

MED BRINE TREATMENT FOR GEOTHERMAL INJECTION

Authors: Thomas Peter Sephton¹, Dr. William Bourcier², Larry Lien³, Richard Simonis⁴

¹*Sephton Water Technology, Inc., USA, tomsephton@sephtonwatertech.com*

²*Lawrence Livermore National Lab, USA, wbourcier@gmail.com*

³*Membrane Development Specialists, USA, Larry@mdsamericas.com*

⁴*Rocky Point Environmental Services, USA, r.simonis@rockypoint-es.com*

Presenter: Thomas Peter Sephton
President – Sephton Water Technology, Inc. – USA

ABSTRACT

The purpose of this study and pilot project was to develop a method to dispose brine concentrate from a geothermal waste heat Multi-Effect Distillation (MED) process by injection into the geothermal aquifer. This would provide environmentally safe brine disposal roughly 2,000 meters below ground into an already hypersaline aquifer. It could also provide a benefit to the geothermal resource by augmenting the 80% to 90% geothermal recharge in practice.

An existing two effect Vertical Tube Evaporator (VTE) pilot plant has been testing the use of waste heat from geothermal steam vented at atmospheric pressure by power plants at the Salton Sea in the Southern California desert in order to reclaim water from that large brine lake for environmental or potable reuse. Disposal of brine concentrate at the inland site is problematic because rising salinity in the brine lake already threatens a critical ecosystem there.

Since the geothermal plants already reinject most of the the geothermal fluid after flashing steam to run turbines, co-injection seems a logical local solution. However, the chemical compatibility of the MED brine with the geothermal aquifer is critical to the geothermal operation. This project investigated the compatibility of the MED brine from Salton Sea feed water with the geothermal aquifer. High sulfate and magnesium in Salton Sea feed water were identified as the primary challenges. For example, sulfate would form gypsum when contacting high calcium in geothermal fluids causing wells to plug.

This project lab tested ion exchange and thermal softening methods, before settling on a nanofiltration approach. Nanofiltration methods were pilot tested with Salton Sea water resulting in a sequential UF/NF process to pre-treat raw Salton Sea water before MED yeilding a brine concentrate compatible with the Salton Sea geothermal aquifer. A subsequent bench test improved the nanofiltration permeate recovery to 95%.

Keywords: Geothermal, Distillation, MED, VTE, nanofiltration



I. INTRODUCTION

The triple flash geothermal power production process has been in use for over forty years on the Salton Sea Known Geothermal Resource in Southern California's Imperial Valley. In addition to flashing hot geothermal brine at three pressures ranging from 270 psig to 48 psig to supply steam turbines, the process includes a final non-power producing flash at atmospheric pressure before the spent brine is reinjected into the geothermal aquifer to reheat and be reused. Steam from this atmospheric pressure flash has been vented to the atmosphere for the last forty years, however, while not economic to drive a steam turbine, the near 100°C temperature provides a good waste heat source to drive a Multi-Effect Distillation (MED) process at very low energy cost.

In prior work [1], a 15 effect MED process was pilot tested with a two-effect Vertical Tube Evaporator (VTE) plant using the adjacent high salinity (now over 60 g/liter TDS) Salton Sea as source water. The pilot testing achieved a high recovery rate of 86% with a performance ratio of 14 [2]. This leaves a 14% fraction of highly concentrated brine to be disposed of without damage to this inland environment. The triple flash geothermal process returns 80% to 90% of the geothermal brine used for power to the salt saturated geothermal aquifer roughly 2,000 meters below ground. This offers an opportunity to make up that deficit with concentrated Salton Sea brine discharged from the MED process, however the chemical compatibility of the MED brine with the geothermal aquifer is critical to the geothermal operation. This project investigated the compatibility of the MED brine, lab tested methods, then pilot tested a sequential UF/NF process to pre-treat raw Salton Sea water before MED yielding a brine concentrate compatible with the Salton Sea geothermal aquifer. This process has other benefits in reducing scale potential in MED.

II. GEOCHEMICAL MODELLING

Dr. William Bourcier led a study that reviewed the chemistry of the geothermal aquifer at the Salton Sea and used computer modelling to identify constraints that MED brine concentrate from Salton Sea feed would have to meet to be suitable for injection in that aquifer. The geothermal fluid produced from the aquifer has a high TDS of 300,000 mg/kg with sodium (53,000 ppm), potassium (16,700 ppm), and chloride (151,000 ppm). Notable was a very high concentration of calcium (27,400 ppm). The fluid has very low concentrations of sulfate (~60 ppm), and magnesium (~35 ppm). By comparison, raw Salton Sea feed without pretreatment had TDS at 59,000 mg/kg with sodium (13,000 ppm), potassium (380 ppm), chloride (20,000 ppm), and comparatively high sulfate (12,000 ppm). Magnesium is also comparatively high in the Salton Sea at 1,600 ppm. The primary constraints on MED brine concentrate identified were:

1. **Sulfate** concentration must be at or below the present levels in the geothermal fluid, at 64 ppm. Higher levels will cause precipitation of calcium sulfate due to the high amount of calcium in the fluid, and the known trend for calcium sulfate to get less soluble with temperature.
2. **Magnesium** concentration must also be equal or lower than the value of about 35 ppm measured in the geothermal brine. Magnesium at higher concentrations is likely to precipitate upon heating, potentially damaging the geothermal reservoir.
3. **Aluminum** should also be equal to or lower than the value of 2 ppm in the geothermal fluid. Aluminum is fairly insoluble at ambient temperature and if present, probably exists in particulate or colloidal form. If so, it should be removed via filtration.
4. **Barium** and **fluoride** should both be at or below their current concentrations in the geothermal fluid. Anti-scalants specific to each of these phases are presently being added to the geothermal fluid to avoid scaling during reinjection.



