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Evaluation of the Aqua Pure Mechanical Vapor Recompression System in the Treatment of Shale Gas Flowback Water

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Acronym and Abbreviations

bbl	Barrel = 42 US gallons
BETX	Benzene, ethylbenzene, xylene, toluene
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
kWh	Kilowatt-hour
mg/l	milligram per liter, approximately part per million by weight
MVR	Mechanical vapor recompression
POTW	Publicly Owned Treatment Works
SCF	cubic foot of natural gas at standard temperature and pressure
TDS	Total dissolved solids (mg/l)
TOC	Total organic carbon
TPH	Total petroleum hydrocarbons

1 Abstract

This report is part of an overall effort to advise and support the natural gas industry in the evaluation and selection of treatment equipment and processes for the treatment and reuse of water used and generated by the industry.

Extensively used by the food, chemical, and pharmaceutical industries, the mechanical vapor recompression (MVR) process is viewed by a number of shale gas companies as one of the most reliable methods of recovering demineralized water from concentrated brines. For this reason, Devon Energy has supported the demonstration of three modular NOMAD units that are manufactured by Aqua-Pure Ventures and operated in the field by Fountain Quail Water Management. This report presents process data on a commercial-scale (6,000-6,800 bbl/day) mechanical vapor recompression distillation (MVR) processing plant treating shale gas hydro-fracture flowback and produced water in North Central Texas (Barnett shale region). Process data were collected during a 60 day period during summer 2011. The pretreatment at this plant included caustic addition and clarification for total suspended solids and iron control. Pretreated water was distilled with three Aqua Pure MVR units, each rated at 2,000-2500 bbl/day. Distilled water recovery averaged 72.5% of the influent to the MVR's The influent total dissolved solids (TDS) fed to the MVR's averaged just under 50,000 mg/l. More than 99% of the TDS was captured in the concentrate stream. The distillate averaged about 171 mg/l TDS. The fate of multivalent cations, total petroleum hydrocarbons (TPH), and benzene, toluene, ethylbenzene and xylenes (BTEX) throughout the treatment system was determined. Most of the iron (90%) and TPH removal (84%) occurred in the clarification step. The removal of iron, magnesium, calcium, barium, and boron from the distillate exceeded 99%. BTEX removal from the distillate exceeded 95%. The power at the facility was provided by two natural gas generators, plus the three generators on the MVR units, making isolation of the MVR energy requirements problematic. Best-fit correlations between treated water and distillate production versus total plant utilization of natural gas indicated that there was a base power load throughout the facility of about 120-140 thousand standard cubic feet of gas per day. Approximately 48 SCF per barrel influent water treated (or 60.5 SCF per barrel distillate produced) was required; this represents an energy cost of less than 25 cents per barrel treated and about 30 cents per barrel of distillate product generated (assuming a natural gas cost of $5/mmBtu). Performance in terms of water recovery and product water quality was stable throughout the 60-day test. The treatment process is available throughout the shale gas industry; Fountain Quail Water Management provides the complete equipment package and operation of the integrated MVR treatment facility on a price per barrel basis. Cost factors and approximate pricing for example applications are included in the report.

2 Introduction

As shale gas emerges as one of the world's most abundant, affordable and clean-burning sources of energy, sustained growth in the development and production of these resources will require intensive levels of sourcing and management of water. In most shale plays, hydraulic fracturing is a necessary step for initiating economical energy production. During the hydraulic fracturing process, between 1 and 4 million gallons of water are mixed with sand (which serves as propant) and chemical additives (e.g. friction reducer polymers, corrosion inhibitors, scale inhibitors, biocides, etc.), and the mixture is injected "down hole" as a necessary step in the well completion process. Vertical wells (representing less than 10% of the wells installed in the Barnett Play) require approximately 1 million gallons and horizontal wells (representing 90% of the wells) require 3-4 million gallons according to a survey among Barnett Shale Producers (Galusky, 2007). About 10 to 50 percent of this water is recovered during the months that follow a well completion. The recovered fluid can contain elevated concentrations of dissolved salt (picked up from mineral solubilization), suspended solids, oils and greases, soluble organics, and low concentrations of chemical additives. Therefore, recovered flowback water and produced water streams present a water management challenge, as well as a significant cost factor in the operation of the well.

The dimensions of water management for each shale gas developer can be more clearly seen when considering that current trends favor the construction and completion of 10 to 30 wells from one or two well pads in each well field (an effort requiring 1-3 years). The installation of dozens or hundreds of well fields within a development area that is roughly the size of a county, could require more than a decade. Under full scale development, hundreds of millions of gallons of fresh water must be found and transported to well sites each year using tens of thousands of truckloads. In addition, the management of flowback water and produced water collected from an ever growing population of completed wells requires options for the transportation and management of thousands of truckloads of brine that usually range in salt content from 30,000 mg/l of TDS (as seen in early flowback water) to more than 150,000 mg/l TDS (as seen in many produced water streams).

Shale gas developers of the Barnett Shale and Marcellus Shale regions have long recognized the potential benefits of reusing flowback water and produced waters for conducting hydraulic fractures of future shale gas well completions. The practice of water reuse usually involves collecting and treating the flowback water from a completed shale gas well and blending that water with supplemental freshwater for use in completing another shale gas well. Benefits of reuse include: 1) The reduction the shale gas industry's demand for fresh water supplies (water conservation is of high importance to drought prone regions such as the Barnett Shale); 2) Significant reduction in volumes of brine requiring final disposal (a particularly attractive benefit to Marcellus Shale companies in Pennsylvania that lack ready access to deep well injection facilities and are prevented from obtaining permits for controlled brine discharges to publicly owned treatment works or POTW's); 3) A significant decrease in water transport truckloads; and, 4) Improved environmental factors that arise from decreased trucks on the road (e.g. traffic congestion, emissions, carbon footprint, etc.).

In view of these advantages, the shale gas industry has explored various options for brine water reuse. In principle, the flowback water and produced water of a completed well are collected, treated and blended with supplemental fresh water at the impoundment that supplies water for the next hydraulic fracture completion of another shale gas well. In the area of treatment for purposes of shale gas water reuse, there are mainly two schools of thought that exist in the industry. One school of thought says: “Clarify the brine and control constituents that cause operational problems without removing the salt.” This approach applies primary treatment (settling and filtering) and chemical disinfection for the control of suspended solids, oils and greases, bacteria and scale forming ions (i.e. constituents that potentially interfere with equipment and infrastructure maintenance with no separation of salts (desalination) prior to reuse. Currently, this approach is being used within the Marcellus Shale as the predominant shale gas water management practice. In practice, flowback and produced waters are processed using primary treatment at the wellhead or in near-field locations at a central processing facility; the clarified brine is then transported to the next shale gas well completion site where the brine is blended with freshwater (at a ratio of about 3-5:1) resulting in a water mixture with salinity of greater than 5,000 mg/l TDS (a salt concentration level of regulatory concern in most states). In working with brine blends, water conveyance and storage impoundments need to be of higher integrity in construction to reduce the likelihood of release of mobile salts (e.g. sodium chloride) into the environment; this, of course, adds to the cost for these components.

The other school of thought says: “Recover demineralized water from the brine for reuse so that water-blend handling equipment and storage structures do not have to be designed to control salt releases.” This approach requires much of the above processing for the removal of suspended solids, oils and greases and scale forming constituents plus the treatment step of demineralization which results in the recovery of a low-TDS water stream that can be easily handled, transported, stored and blended for reuse in hydraulic fracturing. The advantage of this approach would be reduced regulatory concern over minor water releases that might occur with water handling, conveyance and storage systems since the salt content of water blends would be well below 2,000 mg/l TDS. Although demineralization of water adds a cost for flowback and produced water treatment, this approach does allow maximum latitude in using low-cost storage systems and piping systems for inter-field or near-field management of water associated with shale gas developments.

Demineralization of shale gas waters can be performed by several types of processes, including membranes and thermal treatment systems; these classes of separations have been considered by shale gas developers due to their successful historical implementation in the desalinization of sea water and their extensive use for various industrial applications. Membrane-based processes, such as reverse osmosis (RO), have been evaluated, but these processes are limited in application to waters of less than 40,000 mg/l TDS (CSM, 2009; Gaudlip, et al., 2008) if water recoveries of more than 60 percent are to be realized at reasonable pressure drops under 900 psi. Since a good fraction of flowback streams and produced waters can be far higher than 40,000 mg/l TDS, it is necessary to consider alternative demineralization processing based on thermal-mechanical separation.

One of the most efficient thermal processes used for the recovery of water from brine streams is the mechanical vapor recompression process (MVR). Extensively used by the

food, chemical, and pharmaceutical industries, the mechanical vapor recompression (MVR) process is viewed by a number of shale gas companies as one of the most reliable methods of recovering demineralized water from concentrated brines. At a centralized brine processing location accepting flowback and produced waters from multiple well fields, the MVR process offers the potential of recovering substantial volumes of demineralized water from brine that can widely vary in quality. Demineralized water that contains less than 500 mg/l of TDS can then be conveyed and stored for future reuse with minimal regulatory concern for salt release to the environment. For this reason, Devon Energy, one of the largest natural gas developers of the Barnett Shale, has supported the demonstration of the MVR technology at a multiple locations over the past seven years as a part of a larger development effort to improve its near-field water management systems. The MVR system selected for evaluation includes the modular, mobile NOMAD skid units that are manufactured by Aqua-Pure Ventures and operated in the field by Fountain Quail Water Management.

The purpose of this project was to systematically document the field performance of the NOMAD MVR system in the demineralization of shale gas waters in a near-field brine processing facility that was owned by Devon Energy and operated by Fountain Quail. Performance characterization included determination of mass flows, energy flows, fate of constituents of interest, product water yield and product water quality. Importantly, testing under real world conditions allowed the determination of actual field conditions (including feed water quality) on the stability and performance of the entire MVR system, including pretreatment and thermal skid units. Test plan development, coordination and data compilation and analysis were all coordinated by the Gas Technology Institute to provide a third party assessment of the MVR system in the demineralization of a blend of flowback and produced water from shale gas well fields in the Barnett. This report has been prepared by GTI to provide managers and engineers with a technical information base for decision making regarding the value and potential role of the MVR process in the long range management of brines and salts throughout the water-based life cycle of each shale gas development area.

Specifically, this report presents process data on a full-scale (6,000-6,800 bbl/day) mechanical vapor recompression distillation (MVR) processing plant (Maggie Spain site) treating shale gas hydro-fracture flowback and produced water in North Central Texas (Barnett shale region). The Maggie Spain site is owned by Devon Energy Corporation and operated by Fountain Quail Management, a joint venture established between Aqua Pure and the Ellenburg Group. The processes at this site are designed to concentrate solids for deep well injection, and to maximize salt-free water for reuse. The treatment philosophy and management goals represent a proactive and progressive example of environmental stewardship in the shale gas industry.

3 Background

Mechanical vapor recompression is a highly efficient distillation process wherein a mechanically-driven blower or compressor is used to increase the pressure of the vapor that is produced from the boiler in order to improve heat transfer efficiencies. An increase in the water vapor pressure increases the condensation temperature of the steam rendering it useable for heating the original mixture (in the boiler) in a heat transfer device or heat exchanger. This results in the operation of a distillation process at a substantially lower energy demand.

Mechanical vapor recompression has become a standard method of distillation since its commercial introduction in the 1960's. The process has been employed at thousands of facilities for the desalination of sea water (Veil, 2008), the crystallization of sugars in the food industry, dewatering of products in the chemicals and pharmaceuticals industries (Becker and Zakak, 1985), and more lately, in the recovery of industrial wastewaters.

The major advantage of mechanical recompression over conventional distillation is the ability to recycle the latent heat of flashed vapors to the bottom fluids, saving 10-15 % of the total energy of distillation. The recompressed vapors are saturated homogeneous fluids in thermodynamic equilibrium. Becker and Zakak (1985) describe three methods of application, recompression of the top vapors, the bottom vapors, or the intermediary vapor. The choice of the distillation style is dependent on the thermodynamics of the distillation components, and the goals of product recovery. The authors present a series of selection rules for the compressors. Economic case studies are presented for xylene recovery and isobutene extraction at refineries. Cost savings of up to 47% are claimed with payback periods of 1 to 2 years.

Leatherman (1983) reported radical energy savings over conventional distillation by incorporation of MVR technology to the recovery of uranyl nitrate in uranium processing. Steam generation at the plant decreased by 50% and cooling water requirements decreased by 35% compared to conventional distillation. Shake-down tests required about 133 kWh/1000 gallons distillate generated (5.6 kWh/bbl). Full production energy requirements were about 157 kWh/1000 gallons (6.6 kWh/bbl).

Concurrent Technologies (2001) described the advances in MVR technology that allow for the use of the Hadwaco process for treatment of metal finishing wastewater. These include more robust compressor screw designs, new inexpensive materials for heat exchanges to better collect low grade heat, and new evaporator designs with improved scale control. Advantages for the environmental arena are 1) extreme purity of distillate, 2) concentration of all non-volatile components and 3) recovery of solids for recycle or disposal. The process allows for design of nearly complete recycle of process water. Potential disadvantages are high maintenance and operations costs, corrosion control, scaling, and cooling water availability.

