

Extraction of Sodium Chloride and Calcium Chloride From Oil and Gas Wastewater

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Abstract

Eureka Resources, LLC (Eureka) has developed a business model which gives oil and gas operators a sustainable choice for recycling oil and gas wastewaters that targets recovery of useable by-products. Eureka has been operating centralized oil and gas wastewater treatment facilities in Pennsylvania for 10 years and has optimized a model for sustainable treatment and recycling of oil and gas wastewaters. The model involves permitting, designing, constructing and operating comprehensive centralized wastewater treatment facilities focused on maximizing recovery and beneficial reuse of recoverable products (sodium chloride, calcium chloride, methanol, and lithium) and generation of freshwater effluent. There are many challenges associated with operating a centralized oil and gas wastewater treatment system with these objectives. This paper summarizes:

- The challenges/solutions and lessons learned during startup and shakedown of the various unit processes with a focus on the salt crystallization processes.
- Demonstrating that the salt quality generated by the crystallizer is equivalent to manufactured rock salt used for road deicing, and evaporated salt for commercial and industrial uses, etc.
- Establishing characteristics and market value for the concentrated calcium chloride brine purge generated by the crystallizer and the potential market for high purity calcium chloride prills, powder, and flakes.

Eureka has successfully completed a co-product determination for the salt (sodium chloride) generated by the crystallizer at our Standing Stone Facility in accordance with regulatory requirements in Pennsylvania. Eureka has also used this same data to complete multiple beneficial reuse determinations under PADEP guidelines in support of various industrial uses and commercially-salable pool salt.

Keywords: Oil and Gas Wastewater Treatment; Sustainable; Maximizing Recycle; Recoverable By-Products; Salt; Sodium Chloride; Calcium Chloride

Introduction

One of the most prominent of the Shale Basins in the US is the Marcellus Shale Basin – underlying large swaths of New York, Pennsylvania, Ohio, West Virginia, and Maryland. Due to scarcity of water resources as well as regulatory constraints and expensive treatment technologies, E&P companies in all shale basins must develop and implement innovative methods for re-use and adopt more localized and centralized water management systems. E&P companies in various shale plays across the US are now consistently seeking sustainable methods to transport, treat, dispose, and reuse development and produced waters to maximize the profitability of shale gas production and remain competitive in the marketplace.

Eureka has been operating centralized oil and gas wastewater treatment facilities in Pennsylvania for 10 years and has optimized a thermal treatment-based model which provides for environmentally-conscious and sustainable recycling of oil and gas wastewaters. The model involves permitting, designing, constructing and operating comprehensive centralized wastewater treatment facilities utilizing state-of-the-art technologies to achieve the following goals and objectives:

- Continuous improvement in the management/treatment approach for oil and gas wastewaters. Where logistics are favorable, centralized treatment can be cost competitive with UIC disposal.
- Locating centralized treatment facilities in close proximity to major fairways of development activities to minimize hauling and associated costs.
- Providing customers with options for level of treatment with the goal of maximizing recycling of:
 - Pretreated Wastewater - water treated to reduce the suspended solids
 - Distilled Wastewater - water treated to remove dissolved solids
 - Clean Concentrated Brine - heavy (over 10.5 pounds per gallon) water that is very high in dissolved solids
 - De-Wasted Water - water that meets freshwater standards
- Providing a discharge option that returns as much water as possible to the hydrologic cycle.
- Maximizing recovery and beneficial reuse of recoverable by by-products (co-products) such as methanol, sodium chloride and calcium chloride salts, and lithium.
- Reduction of the long-term costs associated with treatment and recycling of oil and gas wastewaters.

History of Eureka

Eureka Resources, LLC (Eureka) currently provides treatment and management of oil and gas (O&G) wastewater from unconventional oil and gas exploration and production (E&P) activities in the Marcellus and Utica Shale plays in Appalachia. Eureka placed its first centralized pretreatment facility into operation in November 2008 in Williamsport, PA. In 2012, Eureka obtained approval to construct two additional facilities – one in Bradford County, PA and a second Williamsport, PA facility. All three of the existing Eureka facilities in PA are permitted as essentially mirror facilities, each with daily throughput capacities of 10,000 barrels per day

(bbl/d) or 420,000 gallons/day and are permitted to allow installation of some or all of several unit processes. Salt crystallizer systems at each plant are capable of recovering 125 tons per day of high-purity sodium chloride evaporated salt, with additional production capacity available via crystallizer expansion at each location.