First Round Nano-filtration Pilot Test at VTE Pilot Plant

Dick Simonis and Bill Bourcier ran a test of nano-filtration with 85° F seawater feed at 50% recovery to reduce sulfate, calcium, and magnesium. Genesis LF was used as an anti-scalant. The membranes scaled up after three hours of operation with Salton Sea water so the test was aborted. A decision was taken to try pre-softening to reduce calcium that could form calcium sulfate and ultra-filtration pre-treatment on the theory that particulates in the feed allowed nucleation of precipitates. New nano-filtration membranes and a set of ultra-filtration membranes were ordered.

A membrane post mortem by Larry Lien restored membrane flow with acid washing indicating the scaling problem was from calcium carbonate. Dick Simonis recommended pretreatment of Salton Seawater with HCl to lower the pH from 8 to 6.5 combined with ultra-filtration prior to nano-filtration to remove particulates that might interfere with the anti-scalant. This would be a 3 pass process.

Second Round Nano-filtration Test at VTE Pilot Plant

Dick Simonis installed ultra-filtration membranes in the pilot test unit and ran ~4,000 gallons of seawater through at 50% recovery while dosing HCl to a pH of ~6.5. Dick Simonis and Bill Bourcier ran two nano-filtration passes on ultra-filtrate at 85 deg F to reduce sulfate, calcium, and magnesium in the seawater to concentrations that would be compatible with the geothermal aquifer after concentration. Samples were taken for on-site and off-site lab analysis. Bill Bourcier tested nano-filtration permeate samples on site for total hardness, calcium, and sulfate. The 1st nano-filtration pass achieved better than 99% rejection of each. The second pass brought calcium, magnesium, and sulfate below levels detectable in the on-site analysis. Based on published detection limits, 2nd pass nano-filtration permeate would meet the targets for geothermal compatibility after 6:1 concentration.

Dick Simonis and Bill Bourcier completed a 1st nano-filtration pass on ultra-filtrate from Salton Sea water at about 50% recovery. Bill Bourcier tested nano-filtration permeate samples on site for total hardness, calcium, and sulfate. Dick Simonis and Bill Bourcier ran a 2nd 50% recovery nano-filtration pass on permeate from Salton Seawater already nano-filtered once. 800 gallons of 2nd pass permeate were stored for later concentration in the VTE. Bill Bourcier tested nano-filtration permeate samples on site for total hardness, calcium, and sulfate.

Dick Simonis ran a nano-filtration test on ultra-filtrate from Salton Sea water to push for 75% recovery per pass. The test was shut down due to precipitation blocking the membranes. Investigation of the choice of anti-scalant showed that the Gensys LS in use was not the manufacturer's best recommendation for high sulfate brine. It was decided to try an alternate anti-scalant, Gensys CAS, designed for high sulfate.

In order to determine the maximum recovery possible with 2-stage NF, a sample of UF-treated Salton Sea feed water was taken to a test facility in San Diego operated by Separation Engineering (SE). The tests were carried out by Larry Lien of MDS, assisted by Tom Sephton and Bill Bourcier. For the testing at SE, the first step was an NF pass at 80% recovery using the sulfate anti-scalant (Gensys CAS) to prevent gypsum precipitation. The concentrate from this step was then forced to precipitate the supersaturated gypsum by addition of lime particulate seeds. The precipitate was then separated and another NF pass carried out to 75% recovery. The CAS anti-scalant from Gensys allows about a 5 times supersaturation of gypsum before initiation of precipitation. With this process 95% of the initial feed is now essentially free of hardness and can be treated to very high recovery using the VTE (80% in the first step, and 75% of the 20% concentrate sums to 95%). It is also possible that the gypsum precipitate could be marketable for drywall manufacture. The test results for the SE tests are shown in Figures 2 and 3.