In the follow-up to the Concurrent Technologies (2001) test plan, Gallerani, Brown, and Moore (2002) reported test results at a copper finishing plant producing 116,600,000 liter/year (734,000 bbl/yr) wastewater. Influent to the MVR during the test period ranged from 600 to 2,600 mg/l TDS. Distillate recovery exceeded 95% of the influent. Copper and sulfate capture exceeded 98%, allowing recovery of 23,900 kg (53,600 lb) copper metal per year. The energy use for generated distillate was 13.9 kWh/1000 liters (6.3 kWh/bbl).

Veil (2008) presented a cursory evaluation of the Aqua Pure MVRs at the Devon Energy water reclamation facility in Decatur, Texas. This site (also called the "Maggie Spain Facility" which is the subject of the present report) treats flowback water and process water from Devon's shale gas wells located at multiple well fields in Denton County. A general flowchart of the process was presented by Veil (2008) but previous literature has been limited in the amount of performance data that has been available on MVR units treating shale gas brines. This report is aimed at presenting performance information that addresses this information gap.

4 Maggie Spain Facility

The sections to follow in this report provide a more detailed description of the Maggie Spain process train and its performance during a 2-month period when samples and measurements were taken to characterize mass and energy flows throughout the entire treatment system. The Maggie Spain Facility is comprised of an influent impoundment and a water preconditioning train followed by multiple mechanical vapor recompression (MVR) modules. The MVR's are operated in parallel to generate a demineralized product water stream and a concentrate stream. The diluate, representing >70% of the water flow is discharged to a product water impoundment. The concentrate, representing less than 30% of the water flow and greater than 90% of the TDS is collected in effluent storage tanks for future disposal. Figure 1 shows a schematic of the entire Maggie Spain treatment facility incorporating the MVRs. This diagram shows the locations in the flowsheet where water samples were taken for analysis (sampling twice weekly). Analyses included conductance, total organic carbon, BTEX (benzene, toluene, ethyl benzene, and xylenes), TPH (total petroleum hydrocarbons), total heavy metals, total dissolved solids (TDS), suspended solids, pH, alkalinity, sulfate, total ammonia, and phosphorus.

All of the energy required by the facility is supplied by natural gas that is provided by the shale gas wells of Devon Energy. The electricity required for pretreatment, and general site needs is supplied by two natural gas driven generators (Photo 1). Each NOMAD MVR skid is powered by an internal combustion engine fueled by natural gas (each engine capable of delivering up to 700 hp). Total energy demand measurements were obtained from daily readings of the natural gas utilization at the facility.

4.1 Preconditioning

For the preconditioning portion of the facility, the treatment objective is to provide suspended solids removal, oil & grease control, iron removal, and calcium-stable water. Water is delivered daily by truck at a rate of approximately 4,000 to 6,000 bbl/d to a 1.4 acre storage reservoir (Photo 2). The chemical analysis of the water leaving the reservoir, (representing influent water to the clarifier) is presented in Table 1. The average total dissolved solids are about 50,000 mg/l. The raw water contains a number of scale forming cations, including calcium, iron, strontium, magnesium and barium. Small amounts of total petroleum hydrocarbons and BTEX are also present.

Photo 1: Gas Driven Generator

Photo 2: Influent Storage Reservoir

Table 1: Influent and Post Clarifier Water Analysis

All units (mg/l) except pH And Conductance (mS/cm)	Influent Water			Post Clarifier		
	Average	Median	Standard Deviation	Average	Median	Standard Deviation
Specific Conductance	55,835	55,650	24,890	57,989	61,050	24,243
Total Dissolved Solids	49,550	44,900	10,959	49,133	46,900	9,921
Total Suspended Solids	1,272	357	3,443	140	132	45
pH	NA	6.9	6.7 - 7.7	NA	3.7	3.1 - 4.6
Alkalinity	405	385	126	12	4	14
Total Organic Carbon	42	12	118	10	9	5
TPH*	388*	19	1,363	5	4	2
BTEX	3.3	2.9	1.4	2.3	2.1	0.8
Ammonia	84	84	26	81	84	24
Sulfate	309	316	153	221	205	123
Phosphorus	3	3	2	2	2	1
Barium	15	7	19	13	6	17
Boron	17	18	4	16	16	3
Calcium	2,916	2,570	975	2,876	2,705	922
Iron	28	27	10	3	2	3
Lithium	12	11	3	12	11	3
Magnesium	316	291	131	319	296	114
Potassium	484	296	524	504	349	494
Sodium	10,741	10,700	3,622	12,400	12,100	2,821
Strontium	505	467	182	528	483	161

Note(*) TPH data overwhelmed by a single event of 5,893 mg/l.
The TPH average is 38 ± 43 when this event is disregarded.

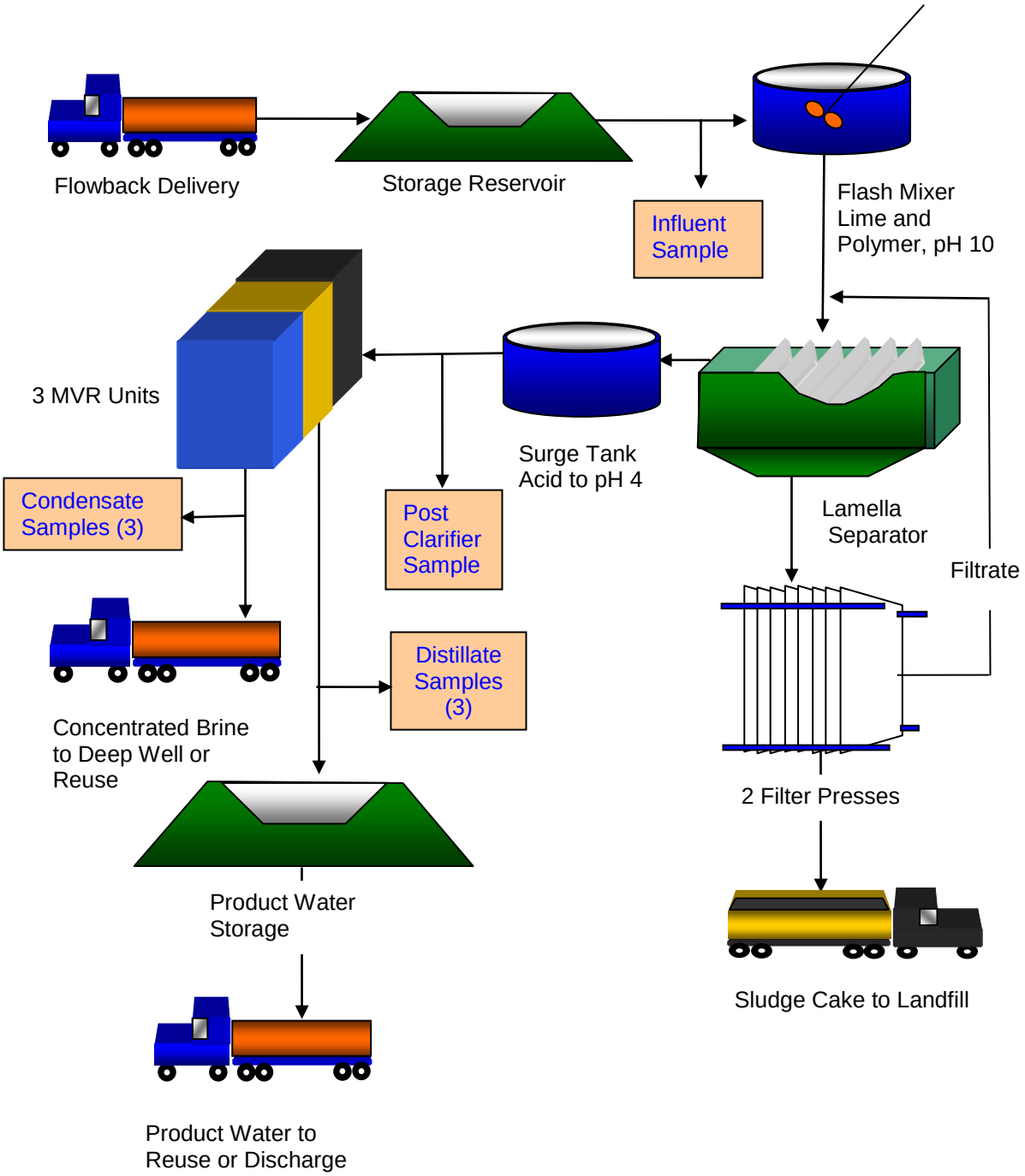

Figure 1: MVR Process Flow Sheet, Maggie Spain Facility

Photo 3: Flash Mixer and Clarifier

Photo 4: Flash Mix Caustic Addition

Photo 6: Details of the Lamella

Photo 7: Filter Presses & Tote

Water from the storage reservoir is sent to a process unit containing a flash-mix chamber and a lamella clarifier (Photo 3). Caustic (NaOH) is added at the flash mixer (Photos 4 and 5) to increase in the pH of the water to about pH10. The shift in pH causes much of the iron to precipitate. Polymer is occasionally added to aide in the coagulation of the solids.

Precipitated iron and other suspended solids are removed across a lamella plate clarifier (Photo 6). The clarifier removes about 90% of the suspended solids, including 90% of the influent iron. The chemical analysis of the post clarifier water is presented in Table 1.

Photo 5: Chemical Storage Facility

The solids from the clarifier are dewatered with a pair plate and frame filter presses (Photos 7 and 8). The solids contribution from the clarifiers to the filter is about 2,500 dry pounds per day.

The cake solids produced (Photo 9) from the presses are about 20-25% dry matter, yielding a wetted solids stream of 10,000 to 12,500 pounds wet solids per day. A 20 yard tote is removed from the site about once per week. The solids are sent to a landfill.

Clarified water is sent to a surge tank where the pH is adjusted to pH 4 to stabilize the scale forming cations, such as calcium. The pH adjusted water is the feed to the MVR units.

Photo 8: Plate and Frame Filter

Photo 9: Typical Dewatered Sludge

4.2 Mechanical Vapor Recompression

The Maggie Spain facility has three mechanical vapor recompression modules (Aqua Pure NOMAD systems) that are powered by natural gas, including the boiler that is used to bring the module up to temperature during startup and the 700 hp natural-gas-fueled internal combustion engine that drives the compressor. Electricity used for ancillary lighting, controls and data acquisition is supplied by one of the on-site generators (Photo 1). The footprint of the NOMAD facility is modest; a three NOMAD processing facility occupies an area of about 250' x 250' (about 1.4 acres). Each module (Photo 10) has a processing capacity of up to 2,800 bbl/d of influent brine.

Photo10: View of a Single Nomad

Photo 11: Pretreatment(L), Engine (C),

Each Aqua Pure NOMAD system consists of chemical conditioning plus three skids. 1) Pretreatment Skid; 2) Engine Skid; and, 3) Evaporator Heat Exchanger Skid. The chemical conditioning consists of anti-foam agents and corrosion control. The pretreatment skid provides 5μ bag filtration and pre-heating economizers. The engine skid houses a mechanical compressor. The evaporator skid (Photo 15) provides the liquid-vapor heat exchangers, evaporator tank, and distillate collection tank. A simplified process flow diagram for the Aqua Pure MVR is presented in Figure 2 (Razzaghi and Spiering, 2002).