Eureka is also in the process of planning additional centralized treatment facilities in Appalachia, as well as expansion into the Permian Basin in Southeast New Mexico, with tentative plans to construct up to 600,000 bbl/d (25,200,000 gal/d) of treatment capacity as part of an initial build-out, capable of generating large quantities of evaporated sodium chloride salt, calcium chloride salt, and lithium, and recovering 23 million gallons per day of freshwater for reuse in the region.

Technology & Drivers

The Eureka treatment process to treat unconventional oil and gas wastewater (patent pending) is comprised of a variable combination of the following unit processes:

- **Pretreatment:**
 - Raw water receiving/screening
 - Primary clarification
 - Methanol rectification
 - Oil separation/recovery
 - Raw water storage
- **Physical-chemical treatment:**
 - pH adjustment
 - Coagulation/flocculation
 - Gravitational settling
- **Phys-Chem Sludge Management**
 - Sludge thickening
 - Sludge dewatering
- **Distillation:**
 - Pretreated water storage
 - Mechanical vapor recompression distillation
 - Concentrated brine purge management
 - Distillate management

- **Crystallization**
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- **Distillate Post-Treatment (Patented)**
 - Membrane biological reactor (MBR) treatment
 - Ion exchange treatment
 - Reverse osmosis treatment
- **Salt By-Product Packaging and QA/QC**
 - Bulk storage (optional)
 - Rotary drying
 - Bagging/Palletizing
 - Product warehousing and QA/QC

Regulatory requirements are a very important driver for determining treatment requirements for oil and gas wastewaters. Regulatory requirements can vary significantly between states. Eureka has developed and maintained a strong working relationship with the Pennsylvania Department of Environmental Protection (PADEP) in order to adjust our business model as necessary to accommodate the ongoing evolution of regulatory requirements.

In addition to regulatory drivers, Eureka's business objectives come into play, including: maximizing recovery of valuable by-products, applying a level of treatment that allows return of water to the hydrologic cycle, minimizing risks associated with transportation and storage of wastewaters by E&Ps, and providing a sustainable choice for oil and gas wastewater treatment when injection is not an option or water supply is limited.

A variety of other factors are taken into consideration regarding selection of the various technologies and technology suppliers, including basin-specific wastewater characteristics, make-up or recycle water requirements, and desired by-product characteristics. For example, even when the decision was made to apply thermal technologies to achieve Eureka's business objectives, selection of the appropriate type of thermal technology was a critical step. Eureka considered several thermal technologies for by-product generation before selecting MVR crystallization based on performance drivers, including higher energy efficiency, ability to handle a wider range of feed qualities, ability to capture condensate, and the potential for expansion in a sequential/modular fashion to achieve recovery of multiple by-products.

Crystallization Technology - Lessons Learned

Eureka has gained valuable experience during the selection, design and operation of a crystallizer-based oil and gas wastewater treatment facility in the Marcellus Play in Pennsylvania. Many lessons have been learned which can be applied to future applications of crystallizer technologies to oil and gas wastewater treatment:

- **Mechanical Vapor Recompressions (MVR) Crystallizer Technology Vendor**

Selection: Application of crystallizer technology for treatment of oil and gas wastewaters is extremely limited. Much of the existing design and operating experience for MVR crystallizers is based on solution mining brine feeds which are nearly saturated with sodium chloride and have a lower variability of impurity levels. Also, much of the non-desalination crystallizer experience is outside the US. There are several factors which must be considered when selecting a crystallizer vendor:

