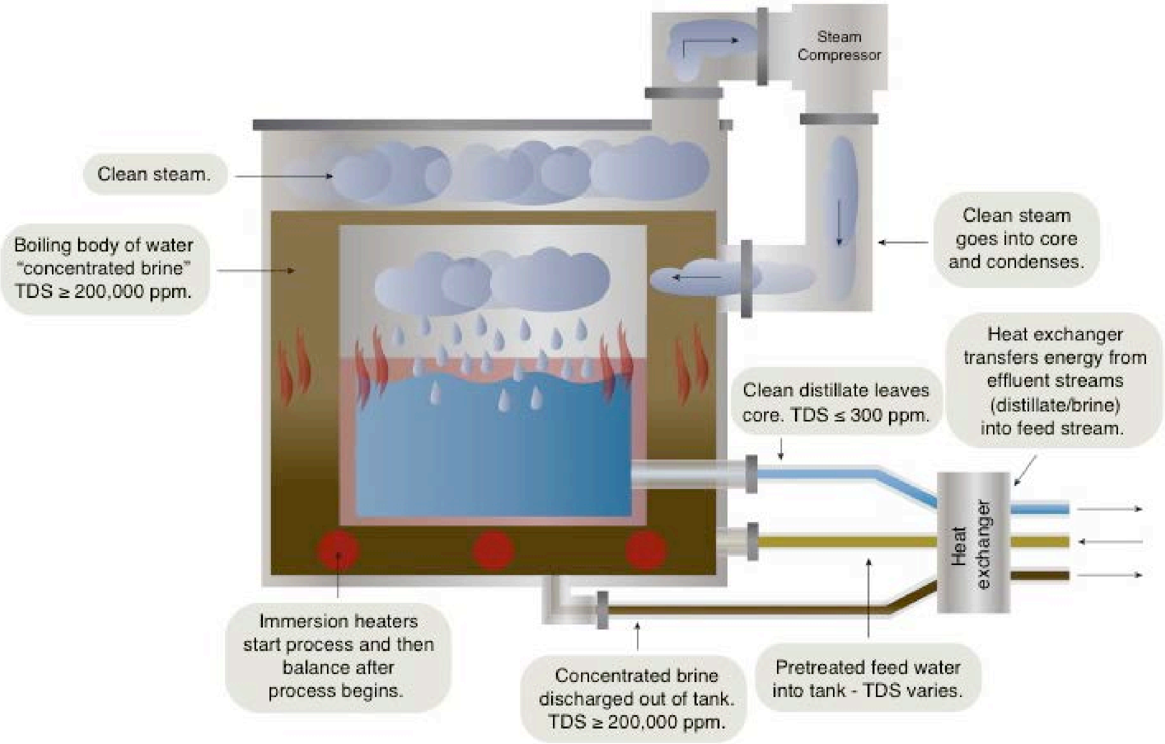


Figure 2-1
AVARA process illustration

Hot water vapor boiling off the brine-laden feed water bath is captured, compressed, and contained on the "high pressure" side of the AVARA core. Pressurized vapor condenses when exposed to the walls of the containment area, gives up its heat of evaporation (enthalpy of vaporization), and collects in the reservoir as liquid distillate. Figure 2-2 further illustrates this part of the process.