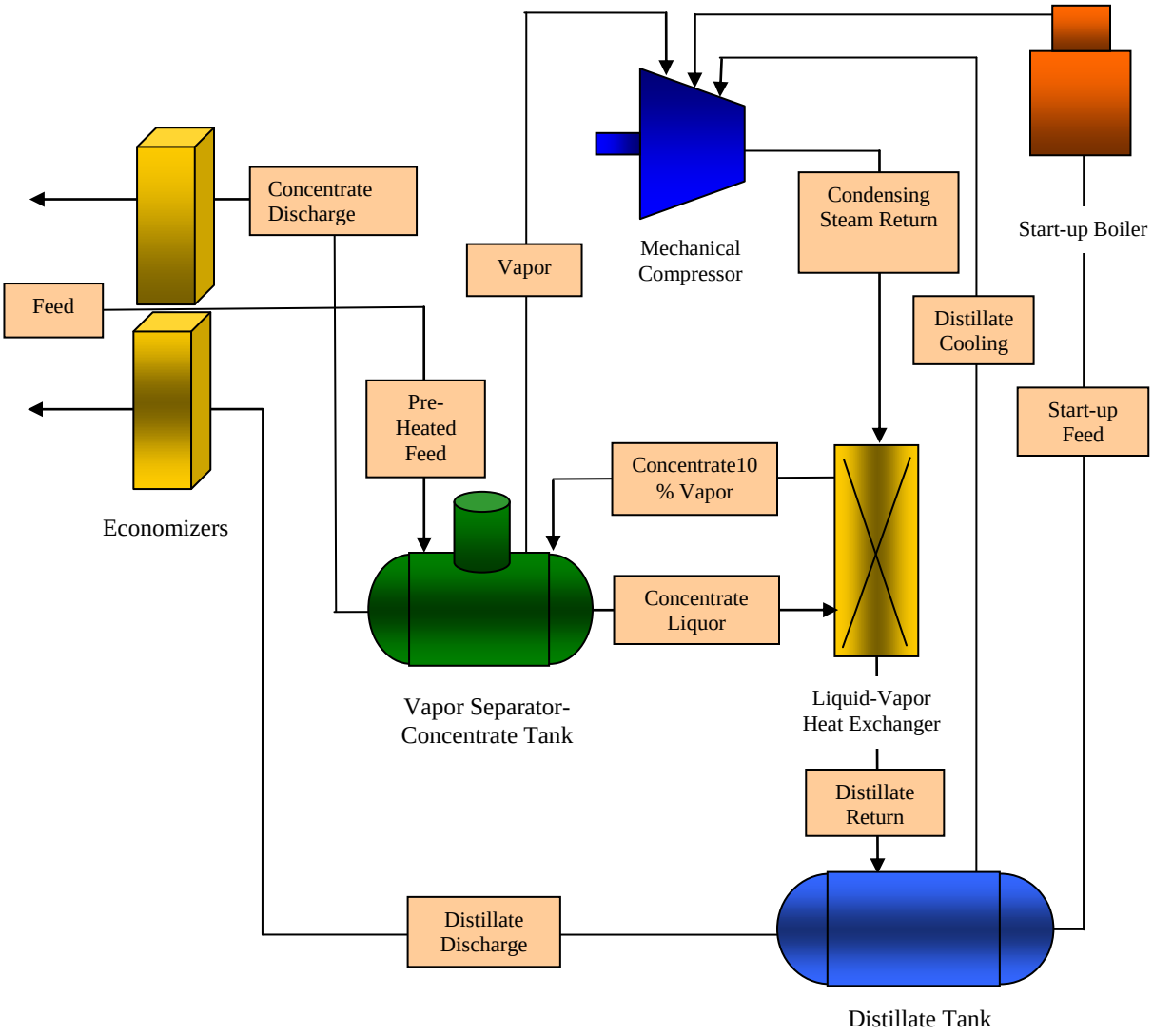

Figure 2: Simplified Flow Diagram for the Aqua Pure Mechanical Vapor Recompression Process

The process is initiated by heating a portion of water from the distillate collection tank with an auxiliary start-up boiler. When the process comes up to temperature, the boiler is extinguished.

The mechanical compressor (Photo 12) is fed a balanced mixture of vapor (fresh distillate) from the vapor separating concentrate tank and water (existing distillate) from the distillate collection tank. The compressor increases the fluid pressure creating a saturated vapor.

The saturated vapor enters a liquid/vapor heat exchanger (Photo 13) on the exchanger skid (Photo 14). The hot side of the exchanger is the saturated distillate vapor. The cool side of the exchanger is concentrated liquor fed from the vapor separating concentrate tank. The process is designed to vaporize about 10% of the concentrate liquor.

Photo 12: Compressor Engine Skid

Photo 13: Evaporator Plates

Photo 14: Evaporator Skid

The partially vaporized concentrate stream returns to the vapor separating concentrate tank. Vapor in this tank is the fresh distillate fed to the mechanical compressor in the continuing cycle.

When the distillate recovery tank is sufficiently full, or the concentrate stream reaches a preset conductivity, then a portion of the distillate and/or the concentrate liquor is discharged. The discharged liquids pass through independent economizers to recover some of the sensible heat in these streams.

The cool side of the economizers is the filtered feed and chemically conditioned water from the pretreatment skid (Photo 15). The preheated feed stock enters the vapor separating concentrate tank and becomes part of the concentrate/vapor distillate cycle.

Technology features of the Aqua Pure MVR system represent an innovative adaption of conventional MVR processing to the highly-aggressive nature of shale gas waters that are characterized by the high levels of scale forming constituents (such as calcium and barium). A detailed discussion of these features is provided in a recent SPE article authored by Aqua Pure staff (Horner, et al., 2011) (see Appendix).

4.3 MVR Process Evaluation Results

Maggie Spain process facility was monitored during a sixty day period during between June and August, 2011. Flow rates to each MVR and total natural gas utilization were measured daily. Water samples were collected twice weekly so that water chemistry data were obtained for eighteen of the sixty days. Chemical analyses included total dissolved solids, selected organic parameters, pH, and a broad range of cations. Summary data for influent to the MVR's were presented in Table 1 (clarifier effluent). Summary data for the effluent (distillate and concentrate streams) from the MVR's are presented in Table 2.

Photo 15: Anti-foam and Corrosion Control with Pretreatment Skid in Background

The purpose of the mechanical vapor recompression process is to produce salt enriched brine (concentrate) and salt-free distillate. Cursory examination of Tables 1 and 2 shows this goal was accomplished. The average influent water contained about 45,000 mg/l TDS, the distillate contained about 1,900 mg/l, and the concentrate contained about 168,000 mg/l.

Figure 3 is an example of TDS data for the influent, distillate and concentrate collected for Nomad No. 3 over sixty days. Data from the other two units was very similar (not presented). The overall performance of the MVR's appeared very uniform throughout the entire sampling period.

Table 2: Chemical Analysis of the Distillate and Concentrate Streams Combined Data from Three MVR's						
All units (mg/l) except pH And Conductance (mS/cm)	Nomad MVR Distillate*			Nomad MVR Concentrate		
	Average	Median	Standard Dev	Average	Median	Standard Dev
Specific Conductance	267	161	280	162,818	158,500	83,327
Total Dissolved Solids	171	103	179	168,465	162,000	29,239
Total Suspended Solids	9	4	12	617	519	319
pH	NA	10.7	10.5-10.9	NA	6.7	6.3-6.8
Alkalinity	263	248	85	162	143	73
Total Organic Carbon	22	16	17	12	12	4
TPH	4.6	4.0	2.3	4.3	4.0	1.1
BTEX	0.2	0.1	0.2	0.0	0.0	0.0
Ammonia	68	64	26	113	114	50
Sulfate	6	5	2	887	793	631
Phosphorus	0.1	0.1	0.2	7	6	8
Barium	0.1	0.1	0.0	27	5	48
Boron	0.4	0.4	0.1	63	62	13
Calcium	3.2	0.8	6.8	9,699	8,960	2,485
Iron	0.1	0.1	0.0	4	2	4
Lithium	0.1	0.1	0.0	42	38	11
Magnesium	0.4	0.1	0.8	1,132	1,055	355
Potassium	0.5	0.1	1.4	2,028	1,675	1,576
Sodium	14.3	3.6	31.6	41,302	39,000	8,046
Strontium	0.5	0.1	1.0	1,739	1,735	430
*Distillate Concentration calculated from Specific Conductance						

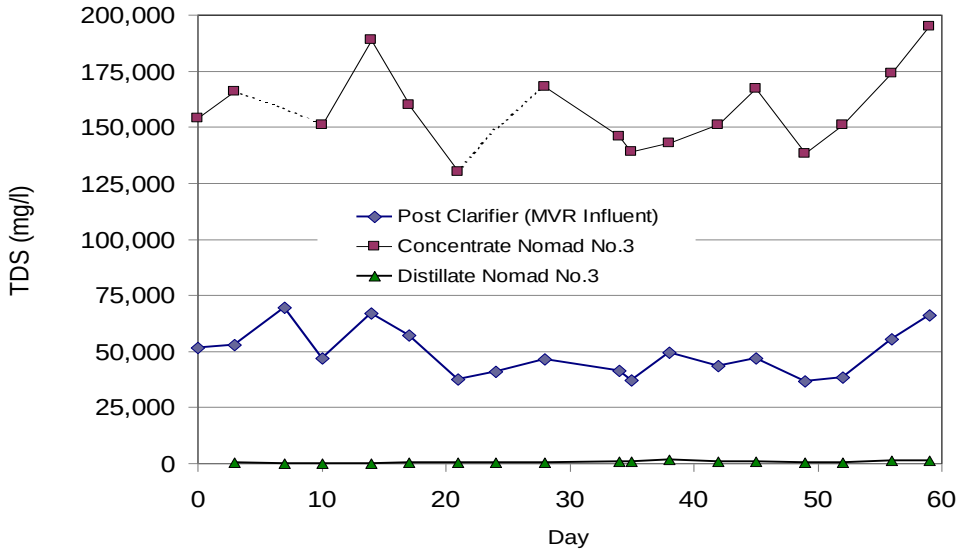

Figure 3: Daily Operation Data for Nomad #3

The overall water balance for typical operation was generated by examining distribution of water between the distillate and concentrate of the individual MVR units. Figure 4 is a plot of distillate and concentrate volume versus the volume fed to each unit. The slope of each line represents the fraction of the influent recovered. The MVRs, as operated in this process period, generated 72.5% distillate and 27.5% concentrate.

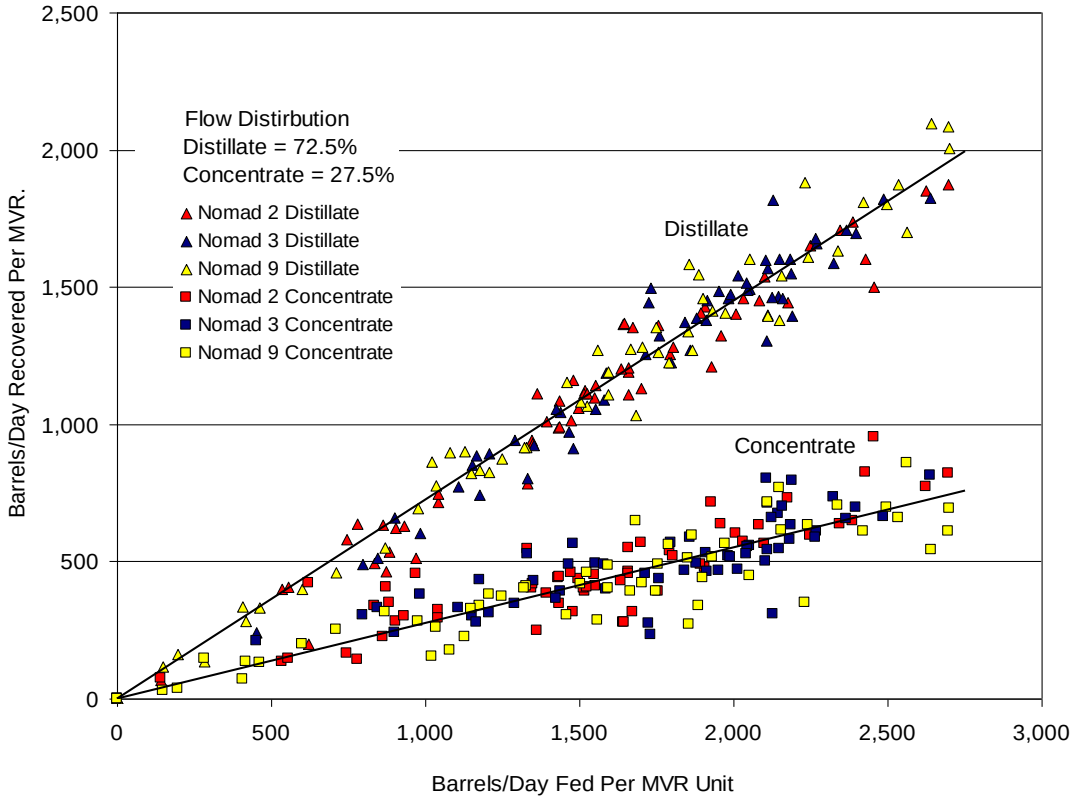

Figure 4: Water Distribution between Distillate and Concentrate During 60 Day Sample Period

The overall salt balance for typical operation was generated by examining the distribution of TDS between the distillate and concentrate of the individual MVR's. This evaluation is presented in Figure 5. The slope of each line represents the fraction recovered in that process stream. The plot shows that the concentrate reliably contains 99.75% of the total salts while only 0.25% remains in the distillate.