Membrane Model: DK1812C-34D 4.5ft. ²										Sample From: Salton Sea													
Normalized net Pressure: 500 psi					Sample ID: Heap Leach																		
Normalized Temperature: 77 F					CAS Antiscalant added 10 ppm																		
Active Membrane Area: 4.5 sq. ft.																							
Date	Time	Temp (C)	Temp (F)	Feed Inlet (psi)	Conc. Out (psi)	Brine Flow (GPM)	permeate collection (ml)	permeate time (sec)	Perm Flow (GPM)	Feed tds (GPD)	Brine tds	Perm tds	syst Rec (%)	Average P (psi)	As Run Flux (GFD)	As Run A-value x100000	cond % Rej	TCF x100000	Norm A-value (GFD)	Norm Permeate (GFD)			
20-Feb	10:15	17.0	62.6	150	150	1.2	0	150	60	0.040	57	3500	3700	8	3.30	150	12.7	5.85	99.8	1.31	7.67	55.37	Pre-test
20-Feb	10:25	17.0	62.6	500	500	1.2	1000	210	60	0.055	80	30000	31000	19080	4.62	500	17.8	2.46	37.4	1.31	3.22	23.26	
20-Feb	10:35	25.0	77	700	700	1.2	5000	300	60	0.079	114	40000	42000	23800	6.61	700	25.4	2.51	42.0	1.00	2.51	18.12	
20-Feb	10:45	27.0	80.6	700	700	1.2	10000	260	60	0.069	99	51000	53000	27500	5.72	700	22.0	2.17	47.1	0.94	2.04	14.71	
20-Feb	10:50	25.3	77.5	700	700	1.2	12500	250	60	0.066	95	52000	54000	28500	5.50	700	21.1	2.09	46.2	0.99	2.07	14.95	
20-Feb	11:30	30.0	86	700	700	1.2	15000	250	60	0.066	95	55000	57000	29100	5.50	700	21.1	2.09	48.0	0.85	1.78	12.85	
20-Feb	12:45	31.0	87.8	700	700	1.2	16000	250	60	0.066	95	60000	62000	33600	5.50	700	21.1	2.09	44.9	0.82	1.72	12.45	
20-Feb	13:00	32.0	89.6	750	750	1.2	19000	200	60	0.053	76	65000	67000	35000	4.40	750	16.9	1.56	47.0	0.80	1.25	9.00	
21-Feb-10	14:00	64	147	150	150	1.2	0	150	60	0.040	57	3500	3700	9	3.30	150	12.7	5.85	99.8	0.32	1.89	13.62	Post-test

Figure 2: Test results for NF high recovery test carried out at the Separation Engineering facilities. 2010

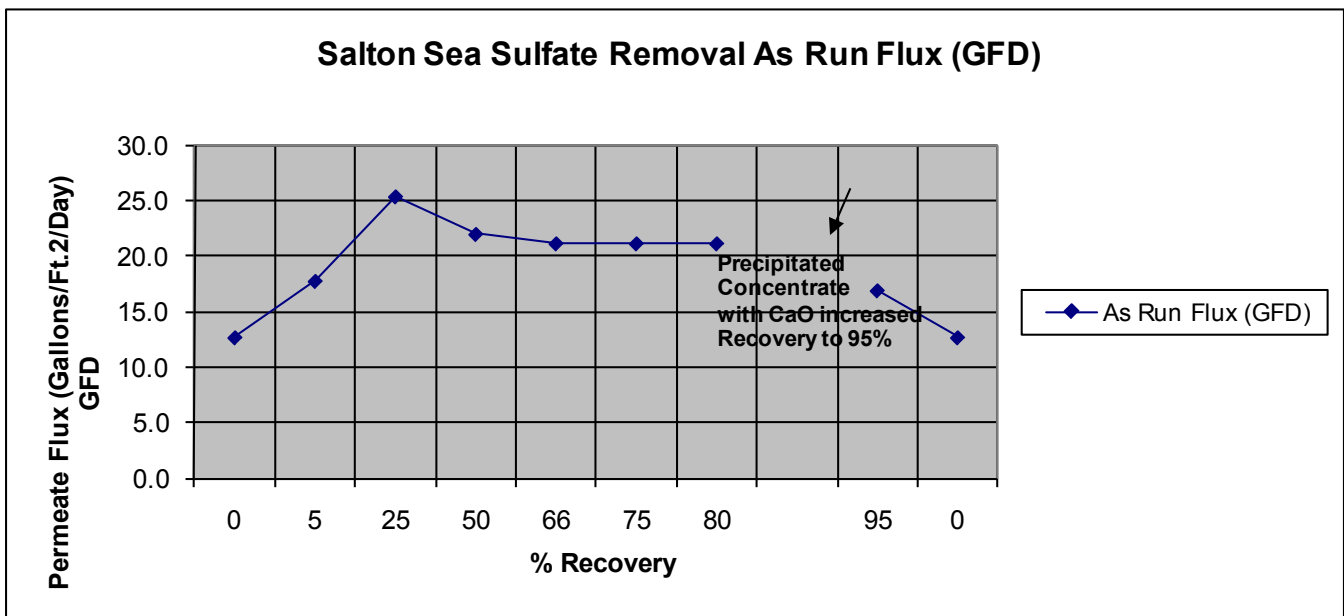


Figure 3: Flux Chart from NF high recovery test carried out at the Separation Engineering facilities.