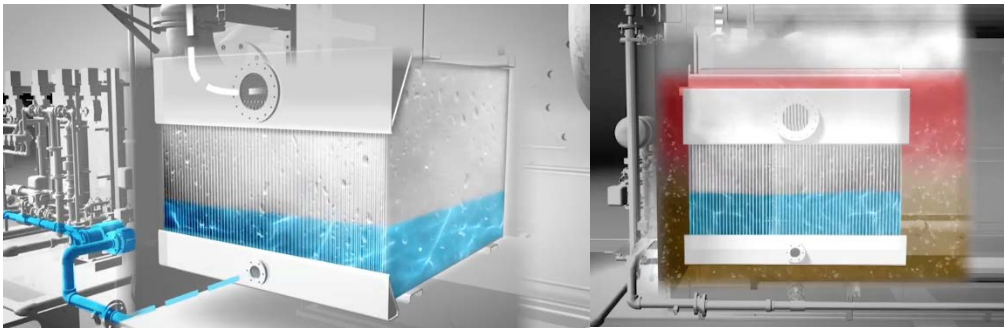


Figure 2-2
Vapor recompression chamber of the AVARA unit

During the vaporization and recompression processes, proprietary control algorithms facilitate optimum heat transfer by controlling fluid levels, compression, and pump-induced flow rates into, throughout, and from the AVARA core. This is shown in Figure 2-3.

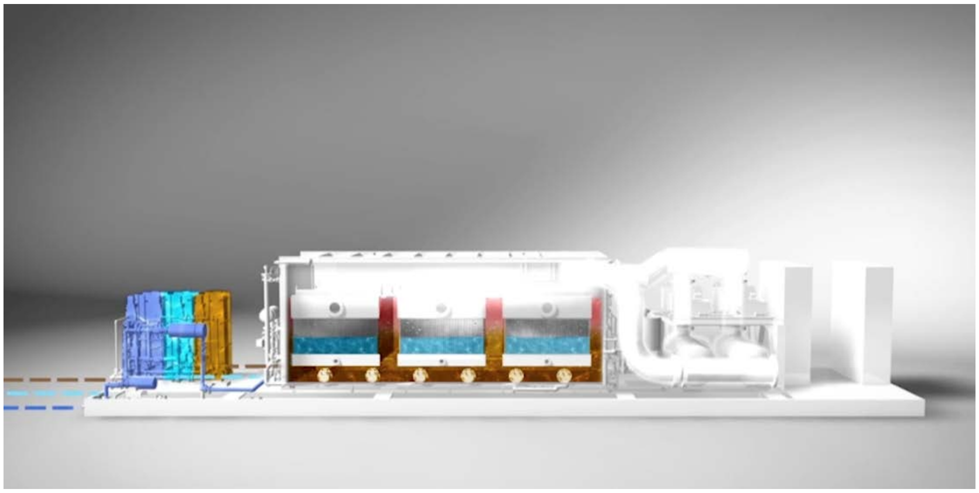


Figure 2-3
AVARA unit side view showing fluid level control

Vent losses to control non-condensable constituents are also part of the controlled vapor recompression process. Wireless transmission and instantaneous upload of operating parameters, diagnostics, and control inputs are a part of the AVARA design.

3

EXPERIMENTAL CONFIGURATION

Boiler Chemical Cleaning Waste Sample

A sample from a large utility boiler chemical cleaning conducted in November 2017 in the United States was obtained and utilized for this evaluation. The cleaning process utilized was high-temperature tetra-ammonium EDTA followed by oxygen addition for passivation. The boiler that was chemically cleaned was a drum unit with all-ferrous condensate and feedwater metallurgy. All the original copper alloy feedwater heaters were replaced as of October 1999, and this was the third boiler chemical cleaning since that time. Low concentrations of copper are still present in the boiler tubes as a result. The unit had been previously cleaned 12 years ago. The waterwall tube scale mass prior to cleaning was 36.9 mg/cm^2 on the hot side of the tube internal surface. The tube was removed from a high heat flux area of the boiler furnace just above the burners, which is the location containing tubes with the highest internal deposit weight in most conventional boilers.

Test Setup

A lab-scale test unit (Figure 3-1) was utilized to evaluate distillate quality and feasibility of the AVARA technology to treat boiler chemical cleaning waste. The test unit was operated at its capacity of 0.2 gallons per minute (GPM) (0.9 liters per minute [LPM]), and is not an exact process replica of the AVARA field unit but simulates the conditions and has been used successfully for feasibility testing on other waste streams. The AVARA components are constructed primarily of stainless steel in both the lab-scale test unit and field units.