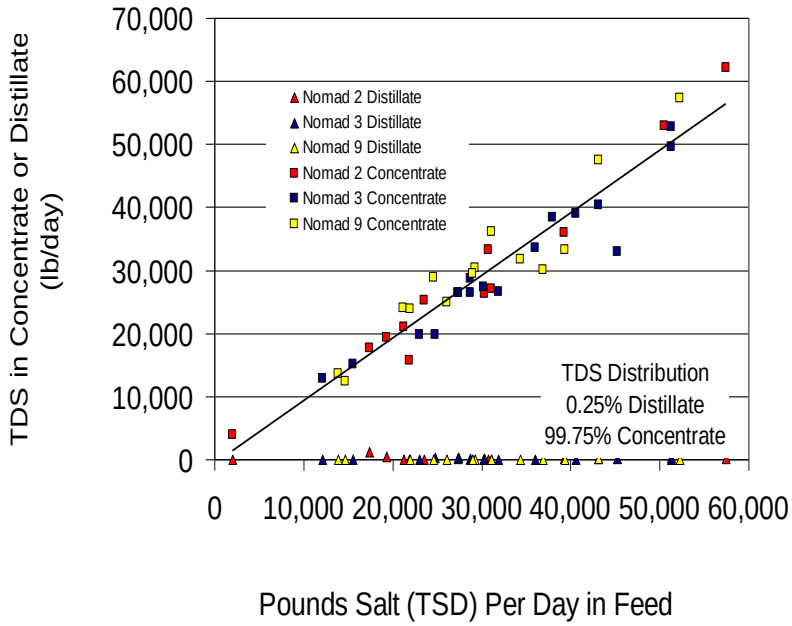

Figure 5: Distribution of Dissolved Salts between the Distillate and the Condensate Streams During 60 Day Sample Period

4.4 Energy Utilization

Total daily natural gas consumption (SCFD) was measured for the entire Maggie Spain facility. Since energy consumption represents natural gas use for the entire plant, characterizing natural gas demand for individual MVR units becomes challenging; for this reason, total natural gas demand was plotted as a function of overall influent loading and product water yield to determine the overall energy requirement for the facility (including MVR operation plus electricity generation). Figure 6 is a graph of total SCF gas utilization as a function of treated water or distillate generated. The plots appear linear with respect to either total volume of water treated, or the volume of distillate produced. The slopes of the lines in this plot indicate that the process requires about 48 SCF/bbl influent or 60.5 SCF/bbl distillate produced above the base loading. Some of the scatter in the data is inevitably due to other process loads on the generators, such as drive motors and hydraulic pumps on the clarifier and filter press skids, site lighting, and miscellaneous office and maintenance activities. The raw gas numbers also include inefficiencies in electricity generation and transmission. Assuming that the field efficiency of the gas generators is about 35% to produce the required electricity, then the value of 60.5 SCF/bbl distillate is equivalent to 6.4 kWh/bbl distillate. This is convincingly within the range of results reported for electrically driven MVR's (Letterman, 1983; Gallarani et. al., 2002). If the apparent base load is added to the incremental processing energy requirements, the overall treatment requires 72 SFC per barrel treated, or 100 SCF per barrel distillate produced.

Some of the scatter in the data is inevitably due to other process loads on the generators, such as drive motors and hydraulic pumps on the clarifier and filter press

skids, site lighting, and miscellaneous office and maintenance activities. The raw gas numbers also include inefficiencies in electricity generation and transmission. Assuming that the field efficiency of the gas generators is about 35% to produce the required electricity, then the value of 60.5 SCF/bbl distillate is equivalent to 6.4 kWh/bbl distillate. This is convincingly within the range of results reported for electrically driven MVR's (Letterman, 1983; Gallarani et. al., 2002). If the apparent base load is added to the incremental processing energy requirements, the overall treatment requires 72 SFC per barrel treated, or 100 SCF per barrel distillate produced.

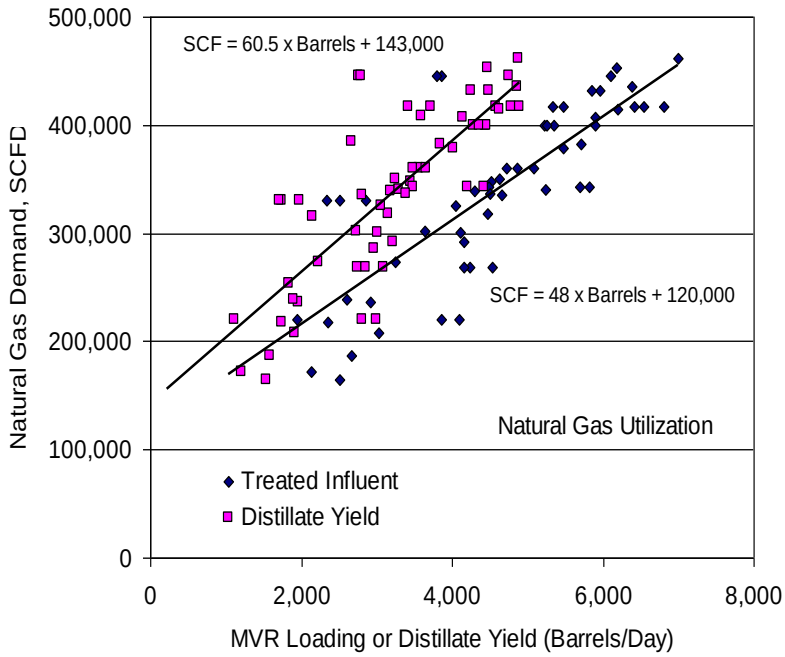

Figure 6: Daily Natural Gas Demand Versus Influent Loading and Distillate Product Yield (Composite of Three

4.5 Fate of Various Chemical Constituents

The following six figures summarize the fate of important environmental constituent at various points in the Maggie Spain pretreatment and MVR processing. Data for these figures were generated from Tables 1 and 2.

Figure 7 re-examines the overall fate of total dissolved solids. The storage reservoir and clarification have no affect on TDS concentrations. The MVR's concentrate the TDS, removing most salts from the distillate stream.

Figure 8 is a summary of the fate of calcium, magnesium, and strontium. These are potential scale forming components. This figure shows that the fate of these compounds is similar to that of the total dissolved solids. The storage reservoir and clarification have no affect on calcium, magnesium, and strontium concentrations. The MVR's concentrates these cations and removes them from the distillate stream.

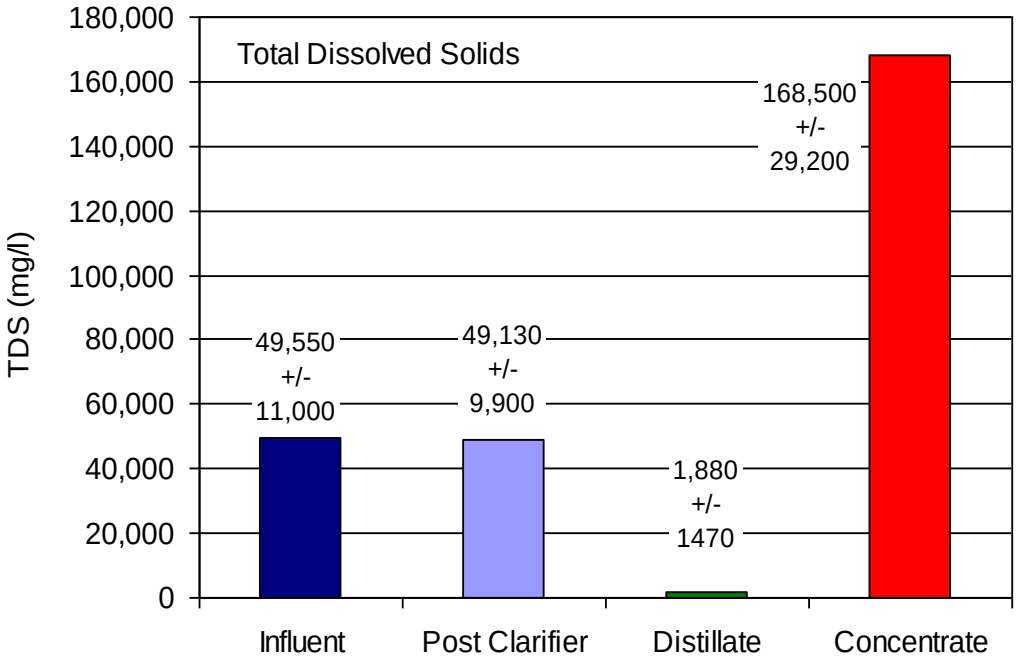

Figure 7: Fate of Total Dissolved Solids in the Maggie Spain Facility

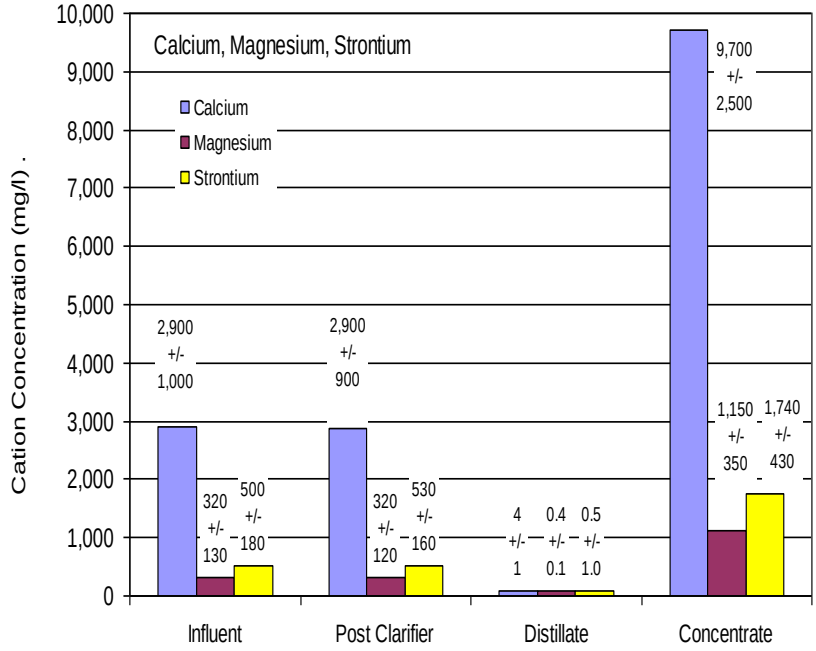

Figure 8: Fate of Calcium, Magnesium, and Strontium in the Maggie Spain Facility

Figure 9 is a summary of the barium, boron, and iron in the water. Barium and boron follow the familiar trend for TDS and are similar to calcium, magnesium, and strontium.

The pretreatment has little affect, and the ions are captured in the MVR condensate stream. Iron, however, is precipiated by the initial caustic addition in the rapid mix tank and much (90%) is removed by the clarifier. Any remaining iron is prefferentially removed in the MVR condensate.

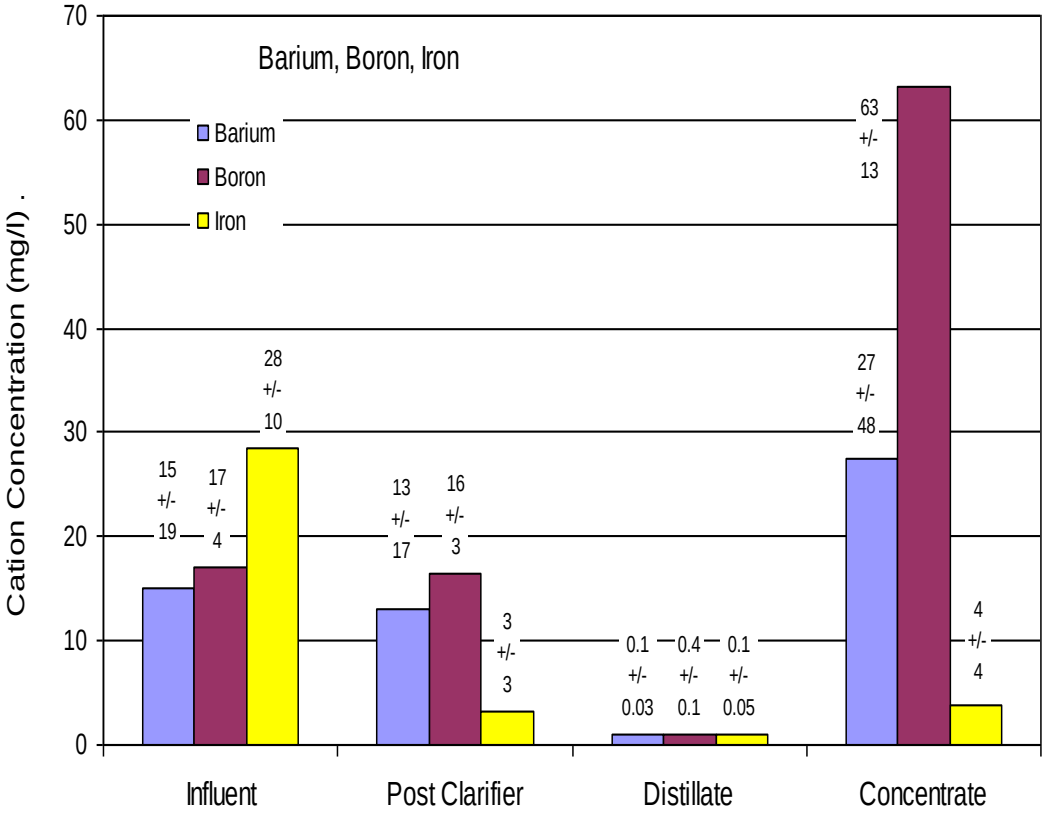

Figure 9: Fate of Barium, Boron, and Iron in the Maggie Spain Facility

Suspended solids removal data are reproduced in Figure 10. About 90% is removed by the clarifier. The remaining suspended solids are removed to the concentrate stream. It is also possible that certain cations, such as barium and strontium, reach saturation equilibrium within the MVR concentrate stream and generate excess suspended material.

The fate total petroleum hydrocarbons (TPH) is apparently intimiately tied to the initial suspended solids (Figure 11). More than 84% is removed by clarification, and presumably is removed with the sludge cake from the filter press. Note that TPH data are overwhelmed by a single event of 5,893 mg/l. The TPH average is 38 ± 43 when this event is disregarded. Figure 11 presents the amended value of 38 mg/l influent.

