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Treatment of Oil & Gas Produced Water

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Treatment of Oil & Gas Produced Water

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Abstract

Production of oil and gas reserves in the New Mexico Four Corners Region results in large volumes of "produced water". The common method for handling the produced water from well production is re-injection in regulatory permitted salt water disposal wells. This is expensive (~ $5/bbl.) and does not recycle water, an ever increasingly valuable commodity.

Previously, Sandia National Laboratories and several NM small business tested pressure driven membrane-filtration techniques to remove the high TDS (total dissolved solids) from a Four Corners Coal Bed Methane produced water. Treatment effectiveness was less than optimal due to problems with pre-treatment. Inadequate pre-treatment allowed hydrocarbons, wax and biological growth to foul the membranes. Recently, an innovative pre-treatment scheme using ozone and hydrogen peroxide was pilot tested. Results showed complete removal of hydrocarbons and the majority of organic constituents from a gas well production water.

ACKNOWLEDGEMENTS

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CONTENTS

FIGURES

TABLES

INTRODUCTION

In 2007, Sandia National Laboratories partnered with ConocoPhillips (CP), Biosphere Environmental (BEST), New Mexico State University (NMSU) and the US Department of Agriculture (USDA) to conduct pilot studies at a coal bed natural gas (CBNG) well site in the Four Corners Region. The project objective was to evaluate the efficiency of ultrafiltration (UF) and reverse osmosis (RO) membrane technologies at removing the high salt content present in the produced water. Several pre-treatment techniques were used to remove the organic materials prior to salt removal. Pre-treatment included the use of cyclone filters, settling tanks, granular carbon and granular zeolites. During this 2007 pilot study, the performance of the membranes was sub-optimal due to problems with the pre-treatment. Failure to remove dissolved and free hydrocarbons, bacteria, and paraffin wax (all of which are often present in Four Corners region gas and oil wells) resulted in pre-mature fouling/plugging of the membranes.

Generally, the primary concern in produced water treatment is the level of total dissolved solids (TDS) which varies by well. The TDS is composed of dissolved matter in the water such as salts, organic material, and minerals. Technology to remove the salts (desalination of sea and brackish water) is well understood and documented; however, high salinity waters containing hydrocarbons and other organic material are not as well understood primarily because of inadequate testing of pretreatment schemes to remove the organics. Often times a sequence of treatment technologies known as a "treatment train" is required to efficiently remove the TDS to acceptable levels.

Background

A 2009 Argonne National Laboratory study estimated that 56 million barrels of water are produced onshore every day, but this study may underestimate the current total volume because it is based on limited, and in some cases, incomplete data generated by the states. Producers of oil and gas can choose from a number of practices to manage and treat produced water, but underground injection is the predominant practice because it requires little or no treatment and is often the least costly option. According to federal estimates, more than 90 percent of produced water is managed by injecting it into wells that are designated to receive produced water. [1]

There is an inextricable link between water and energy production; consequently, considering that fresh water is becoming more scarce every year, efforts towards recycling or re-use of produced water are growing. In fact, just this past year - effective March 31, 2015, the New Mexico Oil Conservation Division (OCD) adopted a new rule that allows the oil and gas industry to store and use recycled water in oil and gas production. [4] The ruling is designed not only to save fresh water but to save the industry dollars normally spent on the transportation of produced water to disposal wells. This change in the regulatory environment provides the opportunity to find an alternative to disposal for water previously considered a waste byproduct; however, the water must be cleaned prior to re-use. This introduces an increased need to understand produced water and what is required to meet the water quality criteria.

TREATMENT PROCESSES FOR PRODUCED WATER

Generally the water quality and volume from any given gas or oil well varies widely based on three factors:

1. hydrocarbon being produced;
2. geography; and
3. production method.

In New Mexico the water quality varies primarily dependent on which formation is being tapped. The water treated during this pilot project was produced from a gas well located near Counselors, NM. The well identified as #1 Gallo Canyon (API #30-039-23391) is within the San Juan Basin, the most productive coalbed methane basin in North America covering an area of about 7,500 square miles across the Colorado/New Mexico line. [3] Figure 1 shows the well identification data.

Figure 1. 1 Gallo Canyon (API #30-039-23391).

Water treatment processes that have been commercially used in the past by the oil and gas industry focused mainly on the removal of oils and greases, scale control, and suspended solids and brine volume reduction using evaporation impoundments. [5] As higher value beneficial use options such as irrigation, livestock watering, groundwater recharge and habitat restoration grow, treatment objectives will require processes that have even greater capability to remove contaminants.

Colorado School of Mines completed a comprehensive technical assessment of produced water treatment technologies in 2009. [2] A total of 54 technologies were reviewed and assessed using the following criteria shown in Table 1.

Table 1. Description of produced water technical assessment criteria. [2]