Testing was conducted over a two-day period in an outdoor test facility at 7°F (-14°C) ambient temperature. Some ammonia vapor (odor) was detected in the non-condensable vent and thus required the testing to be conducted outside.

Figure 3-1
Lab-scale AVARA 0.2-GPM test unit

The boiler chemical cleaning sample was received in a 250-gallon (946-liter) tote that was approximately 80% full. It was dark red in color, as is typical of this type of waste, due to the high ferric iron chelate content. Figure 3-2 shows a picture of the initial as-received waste sample compared to a distillate sample taken during testing.

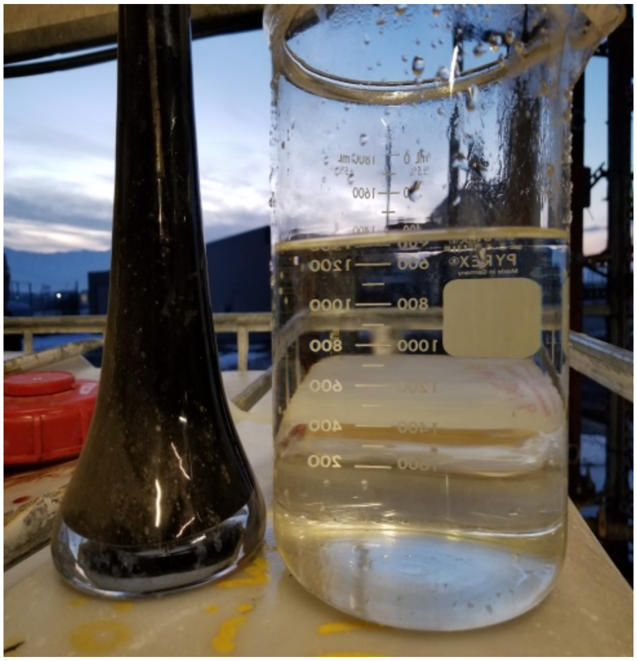


Figure 3-2
Boiler chemical cleaning waste sample (left) compared to a distillate sample (right)

For this test, no anti-foam was added to the influent to the test unit. Neither pH adjustment nor anti-scalant feed was utilized.

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FEASIBILITY TEST RESULTS

Test Results Description

Over a period of 2 days, 140 gallons (636 liters) of the boiler chemical cleaning waste was processed through the test unit. The unit ran for approximately 6 hours each day, producing approximately 105 gallons (477 liters) of distillate and 35 gallons (160 liters) of brine concentrate solution.

Testing was stopped between test day 1 and test day 2. Distillate and brine samples were taken at 10 equal time intervals through the test period. Samples 1–5 were taken on test day 1, and samples 6–10 were taken on day 2. These samples were analyzed by an off-site, third party laboratory. Lab results are presented in the subsection that follows.

No solids or scaling was observed during the testing even as dissolved solid levels increased fourfold. At the conclusion of the test period, the unit was cooled, and no scaling or precipitation of solids was observed.

Lab Results

Table 4-1 displays the initial feed sample analysis of the boiler chemical cleaning waste used in this feasibility test. This waste consisted of the initial spent solvent drain with no rinse water co-mingled. Table 4-2 shows the distillate and brine analysis for samples 1–10.