Total BTEX (benzene, toluene, ethylbenzene, and xylene) represents a volatile fraction of the organic matter in the water stream. Some (30%) of the BTEX is removed between the

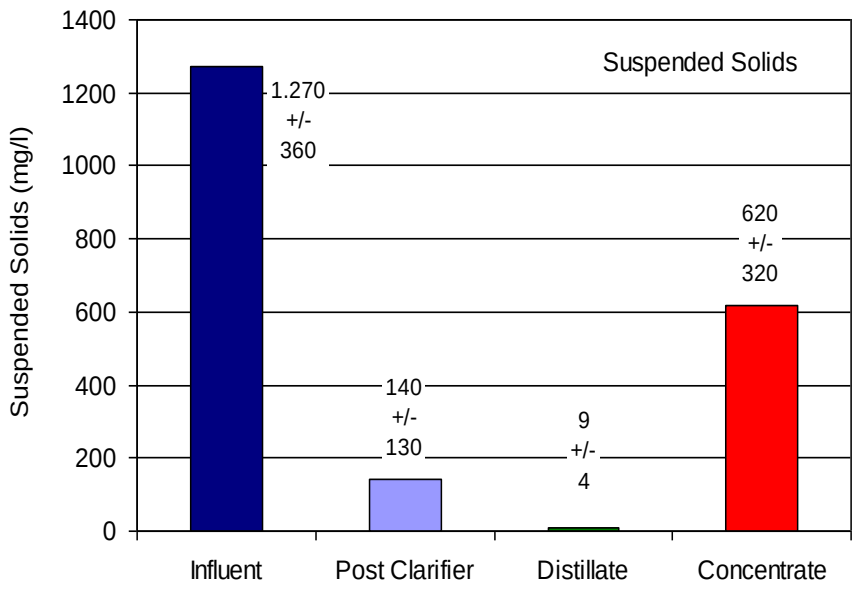

Figure 10: Fate of Suspended Solids in the Maggie Spain Facility

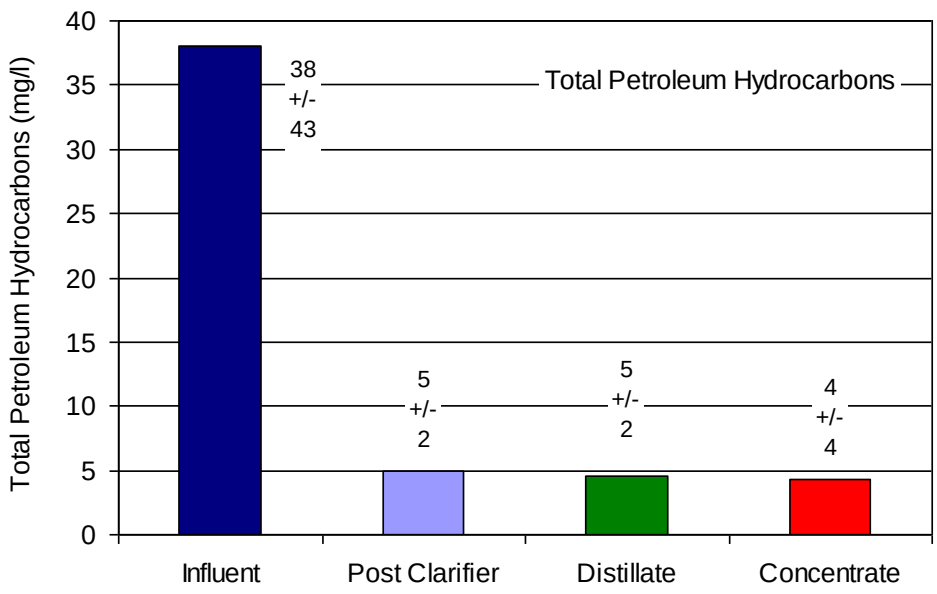

Figure 11: Fate of Total Petroleum Hydrocarbons in the Maggie Spain

influent and the end of the clarification process. Presumably, much of this removal occurs at the rapid mix tank from suface volatility. Much of the remaining BTEX is removed (additional 90-95%) in the MVR process. It is likely that this organic component is volatilized and expelled at degassing or pressure relief valves throughout the separator tank. Notably, the remaining BTEX is prefferentially found in the distilate, indicating that these volatile compounds remain with the vapor side of the MVR process.

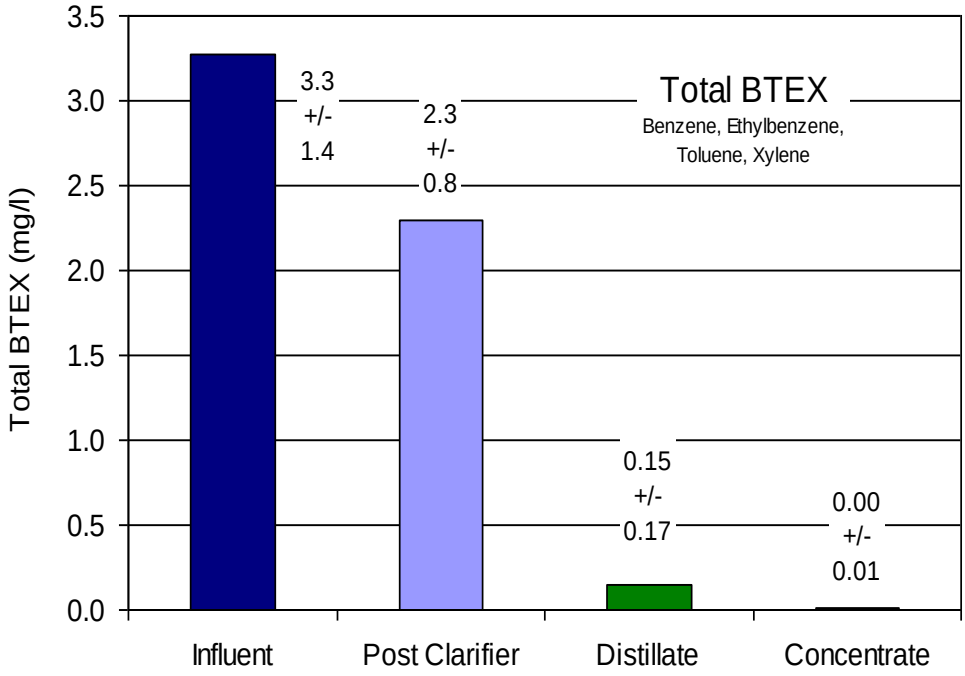

Figure 12: Fate of Total BETEX in the Maggie Spain Facility

5 Discussion

Mechanical vapor recompression has been touted as an attractive alternative for the treatment of various wastewaters, expecially when water or other resource recovery is paramount. This is the case in most Barnett well fields, where fresh water is precious and deep well injection is at a premium.

The Maggie Spain facility discussed in this report is an excellent example of the MVR process as it pertains to the shale gas industry. All unit processes are mobile and can be operated on natural gas, an obvious advantage in a natural gas field. A case-in-point, this facility was moved to a new location prior to the completion of this report.

Advantages of the process are obvious from perusal of the analytical data. Most constituants of interest, including trace organics and multivalent metals, are effectively removed either in pretreatment, or in the distillation process. The distillate is sufficiently pure to be reused in place of fresh process water, or could be discharged to a receiving stream with little or no additional conditioning. The concentrate volume represents less than 28% of the original volume, resulting in lowered ultimate disposal costs.

One disadvantage of the process is the production of solid waste generated from the clarifier solids. This requires some operational expertise and maintenance time, plus additional landfill costs.

The overall treatment (entire facility) requires 72 SFC per barrel treated, or 100 SCF per barrel distillate produced. MVR costs are more difficult to detail from the data as collected. However, best-fit correlations indicate that there is a base natural gas load to the facility requiring 120-140 thousand SCF per day. Energy need per incremental barrel of treating influent water and per barrel of distillate generated was estimated to be 48 SCF

and 60.5 SCF, respectively. Assuming 35% efficiency of electrical power generation from natural gas, the energy requirement is about 6.4 kWh/barrel distillate. The Maggie Spain Facility energy demand in the processing of shale gas waters appears to be as favorably low as the most efficient MVR processing cited in the literature for the treatment of far less aggressive waters in terms of organics and scale forming constituents.

Distilled water recovery averaged 72.5% of the influent to the MVR's. The influent total dissolved solids (TDS) fed to the MVR's averaged just under 50,000 mg/l. The water recovery measured by this evaluation is very close to the 74% water recovery predicted by the AquaPure performance literature that graphically presented in Appendix B.

5.1 Economics

As with the implementation of many water treatment processes, the "per-barrel" pricing for shale gas water treated in the mechanical vapor recompression water reclamation facility depends upon setting and a number of factors (e.g. overall water quality, average salinity of feed waters, actual deliveries of water versus capacity, year-by-year projection of flowback and produced water deliveries, etc.) that affect the efficiency and nature of the operation.

Fountain Quail pioneered shale gas water recycling in the Barnett Shale alongside some of the earliest pioneers in shale gas development. Devon Energy acquired Mitchell Energy and George Mitchell is recognized as the spark that ignited the explosive shale development in North America. As such, Fountain Quail had the privilege of working with some of the founding pioneers behind the development of the Barnett Shale as a commercial gas field. The ability to adapt and react to the changing needs of this rapidly developing new industry is critical.

In order to make recycling cost competitive to disposal in the Barnett Shale, recognized as one of the lowest cost shale plays for disposal, Fountain Quail evaluates each and every cost associated with recycling in an effort to reduce costs and increase efficiency. As such, Fountain Qail often reduces the chemical costs and increase the cleaning frequency if this allows a lower cost of operation. A very practical "oilfield-type" approach to recycling as been enacted: the equipment must be rugged, durable and easy to clean. One cannot afford to complain to the customer when an upset occurs (unexpected water composition, etc). The name of the game is to get back operational quickly. The equipment is designed with this in mind. For example, compressor efficiency was sacrificed by intentionally selecting a low speed engine-driven compressor which is very rugged and durable.

Continuous improvement has also been made. If a certain piece of equipment (e.g. pump) causes significant downtime, it is replaced with a different design so that the overall runtime and efficiency of the system is improved. By remaining competitive in the Barnett Shale, Fountain Quail has developed a wealth of experience and knowledge that has allowed the company to expand into the Marcellus and Eagle Ford shales with NOMAD technology. For example, a new TSS-removal system called the ROVER has been developed, which is able to clean up brine for re-use where customers do not require fresh (distilled) water. The design for the ROVER is based on all the years of testing and trials of different equipment with Devon Energy in the Barnett Shale. Fountain Quail maintains

that recycling must be simple, rugged, proven and cost-effective. ROVER treatment is generally <$1/bbl and NOMAD treatment can be from $3 to $5/bbl, including labor, chemical and equipment.

6 Summary

This report is part of an overall effort to advise and support the natural gas industry in the evaluation and selection of treatment equipment and processes for the treatment and reuse of water used and generated by the industry.

This report presents process data on a commercial-scale (6,000-6,800 bbl/day) mechanical vapor recompression distillation (MVR) processing plant treating shale gas hydro-fracture flowback and produced water in North Central Texas (Barnett shale region). Process data were collected during a 60 day period during summer 2011.

The pretreatment at this plant included caustic addition and clarification for total suspended solids and iron control. Pretreated water was distilled with three Aqua Pure MVR units, each rated at 2,000-2500 bbl/day.

Distilled water recovery averaged 72.5% of the influent to the MVR's. The influent total dissolved solids (TDS) fed to the MVR's averaged just under 50,000 mg/l. More than 99% of the TDS was captured in the concentrate stream. The distillate averaged about 171 mg/l TDS.

The fate of multivalent cations, total petroleum hydrocarbons (TPH), and BTEX) was followed. Most of the iron (90%) and TPH removal (84%) occurred in the clarification step. The removal of iron, magnesium, calcium, barium, and boron from the distillate exceeded 99%. BTEX removal from the distillate exceeded 95%.

The overall treatment (entire facility) required 72 SFC per barrel treated, or 100 SCF per barrel distillate produced. Best-fit correlations between treated water and distillate production versus natural gas utilization indicated that there was a base power load throughout the facility of about 120-140 thousand standard cubic feet of gas per day. Incremental power requirements above the baseline were approximately 48 SCF per barrel influent water treated (or 60.5 SCF per barrel distillate produced).

A new TSS-removal system called the ROVER has been developed, which is able to clean up brine for re-use where customers do not require fresh (distilled) water. Fountain Quail maintains that ROVER (suspended solids removal) treatment is generally <$1/bbl and NOMAD treatment can be from $3-$5/bbl (distillation by mechanical vapor recompression), including labor, chemical and equipment.