- **Domestic vs. Foreign Vendors** – Selection of a foreign vendor can complicate various elements along the lifeline of the project, including general travel and communication (time zone) issues, scheduling and shipment of components, potential management of numerous foreign sub-vendors, challenges associated with procurement of replacement/spare parts during operation to minimize downtime, responsiveness of technical support and operator training, obtaining clear and usable design deliverable and O&M documentation, currency conversions, and units of measure challenges.
- **Heat Source** – Advantages/disadvantages of mechanical vapor recompression- vs. multiple effect systems need to be evaluated. Capital costs, energy use, safety and operating costs should be considered. Visits to similarly sized operating facilities to verify performance are recommended.
- **Turn Down** – The design capacity and ability of the crystallizer to operate at lower than basis of design (turn down) must be well understood. The turn down capability along with the reliability of raw wastewater delivery rates will dictate the need for and size of storage requirements upstream of the crystallizer.
- **Building Codes/Certifications** – Foreign vendors may not be familiar with local, state and federal building codes and certifications which must be factored into the design of the crystallizer process.
- **Materials of Construction** – The corrosive nature of mixed brine solutions must be considered when selecting the materials of construction for the major equipment, vessels and process piping.
- **Fabrication** – Visits to the various major equipment manufacturers/sub-vendors during fabrication must be performed to verify that fabrication activities are on schedule. Delays in fabrication will delay completion of construction.
- **Replacement parts** – Establishing a well-managed inventory of critical replacement components is essential. Clear lines of communication with equipment vendors is a must.
- **Boundary Limits** – Attention to boundary limit requirements is important; including confirming that the necessary utilities are available and accessible to support operation of thermal treatment technologies, and awareness of the challenges that may be faced in any given geographic area (e.g., availability of power, uncontrolled power outages, power supply flickers, availability of natural gas, etc.).

- **Safety:** Oil and gas wastewater treatment facilities typically include multiple technologies and require well trained operators. Inclusion of a crystallization process significantly increases the level of mechanization and incorporates both high temperature and pressure vessels. Safety considerations must be factored into the design of the crystallizer and operators must be educated and trained on safe operating protocols.
- **By-Product Quality Control:** Design and operation of a crystallizer requires a thorough understanding of thermodynamics. Much of the design and operating history for crystallizers is based on sodium chloride brine feeds with consistent characteristics. The characteristics of the mixed brine oil and gas wastewaters can be extremely variable with elevated concentrations of constituents that can complicate treatment, including various alkali earth metal chloride salts (sodium, barium, strontium, calcium, and magnesium chlorides), radionuclides, organics, etc. It is important to understand the range of variability associated with the oil and gas wastewater which will be received at the facility so that the required pretreatment system and residuals management strategies can be selected and designed to generate optimum crystallizer feed quality necessary to achieve and maintain optimum by-product quality.
- **Condensate Management:** Management options for the condensate (sometimes referred to as distillate) produced by a crystallizer must be factored into the design of a centralized oil and gas wastewater treatment facility. Options include recycle and/or direct or indirect discharge. All options require consideration of onsite storage requirements. Direct or indirect discharge may require additional treatment following crystallization due to the presence of elevated levels of inorganics (e.g. barium and strontium), volatile organics, ammonia nitrogen and other constituents that can become present in the distillate generated by the system. Application of additional downstream treatment technologies may be needed to reliably achieve discharge limits and/or reuse standards. The high temperature of the condensate may also be a challenge. For example, if biological treatment technologies are required downstream of the crystallizer, condensate discharge may require cooling prior to biological treatment to protect biomass health.
- **By-Product Market Development:** In order to develop a reliable market for by-products, an understanding of the market for the by-products is required. First, there is the need to demonstrate product quality equivalency which necessarily requires extensive by-product testing. There will also be a need for targeting and engaging potential customers ahead of time, obtaining necessary regulatory approvals for sale of the by-products, and implementing necessary QA/QC procedures and plans.
- **By-Product Management:** In order to develop a reliable market for by-products, investment in equipment to obtain/assure by-product quality may be necessary. Such equipment may include conveyance, processing, packaging, and storage facilities.

De-Wasting Determination

A critical component of Eureka's business model is the ability to treat unconventional oil and gas wastewater to a freshwater level. Eureka has engineered and deployed a patented process for generating de-wasted freshwater from oil and gas wastewater (typically regulated as a residual waste), allowing for the storage and handling of plant effluent as freshwater, and for direct surface water or groundwater discharge with pertinent regulatory approvals. Eureka has successfully obtained a NPDES permit for discharge of treated effluent from the Standing Stone, PA facility. Additionally, Eureka is the only oil and gas wastewater treatment facility to meet the PADEP's de-wasting standard included as Appendix A of the PADEP's WMGR123 residual waste General Permit.

Eureka has worked in parallel with the Center for Responsible Shale Development (CRSD) to characterize final effluent from the Bradford County, PA facility in an effort to support CRSD's development of a performance standard for discharging treated wastewater to surface water. The CRSD is an independent nonprofit organization whose mission is to support continuous improvement and innovative oil and gas exploration and production practices through performance standards and third-party certification. Eureka is the only provider of oil and gas wastewater treatment services to successfully achieve the CRSD wastewater treatment performance standard.