Table 4-1
Boiler chemical cleaning waste feed solution lab analysis

Feed				
Constituent	**Unit**	**Result**	**Minimum Reporting Limit**	**Method**
Ammonia, as N	mg/L	9720	500	SM 4500 NH3 H
pH		9.6	0.1	SM 4500 H-B
Alkalinity (Total, as $CaCO_3$)	mg/L	19800	1.0	SM 2320 B
Total Dissolved Solids (TDS)	mg/L	64400	2000	SM 2540 C
Aluminum, Total	mg/L	18.8	2.0	EPA 200.7
Chromium, Total	mg/L	7.04	0.0500	EPA 200.8
Copper, Total	mg/L	63.4	0.100	EPA 200.8
Iron, Total	mg/L	12700	0.80	EPA 200.7
Nickel, Total	mg/L	18.1	0.0500	EPA 200.8
Zinc, Total	mg/L	11.5	0.40	EPA 200.7
Arsenic, Total	mg/L	0.682	0.0500	EPA 200.8
Barium, Total	mg/L	3.37	0.200	EPA 200.7
Cadmium, Total	mg/L	0.0526	0.0200	EPA 200.8
Calcium, Total	mg/L	379	8.0	EPA 200.7
Lead, Total	mg/L	5.19	0.0500	EPA 200.8
Magnesium, Total	mg/L	67.4	8.0	EPA 200.7
Manganese, Total	mg/L	80.5	0.0500	EPA 200.8
Mercury, Total	mg/L	ND	0.0200	EPA 245.1
Selenium, Total	mg/L	ND	0.0500	EPA 200.8
Silica, Total	mg/L	9.5	4.0	EPA 200.7
Silver, Total	mg/L	ND	0.050	EPA 200.8

Table 4-2
Distillate and brine sample analysis for Samples 1–10

Distillate													
Constituent	**Unit**	**Minimum Reporting Limit**	**Method**	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**Sample 6**	**Sample 7**	**Sample 8**	**Sample 9**	**Sample 10**
Ammonia N	mg/L	200	SM 4500 NH3 H	2700	2740	2860	2990	2590	2980	2830	3180	2900	3040
pH	-	0.1	SM 4500 H-B	10.6	10.4	10.4	10.4	10.4	10.5	10.6	10.6	10.6	10.5
TDS	mg/L	10	SM 2540 C	14	34	12	<10	<10	<10	<10	26	<10	<10
Aluminum	mg/L	0.05	EPA 200.7	0.1	0.08	0.07	0.05	0.06	0.07	<0.05	<0.05	<0.05	0.05
Chromium	mg/L	0.0005	EPA 200.8	0.007	0.0006	<0.0005	<0.0005	0.0007	0.0006	<0.0005	0.0005	0.0006	0.0006
Copper	mg/L	0.0010	EPA 200.8	0.037	0.0108	0.0072	0.0235	0.367	0.0909	0.0509	0.0639	0.0565	0.0462
Iron	mg/L	0.02	EPA 200.7	8.41	0.19	0.09	0.04	0.14	0.09	0.07	0.04	0.02	0.02
Nickel	mg/L	0.0005	EPA 200.8	0.478	0.074	0.0327	0.0093	0.0388	0.0092	0.0064	0.0064	0.0063	0.0068
Zinc	mg/L	0.01	EPA 200.7	0.46	3.36	2.5	2.09	0.82	1.09	0.97	1.67	2.16	2.08

Brine													
Constituent	**Unit**	**Minimum Reporting Limit**	**Method**	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**Sample 6**	**Sample 7**	**Sample 8**	**Sample 9**	**Sample 10**
Ammonia N	mg/L	500	SM 4500 NH3 H	11300	14600	16900	19100	19800	22200	21500	23300	22900	25600
pH	-	0.1	SM 4500 H-B	7.4	7	7	6.9	6.9	6.7	6.8	6.7	6.7	6.7
TDS	mg/L	2000	SM 2540 C	89200	135000	148000	109000	108000	117000	121000	238000	147000	272000
Aluminum	mg/L	50.0	EPA 200.7	0	38.1	45.8	48.4	61.6	55.3	63.9	66.3	58.1	71.3
Chromium	mg/L	0.500	EPA 200.8	11.6	17.7	20	21.4	24	25.2	24.9	29	25.2	27.4
Copper	mg/L	1.00	EPA 200.8	112	154	180	196	200	206	203	227	204	215
Iron	mg/L	20.0	EPA 200.7	13800	27500	33100	34300	44500	41100	44100	47500	42100	52000
Nickel	mg/L	0.500	EPA 200.8	32.7	47	54.7	59.7	66.8	69.6	68.4	79.4	69.8	74.1
Zinc	mg/L	10.0	EPA 200.7	14.8	22.9	27.3	29.7	36.8	33	37.9	39.2	34.8	40.5