IV. DISTILLATION PILOT TESTING

The 2nd pass NF permeate was concentrated 12 fold in a VTE Pilot Plant with heat from 100°C geothermal steam. Heat transfer performance data and samples of brine and distillate were taken at each one-fold increase in brine concentration. Steady heat transfer performance indicated no scaling during brine concentration. All samples were tested for pH and TSS/TDS plus ion analysis in a commercial lab. Magnesium and sulfate levels were higher after introduction of the 2nd pass permeate to the VTE system. This may be caused by dissolving these elements out of slurry deposits from prior raw feed testing. Maximum sulfate was exceeded in the VTE brine concentrate only when going above 5 fold concentration. Higher concentration would be desirable to match the 300,000 mg/liter TDS of local geothermal brine.

Concentration of Nano-filtration Permeate by VTE Pilot Plant

Concentration of 2nd pass NF permeate was accomplished with an isothermal brine concentration in VTE 1 at 100°C geothermal steam temperature conditions running permeate concentration from 1:1 up to 10:1 based on feed rate measurements. Heat transfer performance data were taken at each one-fold increase in brine concentration with sampling of brine and distillate. As seen in Figure 4, there was no indication of scaling during brine concentration with steady heat transfer recorded. The isothermal brine concentration test of 2nd pass NF permeate in VTE 1 continued at 100°C geothermal steam temperature conditions running permeate concentration from 10:1 up to 12:1 based on feed rate measurements. There was no indication of scaling. All samples were tested for pH and TSS/TDS on site.

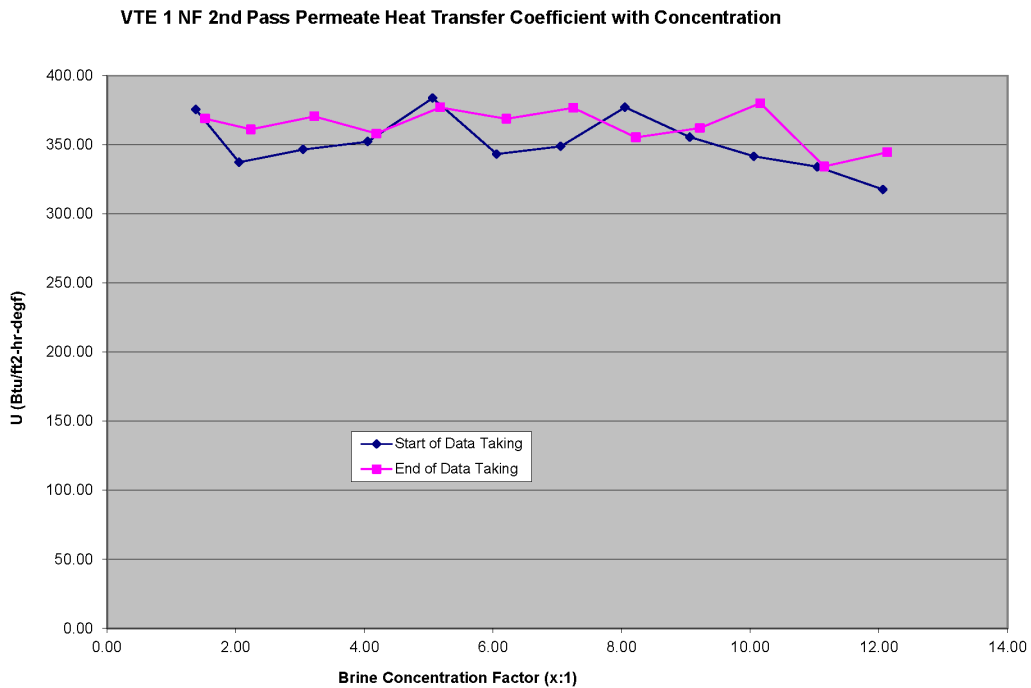


Figure 4. Heat transfer performance in VTE 1 concentrating NF permeate to 12 fold

Lab analysis of major ions, particularly sulfate and magnesium, was needed to confirm whether the brine concentrate will be suitable for geothermal injection. Samples from the isothermal brine concentration test of 2nd pass nano-filtration permeate in VTE 1 were diluted and preserved with nitric acid and shipped out to the Thermochem commercial lab for chemical analysis of major ions to confirm whether the brine concentrate will be suitable for geothermal injection, see Figure 5 for major ions. Lab results received showed 2nd pass nano-filtration permeate met targets with sulfate at 3.86 mg/liter and magnesium at 1.48 mg/liter in a brine calculated to be 19,400 mg/liter TDS, see Figure 6 for minor ions.