By-Product and Beneficial Reuse Efforts

Methanol: Eureka utilizes a methanol rectification column to recover methanol from compressor station wastewaters that typically contain high concentrations of methanol. The recovered methanol by-product contains 97 percent methanol, less than 1 percent ammonia nitrogen, as well as trace levels of BTEX (benzene, toluene ethyl benzene and xylene), MEK (methyl ethyl ketone), MIBK (methyl isobutyl ketone), acetone, zinc, boron, calcium, aluminum and water. Eureka recycles the recovered methanol primarily for reuse in oil and gas field applications.

Salt: Eureka has completed a co-product determination for the evaporated sodium chloride salt by-product generated at the Bradford County, PA facility in accordance with PA regulations. The effort included characterization of the following:

- Eureka's crystallized salt
- Bulk stockpiled road salt samples collected from various storage stockpiles maintained by Penn DOT suppliers for dry application as a road deicing agent
- Bulk stockpiled "solar salt" samples collected from various storage stockpiles maintained by Penn DOT suppliers for wet application as a "pre-wetting" road deicing agent
- Samples of bagged sodium chloride deicing rock salt collected from three different retail outlets within Pennsylvania
- Collection of sodium chloride material from a commercial/industrial that uses salt as a raw material with operations in Southwestern Pennsylvania

The salt samples were analyzed for: a suggested list of parameters provided by the PADEP Bureau of Waste Management; a list of parameters included in the research paper released by

the PADEP and Bureau of Water Standards and Facility Registration in May 2011 (authored by R. Titler and P. Curry); the list of parameters included in the draft WMGR128 general permit previously released by the PADEP for the beneficial use of crystallized sodium chloride and liquid calcium chloride from the processing of oil and gas liquid waste; selected hazardous waste parameter from the list included in 40 CFR Part 261, Appendix VIII; and selected parameters taken from material specifications provided to potential future users of Eureka's salt by their existing sources and/or suppliers. The results of this characterization effort indicated that Eureka's salt was chemically equivalent to commercially available deicing salts. In addition to chemical equivalency, Eureka has demonstrated that driers, compactors and crushers can be installed to generate a graded rock salt equivalent in physical composition to commercially available rock salt.

In response to market demand, Eureka also successfully conducted a similar beneficial use determination process in support of use of the crystallized sodium chloride salt product as pool and/or water softening salt. Eureka currently generates evaporated salt at the Bradford County, PA facility, which is distributed and sold commercially as bagged pool salt.

Calcium Chloride Brine: The brine purge by-product generated by the MVR crystallizer at the Bradford County, PA facility has a calcium chloride concentration of 18 to 22 percent along with varying concentrations of barium, sodium, strontium and lithium chlorides. After extensive research and market assessment, the best end use of this mixed brine purge is in the oil and gas industry to formulate drilling and development fluids. Eureka is also evaluating and pilot testing additional treatment of this mixed brine to recover lithium as a by-product, and to recover calcium chloride as either a liquid brine product or dry product (flakes/granules).

Conclusions/Takeaways

Actual experience treating development and produced wastewaters generated in Pennsylvania as a result of the Marcellus Shale Gas play has indicated the following:

- Eureka has demonstrated that locating centralized treatment facilities (employing crystallization and a group of supporting technologies that maximize potential for recycle and beneficial reuse) in close proximity to major fairways of development activities to minimize logistics and associated costs is a sustainable business model especially when injection is not an option or water supply is limited.
- Eureka has learned many valuable lessons through actual design, construction and operation of a crystallizer on oil and gas wastewater which can streamline future application of crystallization to treatment of oil and gas wastewater.
- Eureka has over seven years of successful experience treating complex unconventional oil and gas wastewaters utilizing a business model that provides:
 - A wide array of treatment options.

- E&P companies with options for selecting the level of treatment necessary to optimize reuse options and reducing the impact on the hydrologic cycle.
- Beneficial reuse opportunities for co-products (by-products) extracted from oil and gas wastewaters.

A forward-thinking strategic position designed to stay at the forefront of emerging regulatory requirements; promoting a close dialogue with state regulators regarding the development of regulations and standards.