References

1. Becker, F.E., and Zakak, A.I., (1985). Recovering Energy by Mechanical Vapor Recompression, Chemical Engineering Progress, Vol. 81, no. 7, pp. 49-53.
2. Concurrent Technologies (2001). Environmental Technology Verification Program for the Metal Finishing Pollution Prevention Verification Test Plan for the Evaluation of Hadwaco MVR Evaporator for the Metal Finishing Industry, U.S. EPA Testing and Verification Program (CR826492-01-0).
3. Drewes, J. (CSM). 2009. An Integrated Framework for Treatment and Management of Produced Water. RPSEA Report No. 07122-12.
4. Evaluation of Hadwaco MVR Evaporator for the Metal Finishing Industry. (2004). US EPA Testing and Verification Program (VR P2 01-04)
5. Gallerani, P.A., Brown,D., and Moore, G., Concurrent Technologies (2002).
6. Environmental Technology Verification Program for the Metal Finishing Pollution
7. Galusky, L.P. and Hayes, T.D. (2011). Feasibility Assessment of Early Flowback Water Recovery for Reuse in Subsequent Well Completions. RPSEA Report No. 08122-05.07. October.
8. Gaudlip, A.W., L.O. Paugh and T.D. Hayes. 2008. “Marcellus Shale Water Management Challenges in Pennsylvania.” Proceedings of the 2008 SPE Shale Gas Conference, Fort Worth, TX, November 16-18, Paper No. 119898-PP.
9. Horner, P., B. Halldorson, and J. Slutz. 2011. “Shale Gas Water Treatment Value Chain – A Review of Technologies, Including Case Studies.”, Proceedings of the 2011 SPE Annual Technical Conference and Exhibition, Denver, October 30 – November 2.
10. Leatherman, H.R.(1983). Cost Effective Mechanical Vapor Recompression, Chemical Engineering Progress, Vol. 79, no. 1, pp. 40-42.
11. Razzaghi, M., and Spiering, R., (2002). Mechanical Vapor Recompression Separation Process, U.S. Patent 6,375,803.
12. Veil, J.A., (2008). Thermal Distillation Technology for Management of Produced Water and Frac Flowback Water, Argonne National Laboratory, Water Technology Brief # 2008-1.

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Appendix A

Information from Fountain Quail and Aqua Pure on the Mechanical Vapor Recompression System

Horner, et al., 2011

SPE 147264

Shale Gas Water Treatment Value Chain - A review of Technologies, including Case Studies

Patrick Horner, P. Eng., Aqua Pure Ventures and Brent Halldorson, P.Eng., Fountain Quail Water Mgmt and James Slutz, SPE, Global Energy Strategies LLC

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Abstract

North American shale gas plays discovered over the past ten years contain an abundant tcf of natural gas, providing a long term, low carbon domestic energy source. Drilling and completing techniques developed in the Texas Barnett Shale over the past ten years have unleashed an unprecedented new shale gas industry across North America. The most effective completion technique is known as hydraulic fracturing (or "fraccing"), a process that involves injecting a large volume (60,000 to 140,000+ bbls) of fresh water underground to fracture the formation, increasing permeability and thus gas flow. After a frac is completed, a large portion of the frac fluid returns to the surface as "flowback" water which contains high concentrations of dissolved salts, frac chemicals, and formation minerals.

The costs and logistics of managing both fresh and flowback water in shale gas plays are problematic. Development of North America's shale gas resources will require well developed water management strategies that include the effective implementation of water recycling technologies. Treating flowback for re-use as frac fluid reduces the impact of key issues associated with shale gas water management including cost, truck traffic, water availability, and disposal availability.

Factors including salinity, residual frac chemicals (polymers), H_2S, NORM, carbonate scales, iron scales, and sulphate scales make the treatment and handling of flowback complex. The overall water management strategy is a function of water sourcing and disposal cost and availability, formation geology and how that impacts both flowback water chemistry and frac fluid compatibility, the regulatory environment, and the availability of commercialized and cost-effective technology.

This paper explores the challenges associated with treating shale gas flowback for re-use and evaluates the role and cost of available commercial technology. Cases studies of technology applications that have been used during the past seven years in major shale basins will be included.

INTRODUCTION

North American shale gas plays discovered over the past ten years contain an abundant tcf of natural gas, providing a long term, low carbon domestic energy source. Drilling and completing techniques developed in the Texas Barnett Shale over the past ten years have unleashed an unprecedented new shale gas industry across North America. The most effective completion technique is known as hydraulic fracturing (or "fraccing"), a process that involves injecting a large volume (60,000 to 140,000+ bbls) of fresh water underground to fracture the formation, increasing permeability and thus gas flow. After a frac is completed, a large portion of the frac fluid returns to the surface as "flowback" water which contains high concentrations of dissolved salts, frac chemicals, and formation minerals. The flowback water is highly variable and its composition is affected by factors such as the subsurface geology, the length of time the water has been in contact with the formation and the chemical composition of the frac water used. The costs and logistics of managing both fresh and flowback water in shale gas plays are problematic. Development of North America's shale gas resources will require well developed water management strategies that include the effective implementation of water recycling technologies. Water and the key role it plays in the development of non-conventional oil and gas reserves such as shale gas is becoming a very contentious public issue, particularly in light of the recent development of the Marcellus Shale in the northeast United States. This is emerging as a very important environmental issue for operators and indeed for the entire gas shale industry. By making the recovery of and beneficial re-use of a portion of the brackish produced water from these shales efficient and cost-effective, an environmental liability can be turned into an asset.

FLOWBACK OVERVIEW

Flowback is defined as the return of the fluid to the surface after a completion or frac job. The quality and quantity of the flowback is a function of a number of key factors: the quality of the initial source water used to make the frac fluid, the frac fluid chemical program, the formation geology, contact of the frac fluid with formation waters, and the time the fluid spends both underground and on the surface after the frac. The source water makes up over 99% of the total frac fluid and as a result impacts the quality of the resulting flowback. Components in the source water such as dissolved salts, minerals, organic material and/or bacteria will either return to the surface in the flowback or have the potential to react with the frac or formation chemistry. Chemical additives (primarily polyacrilaymide friction reducers in shale gas slick fracs) are another key component of flowback. The type and amount of chemical additives varies depending on the specifics of the geology and the completion strategy. The chemical additives used during fraccing are designed to remain dissolved in the frac fluid under a wide range of conditions and, as a result, return to the surface in the flowback. The formation geology is another key factor impacting flowback quality. The shale formations are a composite matrix of carbonate shale and salt crystals. During the frac operation, the frac fluid comes in contact with the formation geology and dissolves salt and formation minerals, returning these to the surface in the flowback. The amount of dissolved material in the flowback is a function of the formation geology and the length of time spent underground. The longer the flowback remains in the formation, the more contact it has with formation geology and, as a result, the more dissolved solids it will contain. The solubility of the formation is also a key factor impacting the amount of dissolved solids in the flowback. If the formation is in communication with an aquifer or other subsurface formation waters, the frac fluid will blend with this formation water. Formation waters in contact with shale gas formations typically have very high levels dissolved solids (>100,000 mg/L). Flowback from completions in contact with formation waters is generally higher in levels of dissolved solids and volume. Time is another critical factor impacting the quality of flowback. As discussed, the time spent underground increases the level of dissolved solids. After the flowback returns to the surface, time is also an issue as bacteria will start to grow resulting in the breakdown of organic material and if sulphates are present, can cause the formation of hydrogen sulphide (H_2S).

When the flowback returns to the surface it contains dissolved salts, dissolved minerals, residual frac chemicals, frac chemical degradation products, bacteria, suspended solids, normally occurring radioactive material, volatile organics, hydrocarbons, and ammonia. The concentration of these materials varies from play to play from well to well within the same play and from day to day on the same well. Average flowback compositions from the Fayetteville, Marcellus, and Barnett as as follows:

		Fayetteville	Marcellus	Barnett
Na	(mg/L)	5362.6	24445.0	12453.0
Mg	(mg/L)	77.3	263.1	253.0
Ca	(mg/L)	256.3	2921.0	2242.0
Sr	(mg/L)	21.0	347.0	357.0
Ba	(mg/L)	0.8	679.0	42.0
Mn	(mg/L)	0.5	3.9	44.0
Fe	(mg/L)	27.6	25.5	33.0
SO4	(mg/L)	149.4	9.1	60.0
HCO3	(mg/L)	1281.4	261.4	289.0
Cl	(mg/L)	8042.3	43578.4	23797.5
TDS	(mg/L)	15,219	72,533	39,570
S.G.		1.010	1.050	1.030

Flowback water is challenging to treat due to the high degree of variability, the high fouling potential and the wide range and concentration of key components. These fouling mechanisms can be broken down into the following five catagories:

Suspended Solid Accumulation

Residual suspended solids that are not removed in the pre-treatment system have the potential to settle at low velocity points or deposit on surfaces within the unit. Suspended solids can also precipitate (metal hydroxides, etc.) due to increases in temperature and concentration.

Organic Fouling

Organic material in the feed water, primarily polymers (friction reducer and residual flocculent) can precipitate with an increase in concentration and/or temperature. This material can deposit on surfaces and/or flocculate smaller suspended solid particles that wouldn't otherwise be a problem.

Carbonate Scale

The presence of calcium and carbonate in sufficient concentrations can cause $CaCO_3$ scale. The potential for $CaCO_3$ scale formation increases as temperature and concentration increase. Carbonate scales are generally white, chalky and acid soluble.

Sulphate Scale

The presences of sulphate and barium, strontium, and/or calcium in sufficient concentrations can cause $BaSO_4$, $SrSO_4$ and/or $CaSO_4$ scale. The potential for sulphate scales to form increase as concentration increases. Sulphate scales are generally white, hard or glass like, and acid insoluble.

Silica Scale / Deposition

Silica can precipitate out of solution and form solids in one of three ways: surface deposition (depositing directly to surfaces), bulk precipitation (colloidal particles collide to form larger particles), complexing (metal hydroxides bind with silica to form colloidal particles) and silica polymerization (silica molecules combine to form long strings). As silica fouling is greatly impacted by metal hydroxide precipitation, it's potential increases with temperature, concentration, and is highly impacted by pH. Silica deposits can range from quartz-like hard scale to slimly deposits (generally white, grey, green or brown - the colour can vary depending on the type of metal hydroxides involved). Silica deposits are generally partially soluble in either high or low pH solutions.

WATER MANAGEMENT DECISION FACTORS

An effective shale gas water management strategy is a balancing act between several key factors. Public safety is of paramount importance. There is no evidence to suggest that shale gas fraccing poses a risk to drinking or surface water contamination (assuming the well is properly constructed and cased), yet management of shale gas flowback on the surface

does present handling risks including spillage, potential vehicle accidents and the possible release of flowback into surface water as the result. More fatal work injuries result from transportation incidents than from any other event. Highway incidents alone accounted for almost one out of every four fatal work injuries in 2008 (U.S. Bureau of Labor Statistics, U.S. Department of Labor, 2010). Reducing the truck traffic associated with water hauling is the most effective way to reduce the risk of both accidents and the release of flowback to the environment. Water hauling truck traffic is also one of the greatest impacts to communities affected by shale gas development. The high level of truck traffic causes damage to existing road infrastructure (often not designed for heavy hauling), and can create high levels of traffic conjestion, pollution and dust. High truck traffic is often one of the greatest concerns for local communities and strategies that minimize traffic often improve the willingness of land owners and communities to cooperate with producers. The regulatory environment also influences how the overall water management strategy is put together. Regulations often dictate how much water can be stored on the surface, the type of containment needed for storage, the types of pipelines allowed (either temporary or permanent), and the rules around discharge and disposal. Environmental liability is another key concern. Spill related incidents related to the transportation and storage of flowback can be exteremly costly. Spill risk management is an important factor to take into consideration. Reducing the risk of flowback spills is a critical risk management objective. Clean-up of salt water spills, specifically in environmentally sensitive areas or near watersheds can be expensive. A management plan that reduces the potential for spills and releases will go a long way to reducing long term costs. Shared long term access to source water and disposal is also critical. Water and disposal sources often have sufficient supply in the early stages of field development but this demand increases as activity increases, and the collective water demand can often exceed the supply. Producers need to look at long term overall supply with respect to the collective demand of all water users in the area, including other producers, other industries, agriculture, and municipal water supplies. Water supply issues can become increasing complex in areas where competition for water sources is already high such as in arid climates, urban areas, or regions that require large volumes of water for industrial or agricultural use. Industrial or municipal waste water sources can often be used as source water for frac fluid with minimal treatment and facilities accepting flowback can be designed to accept other industrial waste which can reduce overall treatment costs and create more make-up water for re-use.

The quality of water used to develop the frac fluid and how this impacts well production is a critical factor in developing a water management strategy. Multivalent ions (Fe, Ca, Mg, Ba, Sr) and chlorides in the water can limit friction reducer effectiveness and drive up horsepower costs for the producer's frac pumping operation. The type and dose of friction reducer can be adjusted to accommodate for higher TDS water but at an added cost. Scaling tendency of the source water and/or poor compatability of source water with formation water, and/or poor compatability of re-use water with make-up water can result in scaling. The scaling can occur within the formation creating the potential for reduce permeability and ultimately reduced gas production. Scaling can also occur in equipment casing which can damage equipment or reduce the equipment functionality. Bacteria in the frac fluid can cause formation biofouling, reducing permeability and gas production. The presence of sulphate reducing bacteria (SBR) can form hydrogen sulphide (H_2S), making the well sour, creating safety issues and increasing overall costs. Metals in the water, specifically iron, can oxidize and form deposits, reducing permeability and gas production. Suspended solids in the frac fluid such as sand, silt, clays, and scale particles can lead to reduced permeability and gas production. As shale gas formations are a composite of carbonate shales and salt crystals, the use of low TDS frac fluid will increase dissolution of formation salts, potentially increasing reservoir permability and gas production. A qualitative understanding of the relationship between frac fluid water quality and long term well production is key to the cost / benefit analysis of the level of water treatment technologies encorporated into the water management plan.