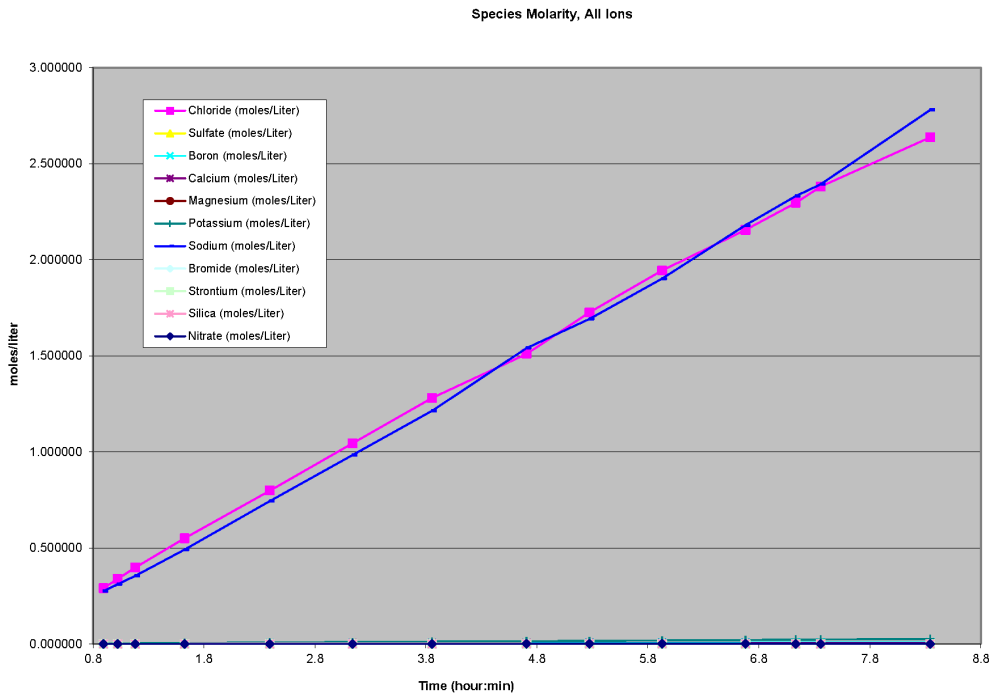


Figure 5. Major ions in NF permeate concentrating 12 fold in VTE 1

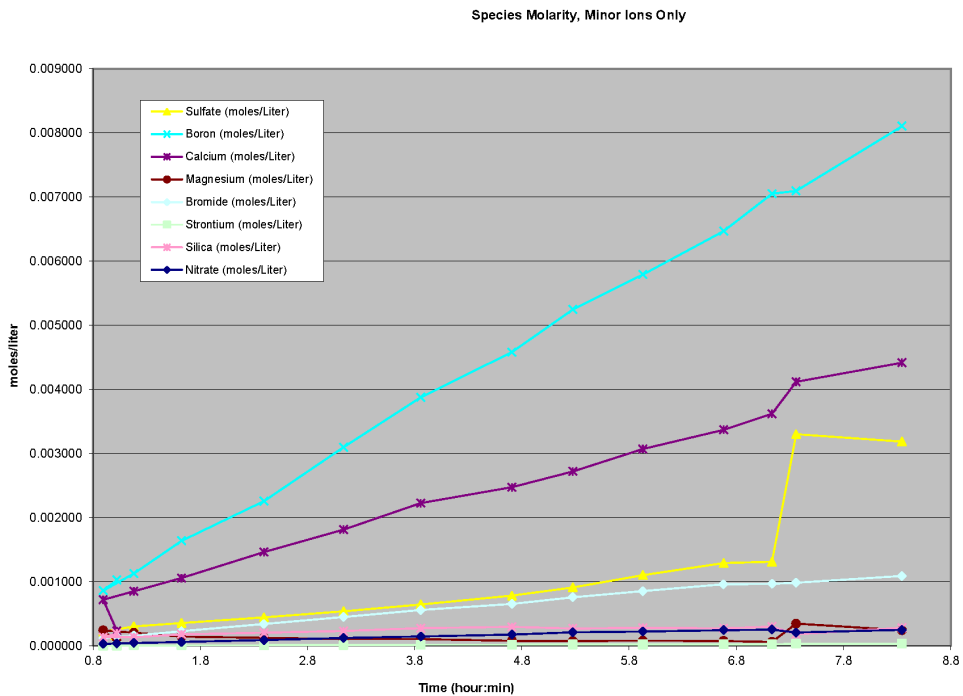


Figure 6. Minor ions in NF permeate concentrating 12 fold in VTE 1

The 2nd pass permeate could, in theory, be concentrated 16 fold to 310,400 mg/liter TDS before exceeding the maximum 65 mg/liter target for sulfate or 35 mg/liter for magnesium in the geothermal aquifer. In the



brine concentration test, magnesium and sulfate levels were higher after introduction of the 2nd pass permeate to the VTE system. This may be caused by dissolving these elements out of slurry deposits that were not adequately removed from the VTE equipment after flushing several times with freshwater and distilled water or by some unknown mechanism. The maximum sulfate target was exceeded in the VTE brine concentrate only when going above 5 fold concentration, see Figure 6. This level of concentration would be adequate if the starting material were raw Salton Sea water, but nano-filtration reduced sodium and chloride in the permeate along with the divalent ions targeted so a higher concentration would be desirable to recover more distilled water and match the 300,000 mg/liter TDS of local geothermal brine. If the nano-filtration pre-treatment were used for a large scale process, permeate should be distilled and concentrated by separate clean VTE equipment that had not been exposed to raw Salton Sea water, slurry, or nano-filtration reject brine.