Results Discussion

As shown in Table 4-2, distillate quality from the test unit was relatively consistent even as the brine concentrated to levels four times the initial values by the end of the test period. With the exception of Sample 1, iron concentration was less than 1 ppm in the distillate. Total dissolved solids (TDS) averaged 8.6 ppm with a standard deviation of 12.6. The highest TDS value was 34 ppm. It was observed that the initial distillate sample (sample 1) was turbid and red in color, indicating that either the test unit was not fully cleaned between this test and the previous test or that some carryover occurs when the unit is started. This is a potential cause for the higher iron concentration (8.41 ppm) in the first sample. All other metals, except for zinc, were considerably less than 1 ppm through the test period. The higher zinc concentrations cannot be explained. It is possible that the materials of construction of the vapor compressor or residual material from previous testing contributed to this zinc concentration. The average pH of the distillate samples was 10.5 due to the ammonia concentration.

The brine solution concentrated dissolved solids approximately four times the initial waste feed to the test unit. No precipitation or scaling issues were noted. The final brine pH was 6.7. As expected, ammonia distributed to the distillate, as indicated by the odor and pH of 10.5. However, some ammonia remained in the brine solution, although only concentrated by 2.6 times the initial value, which is lower than the concentration factor measured in other constituents.

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CONCLUSIONS AND RECOMMENDATIONS

Based on the lab-scale feasibility testing performed, AVARA thermal evaporation technology shows potential as a viable alternative for reducing the volume of a tetra-ammonia EDTA boiler chemical cleaning waste (BCCW). Additional testing should be conducted on a larger scale. The process produced a relatively consistent distillate quality with carryover of ammonia and notable amounts of zinc. Mass balance shows that approximately 60% of the ammonia is concentrated with the brine and the balance is vented with non-condensables or condensed with the distillate. Based on the sample tested, it is anticipated that AVARA can feasibly reduce the waste volume of an initial spent solvent drain BCCW by about 75%. Additional testing should be conducted before attempting to reduce initial spent solvent BCCW to a greater degree. Additional testing should also be conducted before this process is utilized to reduce BCCW from a mineral acid, such as hydrochloric acid, or other organic acid solvents, such as diammonium citrate or hydroxyacetic formic acid.

The distillate stream shows potential for re-use as feed water in the plant boiler and turbine steam cycle makeup water treatment process assuming it is properly treated with a reverse osmosis and ion exchange process to remove the remaining dissolved solids. A plant specific technical and environmental analysis should be conducted to evaluate feasibility of distillate re-use or discharge.

The brine solution concentrates dissolved and suspended solids, including heavy metals, and for this reason will likely be characterized as a hazardous waste based on current U.S. regulations [6]. The total chromium content of the initial drain of spent solvent EDTA BCCW was reported to average 9.1 ppm in a previous EPRI report [3]. Brine resulting from AVARA processing will increase the initial BCCW chromium concentration by at least a factor of 4 at a target volume reduction of 75%.

A larger scale AVARA modular unit is available for mobilization to a plant site so that the BCCW is treated on site. Further testing will help to confirm treatment feasibility and further explore environment aspects. Additional determination of the following should be made with additional testing:

- Evaluate energy consumption and operating conditions (temperatures, pressures, recirculation rate, etc.)
- Analyze feed and final waste for total suspended solids (TSS)
- Conduct internal inspections of the core to further evaluate scaling
- Evaluate increased waste volume reduction at >75%

6

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6. 40 CFR 261.24(b)

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