TREATMENT OPTIONS

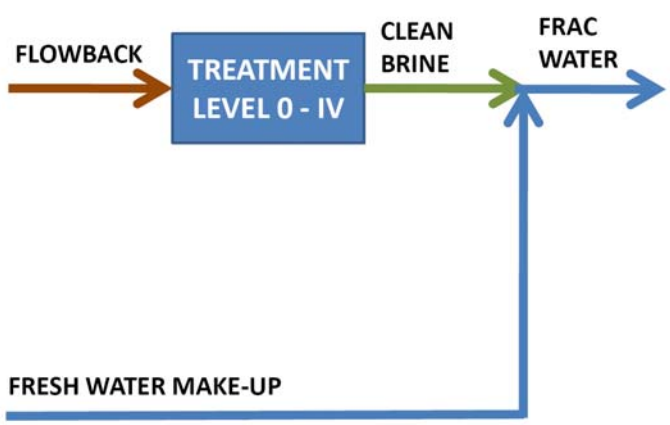
Flowback management strategies can be broken down into three key types: disposal, re-use and recycling. In disposal scenarios, fresh water is transported to site from available sources and flowback is transported to an injection well for disposal. The disposal scenario is often chosen if there is an inexpensive, abundant supply of fresh water nearby and nearby injection wells are able to handle the flowback disposal volumes. As fresh water availability decreases, costs increase and/or distance to injection wells for disposal increases, the disposal scenario becomes less appealing. Re-use strategies involve primary treatment of the flowback to remove suspended solids and soluble organics and then blending the treated water with fresh water to generate the frac fluid for a new well. Re-use strategies reduce the amount of fresh water required and can eliminate the need for disposal provided all of the flowback can be treated and re-used. Re-use is often the least expensive strategy, especially in areas with high disposal costs. Recycling strategies involve high level treatment of the flowback water producing a fresh water quality product. The recycled water is blended with make-up water from freshwater sources to generate a low TDS flac fluid. Recycling is used when fresh water costs are high or a high quality, low TDS frac fluid is desired or when other logistics (such as fraccing schedules) do not permit re-use strategies. Producers that transfer the frac fluid via temporary above ground pipelines (known as "fastlines") may choose the recycling option to minimize the potential environmental liability from a spill or fastline rupture.

The level of treatment required can vary depending on the quality of water required for frac fluid. Available levels of treatment as as follows:

REUSE TREATMENT	LEVEL 0 – No treatment, direct blending of flowback with make-up water.	TSS – No Change TDS – No Change 100% available for re-use
	LEVEL I – Basic TSS Removal.	TSS - < 25 mg/L TDS – No Change 100% available for re-use
	LEVEL II – Low Polish, basic TSS removal followed by media filtration.	TSS – Filtered to 5 um TDS – No Change 100% available for re-use
	LEVEL III – High Polish, basic TSS removal followed by membrane filtration.	TSS – Filtered to < 1 um TDS – No Change 100% available for re-use
	LEVEL IV – Selective Ion Removal, basic TSS removal followed by membrane filtration and ion exchange or nanofiltration.	TSS – Filtered to < 1 um TDS – Divalent ions removed as required 100% available for re-use
RECYCLE TREATMENT	LEVEL V – Distillation, basic TSS removal followed by MVR Evaporator (TDS removal).	TSS - < 10 mg/L TDS < 100 mg/L 60 to 90% Available for re-use
	LEVEL VI – Crystallization, basic TSS removal followed by MVR Evaporator and crystallizer (TDS removal) or direct fired evaporator.	TSS - < 10 mg/L TDS < 100 mg/L 100% available for re-use

TSS – Total Suspended Solids TDS – Total Dissolved Solids

RE-USE TECHNOLOGY



During an active hydraulic fracturing program, natural gas producers are faced with inconsistent flowback water containing total suspended solids (TSS) ranging from 100 to 3,000 ppm and total dissolved solids (TDS or Salts) ranging from 5,000 to 100,000 ppm. Recent legislation enacted in Pennsylvania, heart of the Marcellus play, requires a maximum TSS of 250 ppm with a maximum combined TSS/TDS of 500 ppm to obtain a new or expanded discharge permit for treated flowback. Aqua-Pure piloted and tested 12 individual technologies in the development of a robust and adaptable clarifier applicable to the wide spectrum of oilfield conditions. The re-use technology in Aqua-Pure's ROVER Mobile Clarifier has

been in continuous and successful operation for 6+ years with a major gas producer. The re-packaging of this technology has enabled a mobile unit aligning with the natural portability of oilfield services. Aqua-Pure's ROVER Mobile Clarifier consists of a low profile, clarification trailer and auxiliary support trailer. Flowback is pumped from the customers' source (frac tank, pit, etc.) into the unit via an adaptable location feed pump. Suspended solids and organics are precipitated from the solution using an adjustable chemical system. The solids settle to the bottom where they are collected and de-watered. Clean brine is pumped out of the system to a designated location specified by the customer. This mobile clarifier allows producers to recycle water on-demand, providing a powerful and flexible tool in managing oilfield operations. Capacity is 10,000 bbl/day of feed water. The unit is DOT approved for non-permitted transportation in the United States and Canada. Deployment of ROVER Mobile Clarification technology has many benefits for the industry. The direct costs associated with water transportation are significant and well documented. The social cost of water transportation, heavy truck traffic in often rural and small towns with limited road networks is an ongoing legal, public relations and insurance risk. Allowing water to be treated and recycled at or very near the wellhead reduces this impact by reducing water transportation needs. Availability, cost and the complex logitics of acquiring fresh water must be considered in the financial analysis of mobile clarification technology. Migration of the treatment process near the wellhead is quickly becoming an industry best practice and aligns closely with the risk management policies of many stakeholders.

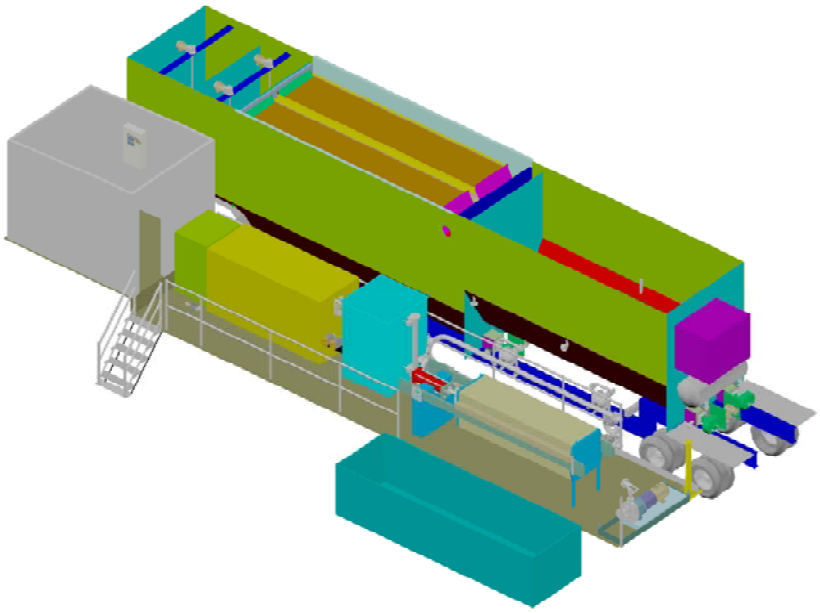
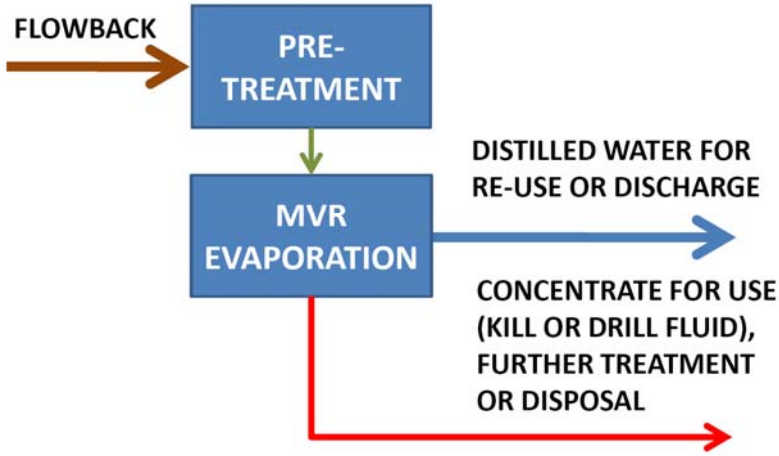


Figure 1. Aqua-Pure ROVER Mobile Clarifier

RECYCLING TECHNOLOGY



Recycling technologies for flowback generally include two main categories: (1) membrane-based systems, and (2) thermal (evaporator) systems. Membrane technologies have generally proven ineffective in shale gas flowback recycling to

date and are not discussed in detail in this paper. Membrane systems are most effective when treating water with consistent levels of specific contaminants. Variations in the type and concentrations of contaminants will cause these systems to fail, requiring frequent cleaning or recalibration. Increasing the energy efficiency of thermal evaporator systems reduces operating costs and carbon emissions. Increasing the utilization factor allows for better use of all associated resources, ensuring that the maximum volume of water is recycled for fixed capital and operating costs. This reduces costs on a per volume basis so that recycling operations are economically sustainable and able to grow to meet market demand. In 2003 Fountain Quail made contact with shale gas producers in the Texas Barnett field and began a search for solutions to managing shale gas water. Aqua-Pure Ventures ("Aqua-Pure") from Calgary (Canada) worked with Texas-based Fountain Quail Water Management ("Fountain Quail") to design the NOMAD 2000 - a mobile, modular version of Aqua-Pure's process patented Mechanical Vapor Recompression ("MVR") evaporation technology, specifically for operation in shale gas fields. The Aqua-Pure MVR technology was already in use for heavy oil applications at that time, and the NOMAD 2000 design built on Aqua-Pure's experience in handling oilfield produced water. Aqua-Pure eventually acquired Fountain Quail and established it as a service company based in Texas that owns and operates the equipment and charges producers for the water processed on a per volume basis. For the past seven years Fountain Quail has owned and operated its own equipment and used it in aggressive, high fouling water recycling applications. Fountain Quail monitored the performance and problems with the equipment designs and has made a series of design changes that have led to step improvements in both system efficiency and reliability. A high level of in-house knowledge has been accumulated on corrosion, metallurgy, scaling and fouling, water chemistry, process optimization, and innovative construction techniques. The NOMAD 2000 MVR Evaporator is a highly energy efficient process for producing distilled water from wastewaters contaminated with dissolved salts. Evaporative treatment involves boiling a solution such that contaminants remain in the liquid phase, while pure water vapor evaporates and can be condensed into distilled water. MVR evaporation differs from conventional evaporation in that a compressor is used to input the energy required to generate steam rather than a heat source such as a boiler. The high energy efficiency is achieved by utilizing the latent heat of the condensing steam as the primary energy source for boiling the wastewater. Conventional distillation requires 1,000 BTU/lb of steam, while MVR evaporation requires a theoretical 25 BTU/lb of steam produced. The energy input by the compressor for MVR evaporation is required to compensate for the difference in latent heat of vaporization between the boiling brine and condensing steam, heat losses in the pre-heat exchangers, and energy loss of the system to the environment. The NOMAD produces steam for approximately 50 to 75 BTU/lb (shaft input at the compressor). The NOMAD is designed to remove soluble dissolved salts from wastewater at the lowest possible energy cost while at the same time allowing for ease of cleaning and serviceability. Insoluble or sparingly soluble material such as oil, suspended solids, or mineral compounds suspected of forming high quantities of scale (that cannot be managed with inhibitors) must be removed prior to treatment with the NOMAD or fouling can occur, which reduces both the capacity and recovery efficiency of the unit.

A primary innovation of the Aqua-Pure technology involves circulating concentrate through the evaporator side of the evaporator exchanger. This circulating concentrate will contain a precisely controlled vapor fraction from 1% to 50%. With this controlled low vapor fraction, the concentrated fluid within the evaporator exchanger is subjected to an additional localized concentration factor of less than 1.1, avoiding localized precipitation of scaling compounds. As the vapor fraction increases while passing through the evaporator exchanger, the steam velocities increase significantly, reducing the risk of fouling. The temperature rise of the evaporating side of the evaporator exchanger is kept very low, resulting in low energy for compression. By adjusting the heat flux, the temperature of the wet surfaces for condensing and evaporating are maintained near that of the saturated steam condition. The type of boiling experienced will range from primarily forced convection to stable nucleate boiling of the wetted surfaces.

A secondary innovation of Aqua-Pure technology involves the use of a highly efficient specialized plate and frame heat exchanger. The plate type exchanger used offers a low, fixed static head and very low pressure drop on the concentrate circulating fluid or evaporating side, while providing a relatively high heat transfer coefficient. The heat flux can be easily adjusted by adding more surface area or plates in a given frame. The highly effective heat transfer coefficient allows the surface temperature to be very near to both fluid stream temperatures, reducing the risk of fouling. There are no hot or cold spots and no dead flow zones, which subsequently reduces the risk of fouling or scaling. The compact size can be provided cost effectively with exotic alloy plates (i.e. titanium) to resist fluid corrosion and stress corrosion cracking, common to desalination type evaporator applications. The compact size also allows for modular construction, reducing both overall size and capital cost.