Concentration of Nano-filtration Reject by VTE Pilot Plant

The nano-filtration reject is a reject stream not suitable for geothermal injection. This brine could be suitable in the locality as a brine source for salinity gradient solar ponds. These ponds would benefit from a brine source delivered near saturation. In any case, minimizing the volume is preferable, so concentration of this challenging brine in the VTE would be useful in a very low liquid discharge process. The quantity of 1st Pass Nano-Filtration Reject saved from the final NF pilot test was about 1,500 gallons, sufficient for only one chance at a concentration test with NF Reject as the feed source. The NF Reject had elevated levels of scale forming ions such as calcium, magnesium, and sulfate.

A series of tests with freshwater feed were run to select an optimal operating condition and concentration of the anti-scaling surfactant Linear Alkylbenzene Sulfonic Acid (LAS-99 from Pilot Chemical or LAS). In prior tests, LAS concentrations of 10 mg/liter and above showed excessive foaming at the highest operating temperatures in VTE 2 unless the brine recycle rate were reduced. VTE 1 was less prone to foaming. A multi-effect simulation test of VTE 1&2 in two-effect operation with 2 mg/liter LAS in freshwater, feed preheating by heat exchange with de-superheating condensate, forward feed from VTE 1 to VTE 2, and brine re-injection from VTE 2 back to VTE 1 was run at ½ the typical brine recycle rate or ¾ gpm per tube. This had no impact on heat transfer performance at lower operating temperatures, but caused up to a 20% reduction in the measured heat transfer coefficient at higher temperatures. Similar multi-effect simulation tests were run with LAS dosed at 10 mg/liter and at 20 mg/liter using the ¾ gpm per tube brine recycle rate. The lower recycle rate and improved control of the LAS concentration in the brine made it possible to operate without excessive foaming. LAS concentrations of 10 mg/liter and 20 mg/liter gave an improvement in the heat transfer coefficient of about 10% in VTE 2 over 2 mg/liter LAS. There was minimal difference in VTE1. The performance benefit of higher LAS in VTE 2 was offset by the need to operate at a reduced brine recycle rate risking tube dry out, so the 2 mg/lit LAS condition was chosen with VTE 2 brine recycling at 1.5 gpm per tube.

1st Pass NF Reject was mixed with all available CaSO₄ slurry to 1.5% TSS and used to charge VTE 1&2. LAS was dosed at 2 mg/liter. Samples were taken for analysis. The pilot plant was brought to the Effect 15 low temperature condition of 51°C with geothermal steam heat. To provide a standard curve of brine conductivity against concentration (TDS), the 1st Pass NF Reject slurry was concentrated isothermally up to 4:1 with samples taken for analysis at 1:1, 2:1, 3:1, and 4:1 concentration factors. All major ions showed a steady rise in concentration except calcium, which declined steadily across the test range indicating precipitation of CaSO₄. Sulfate was in 8.7 fold molar excess over calcium, so precipitation is not obvious in the sulfate data. Also carbonate was converted fully to bicarbonate between 2:1 and 4:1 brine concentration.



A multi-effect simulation test of 1st Pass NF Reject was run immediately after brine concentration. VTE 2 brine was held at the 4:1 concentration factor with 51°C effect 15 temperatures while taking thermal performance data. VTE 1&2 were operated with 2 mg/liter LAS, feed preheating with geothermal condensate to VTE 1, then to VTE 2, and brine re-injection from VTE 2 back to VTE 1. VTE 2 was run at the typical brine recycle rate of 1.5 gpm per tube. The brine concentration was brought down with excess blowdown and the operating temperatures raised for an Effect 11 and an Effect 7 simulation of a forward feed multi-effect system. The supply of 1st Pass NF Reject ran out after the Effect 7 simulation so the high temperature 100°C steam, low brine concentration Effect 1 condition could not be tested. Heat transfer coefficients operating with 1st Pass NF Reject ran about 10% below a prior freshwater baseline test in both evaporators. Slurry (as TSS) rose steadily during the isothermal brine concentration to 2.8%, but was reduced to very low levels when driving down the brine concentration during the test.

To evaluate possible scaling of VTE 1 and VTE 2 during the multi-effect simulation test with 1st Pass NF Reject feed, both evaporators were drained and recharged with freshwater and 10 mg/liter LAS. A baseline multi-effect simulation test of VTE 1&2 was run in two-effect operation with feed preheating by geothermal condensate, forward feed from VTE 1 to VTE 2, and brine re-injection from VTE 2 back to VTE 1. The same test procedure was repeated after draining, flushing, and recharging both evaporators with freshwater and 2 mg/liter LAS. Heat transfer performance data was taken and compared with baseline tests run with 10 and 2 mg/liter LAS in freshwater before the 1st Pass NF Reject test.