The NOMAD system has the ability to process highly variable oilfield wastewater and return to the producer approximately 85% of the feed volume as distilled freshwater that can be re-used (Barnett Shale example). The NOMAD evaporator system is truly revolutionary. It is a system capable of addressing one of the greatest challenges of economically treating contaminated water that is the challenge posed by the variable nature and concentration of oilfield wastewater contaminants. In order to control the level of dissolved solids in the concentrated boiling fluid, a constant stream is drawn off. This is called concentrate. All of the dissolved solid contaminants that enter the system in the Feed water leave the system in

the concentrate. For example, a Feedwater stream consisting of dissolved solids (Sodium Chloride (NaCl) Salt) will produce a distilled water stream and a stream of concentrated Sodium Chloride.

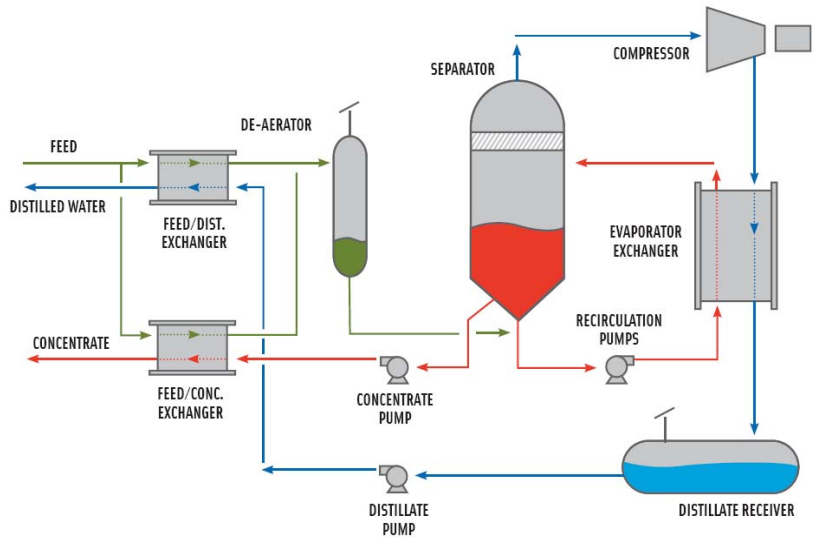


Figure 2. MVR Evaporator Process Flow

The Feedwater enters the NOMAD, breaks into two streams and flows through the Pre-Heat Exchangers. One Feedwater stream cross exchanges with the Distilled Water leaving the system and the other with the Concentrate leaving the system. Both the Distilled Water and Concentrate streams are very hot (near boiling) and transfer heat to the incoming Feedwater. The two hot Feedwater streams re-combine and pass through a De-Aerator. In the De-Aerator, dissolved gases (such as Carbon Dioxide) in the Feedwater are released and vented. The hot de-aerated Feedwater then enters the Recirculation Loop.

The Recirculation Loop consists of boiling Concentrate flowing from the Separator to the Circulation Pump to the Evaporator Exchange and back to the Separator. The Circulation Pumps transfer the hot Concentrate from the Separator up through the Evaporator Exchange. In the Evaporator Exchanger, a portion of the hot Concentrate is boiled into steam. A mixture of Steam and boiling Concentrate exits the top of the Evaporator Exchanger and flows into the Separator. Inside the Separator the Steam is separated from the boiling Concentrate. The Steam is drawn from the Separator with the Compressor. The Compressor boosts the pressure of the Steam and this causes the temperature of the Steam to go up. The high temperature, high pressure Steam is driven down through the Evaporator Exchanger. As the high temperature, high pressure Steam condenses into Distilled Water, it passes heat to the boiling Concentrate making it boil into Steam.

Hot Distilled Water flows from the bottom to the Evaporator Exchanger into the Distillate Receiver. The hot Distilled Water is pumped from the Distillate Receiver through the Feed/Distillate Pre-Heat Exchanger where it cools down, passing heat to the incoming Feedwater. The cool Distillate Water then exits the system and flows to the Distillate Pit. To prevent the Salt concentration from getting too high in the Recirculation Loop, a constant stream of boiling Concentrate is drawn from the Separator with the Concentrate Pump. The boiling Concentrate is pumped through the Feed/Concentrate Pre-Heat Exchanger where it cools down, passing heat to the incoming Feedwater. The cool Concentrate then exits the system and flows into the Concentrate storage tanks. Boiling water on the stove requires 1,000 BTU of energy to product 1 pound of Steam. MVR Evaporation uses a theoretical 50 BTU of energy to produce 1 pound of steam (5% of the energy of conventional evaporation).

The key to the success for the technology requires that the cost of treatment has to be less than the cost of disposal to make the technology viable. The success of the NOMAD technology is based on patented evaporator design allowing the unit to be portable, self sustaining and treating the water to allow reuse and recycle. Fountain Quail (Aqua-Pure) MVR Evaporators remain one of the only technologies operating in shale gas flowback recycling applications due to their high recovery efficiency and resistance to scaling and fouling. To date over 14,000,000 barrels of hydraulic fracturing flowack and produced waters have been recycled for re-use in the Barnett Shale. As other shale gas plays are being developed, Fountain Quail technology is being looked at as a leading example of effective shale gas water management recycling technology.

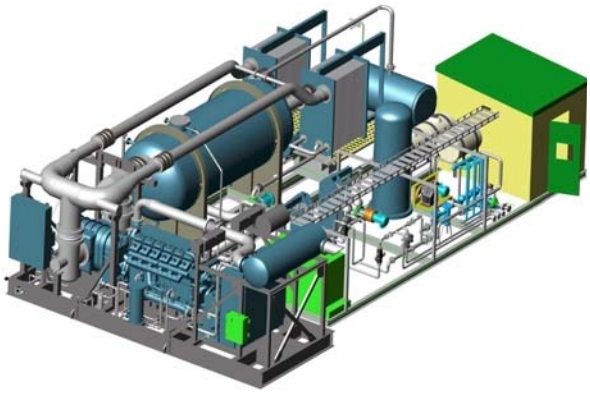


Figure 3. Aqua-Pure NOMAD MVR Evaporator

CASE STUDIES

FOUNTAIN QUAIL BARNETT SHALE RECYCLING FACILITY

Fountain Quail's Barnett shale recycling facility consists of a level V treatment system (Pre-Treatment + MVR Evaporators). The facility is set-up in an area with high drilling density in the immediate vicinity. The photograph below provies a good overview of the recycling logistics. Three well pads surround the recycling facility. Each well pad contains four horizontal wells (twelve in total between the three pads). Fresh water is pumped via fast line (aluminum irrigation pipeline) from a fresh water pit directly to the frac. After the frac is completed, flowback is returned to the flowback pit at the recycling facility via a temporary 3" poly pipeline. The flowback is processed to distilled water quality at the recycling facility and returned to the fresh water pit to be blended with make-up water for re-use. Locating the recycling facility this close to the operation drastically reduced the number of trucks required to move in fresh water and haul out wastewater for disposal. As transporation is generally the largest cost associated with water management, the proximity of the recycling facility helped reduce overall completion costs significantly. Fountain Quail has operated up to four concurrent recycling operations in the Barnett Shale with a combined capacity of close to 20,000bbl/d of flowback treatment.

Figure 4 – Fountain Quail Barnett Shale Recycling Facility with 2 NOMAD evaporators. There are 3 frac operations surrounding the facility.

EUREKA RESOURCES MARCELLUS SHALE RECYCLING FACILITY

Eureka Resources Marcellus shale recycling facility consists of a level V treatment system (Pre-Treatment + MVR Evaporators). Transporation to disposal is very expensive in the Marcellus shale due to the low availability of disposal wells. The Eureka facility is used to treat flowback to distilled water quality and discharge it to a municipal wastewater facility (POTW) that blends the distillate with treated municipal waste and discharges it to the river. The facility is located closer to the source of drilling than available disposal wells and as a result, reduces flowback transportation costs.

Figure 5 – Eureka Facility (Williamsport, PA) Utilizing Three Aqua-Pure NOMAD Evaporator Systems.

Aqua-Pure technology and solutions can be customized to meet a wide range applications and capacities.

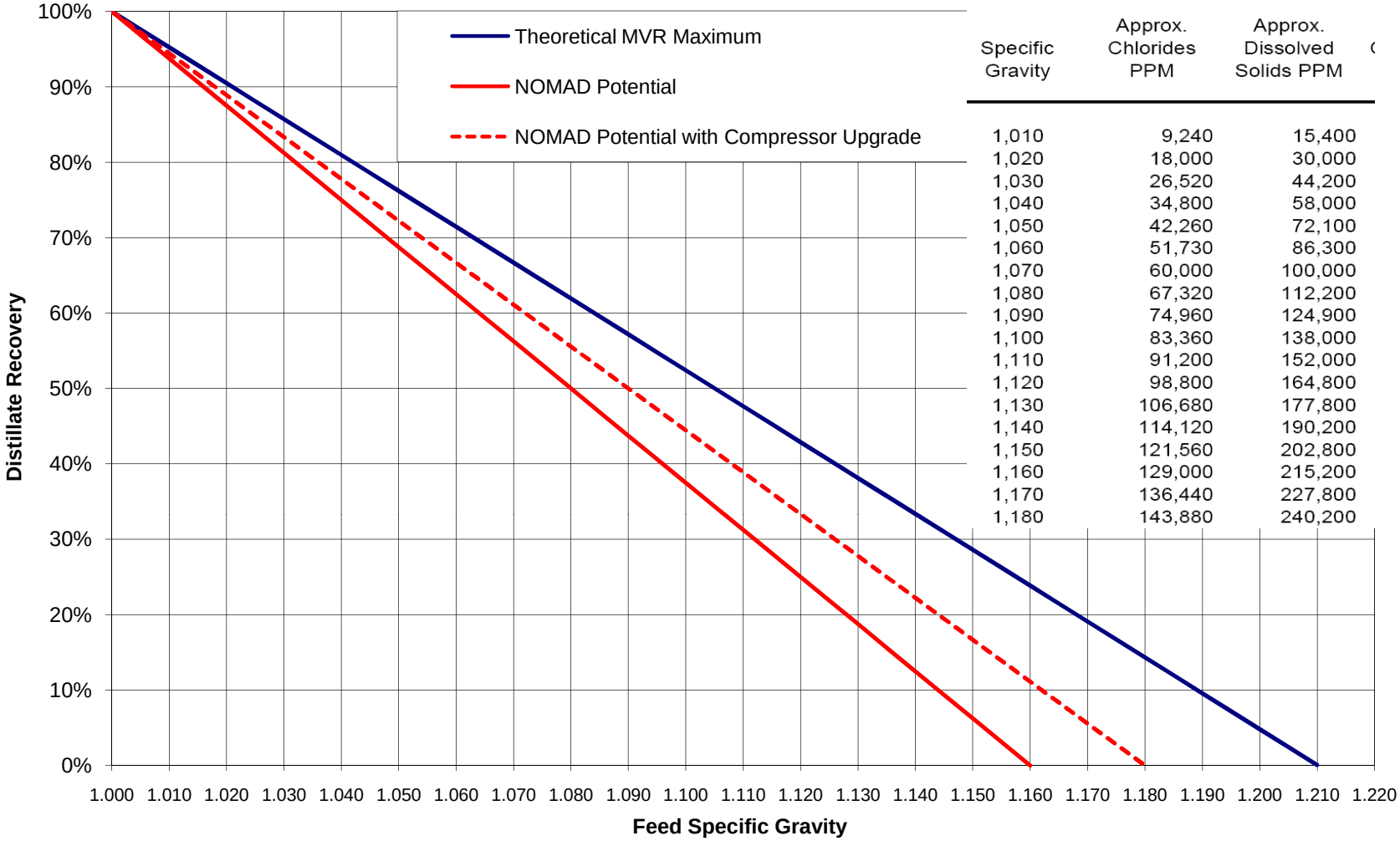
Appendix B

Graph from Fountain Quail and Aqua Pure on the Water Recovery Performance of the Mechanical Vapor Recompression System

Brent Halldorson, 2012

AQUA PURE
CLEAR SOLUTIONS

MVR Evaporator Revovery as a function of Feed Gravity for Oilfield Brine



Specific Gravity	Approx. Chlorides PPM	Approx. Dissolved Solids PPM
1,010	9,240	15,400
1,020	18,000	30,000
1,030	26,520	44,200
1,040	34,800	58,000
1,050	42,260	72,100
1,060	51,730	86,300
1,070	60,000	100,000
1,080	67,320	112,200
1,090	74,960	124,900
1,100	83,360	138,000
1,110	91,200	152,000
1,120	98,800	164,800
1,130	106,680	177,800
1,140	114,120	190,200
1,150	121,560	202,800
1,160	129,000	215,200
1,170	136,440	227,800
1,180	143,880	240,200