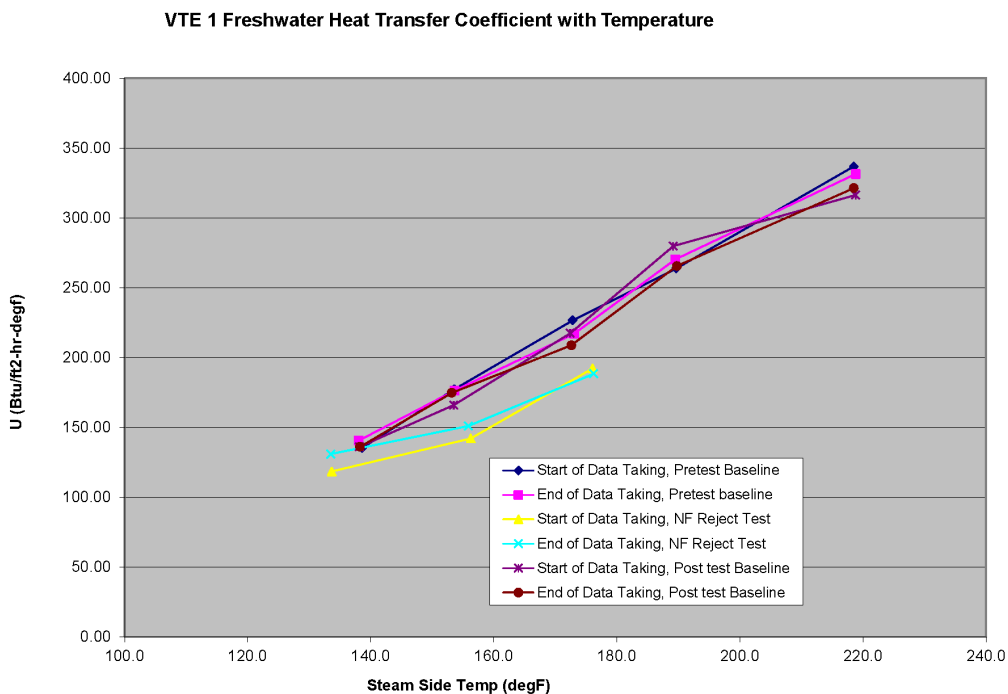


Figure 7. VTE 1 heat transfer coefficient concentrating NF Reject with freshwater tests for scaling

The heat transfer coefficient was not reduced in VTE1 (Figure 7) under either test condition indicating no measurable scaling during the test using 1st Pass NF Reject as feed. A slight reduction in heat transfer performance was seen in VTE 2 (Figure 8). The NF reject feed source was very high in scale forming ions. The multi-effect simulation with 1st Pass NF Reject feed tested the low temperature with high brine concentration condition that would be used in a multi-effect system configured for forward feed. This result supports a forward feed process, however there was not enough 1st Pass NF Reject to test all forward

or reverse feed conditions. Buildup of flakes in the VTE 1 strainer occurred in both freshwater tests requiring strainer screen cleaning after each test run.

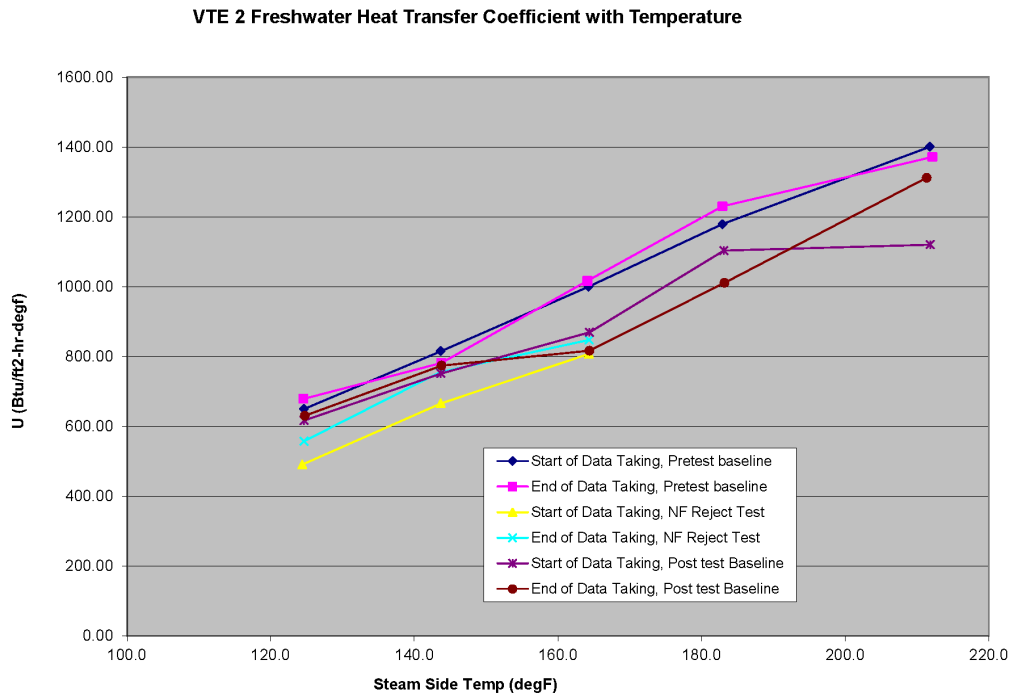


Figure 8. VTE 2 heat transfer coefficient concentrating NF Reject with freshwater tests for scaling

V. CONCLUSIONS

Pilot testing showed that a two pass NF process, after removal of all particulates by UF and pH adjustment to remove carbonate, can achieve the very low levels of magnesium and sulfate in brine concentrate required. The permeate from NF could be concentrated up to 12 fold in the VTE without scaling while recovering about 90% of the water as distillate. The UF/NF pretreatment process on Salton Sea feed water can enable disposal of MED brine concentrate in the geothermal aquifer without harm to the aquifer or the surface environment and with a possible recharge enhancement benefit to the geothermal resource.

The testing undertaken developed the preferred high recovery NF process on only a small batch basis at the Separation Engineering facility. The test data would be more complete and reliable if the preferred process were tested at pilot scale at the VTE facility to verify the high recovery ratios are actually achievable in practice. Figure 9 outlines the overall high recovery test process.

Removal of scale forming divalent ions may enable higher VTE-MED top brine temperatures. While the VTE process development has aimed at a waste heat process with a top brine temperature slightly under the 100°C atmospheric flash steam, higher temperature steam is available at the VTE site. Enhancing VTE-MED performance with a higher top brine temperature and more effects would provide information applicable to a wider range of steam sources that could be tested at the existing VTE site.

UF/NF Ion Separation with VTE Concentration, Test Schematic

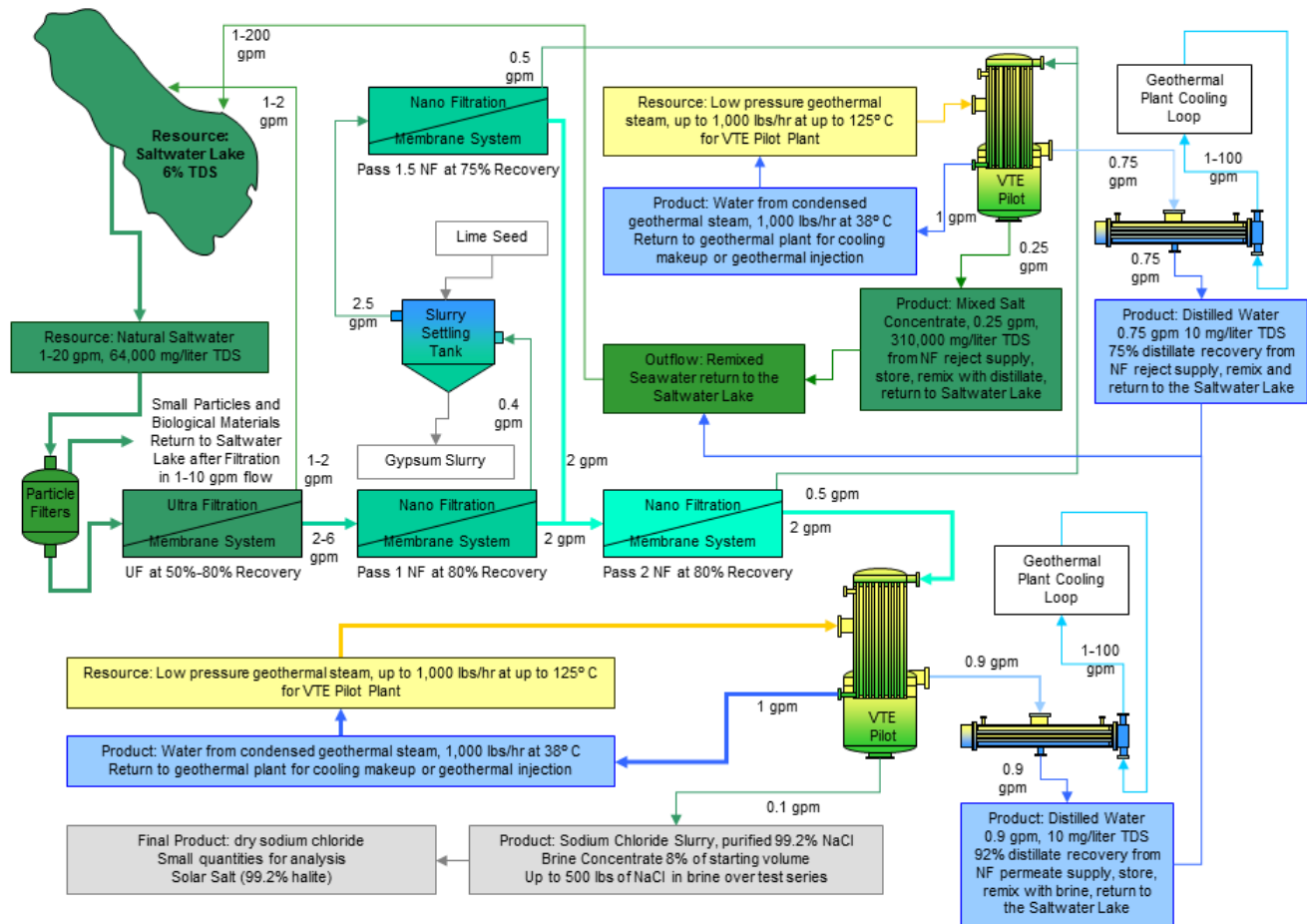


Figure 9: Diagram of NF High Recovery Overall Test Process

VI. REFERENCES

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