Criteria	Description/Rationale
Industrial status	Emerging or existing technology in which industry, whether being previously employed for produced water treatment and to what level (full-scale, pilot-scale, bench-scale), whether it is a competitive or non-competitive vendor market (including supplier names), minimum and maximum plant size
Feed water quality bins	Applicable TDS range, types of water chemistry makeup, constituents of concerns including: hydrocarbons, suspended solids, hardness, boron, silica, barium, iron, manganese, etc
Product water quality	Overall reported or estimated rejection in terms of TDS, sodium, organic constituents, heavy metals, ammonia, and others
Production efficiency (recovery)	Specific production efficiency in terms of reported and/or estimated product water recovery
Infrastructure considerations	Known infrastructure constraints or considerations such as modularity, mobility, energy type, relative footprint, electrical supply, housing, brine discharge, chemical storage, etc.
Energy consumption	Types of energy needed and power requirements
Chemicals	Types of chemicals required for process control (such as for regeneration, fouling, scaling, alkalinity, corrosion, and disinfection) and cleaning
Life cycle	Expected life of the process and replacement needs
O&M considerations	Levels of monitoring and control required, including quality control Level of skilled labor required Level of flexibility: easy to adapt to highly varying water quantity and quality Level of robustness: ability of the equipment to withstand harsh conditions, such as cold weather climates, shut-down and restart Level of reliability – little down time, need for maintenance Types of energy required
Overall costs	Reported treatment, capital, operation, and maintenance costs. Identification of major cost components including waste disposal. Identification of components offering most cost reduction opportunities
Pre-and post treatment	Types and levels of pre- and post-treatment required by the technology
Concentrate management or waste disposal	Waste to feed volume ratio. Concentrate treatment and/or available disposal options of concentrate or solid wastes. Special disposal considerations, if any
Applicability in produced water treatment	Qualitatively scoring the technology for the produced water application criterion (excellent to poor)

An important note is that each criteria is not weighted therefore technology users often focus on certain criteria while neglecting others. Failure to consider all criteria when making a decision on water treatment can lead to problems as seen in the 2007 Sandia National Laboratories pilot demonstration where the pre-treatment was not given enough importance during the pilot design. The critical issue when using a membrane based demineralization process such as RO is protection of the membranes from suspended solids, oil and grease and biological fouling. As such, it is important to have a pre-treatment process that will remove the suspended solids, and destroy the organics (oil, grease, waxes, and microorganisms). Generally the use of chlorine products having a chlorine residual are great for limiting biological growth; however, they can damage pressure membranes so a technology that destroys organics but has no adverse effect on the membranes is preferred. Much of the previous work using RO membranes has shown good demineralization performance of produced waters; however, premature degradation of the membranes is common. Figure 2 is an example of what happens to the membranes as treatment progresses. This figure exhibits how performance of an RO membrane degrades with each

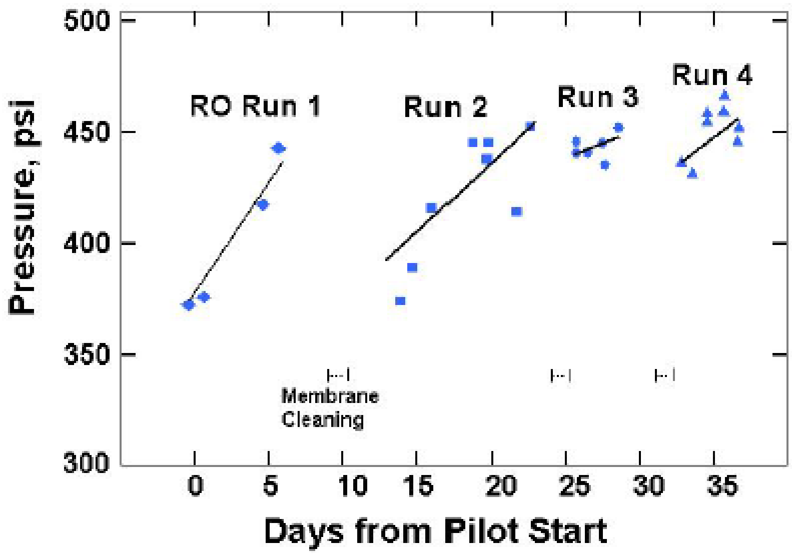

Figure 2. Pressure drop accumulation profile of reverse osmosis pilot. [5]

membrane cleaning. The cause is typically fouling of the membrane surfaces increasing the pressure drop across the membrane, decreasing efficiency of the water treatment, eventually to the point where the membranes need replacement at a significant cost.

This information, together with the body of experience with RO in the oil and gas industry, suggests that increased emphasis needs to be placed on high-performance preprocessing to remove oil and grease as well as total organic carbon to sustainable low levels and to minimize detrimental impacts to the expensive membrane components that carry out demineralization. [5]

NEW OPPORTUNITY FOR ALTERNATIVE WATER USE STUDY

In response to the new ruling by the New Mexico OCD promoting recycling and reuse of produced water, Sandia National Laboratories re-visited the problems encountered during the 2007 pilot study. In 2015, a new project directed at finding a solution to the produced water pre-treatment issues in the Four Corners region of NM was funded. The solution involved three tasks:

1. evaluate potential pre-treatment options that could remove the hydrocarbons and other organic materials;
2. identify the optimal pre-treatment option; and
3. conduct a field pilot test to collect actual data on performance of the selected pre-treatment option.

Pre-Treatment Option Evaluation

A comprehensive literature search evaluating conventional and innovative technologies for cleaning produced water was conducted. A report published in 2009 by the Colorado School of Mines entitled "An Integrated Framework for Treatment and Management of Produced Water, Technical Assessment of Produced Water Treatment Technologies, 1st Edition" [2] provided the most comprehensive, detailed review of applicable technologies available. Each technology was summarized and evaluated against the criteria listed in Table 1 above. The 54 technologies discussed in the report were evaluated for applicability to the Four Corners produced water. Some of the technologies are stand-alone and others are multi-technology processes. Technologies that are capable of removing the organic constituents and metals such as iron or manganese that could foul a membrane were considered for this pilot project. A combination of bag filtration, advanced oxidation using ozone and hydrogen peroxide (as needed) and chemical precipitation were chosen for the pilot test at #1 Gallo Canyon.

Ozone and Chemical Precipitation

Several of the reviewed technologies could to treat the Four Corners CBM produced water; however, considering the past difficulties with the potential for microorganisms (algae and bacteria), paraffin wax, hydrocarbons, iron and manganese the best choice for a pilot demonstration appeared to be a proprietary process which includes a combination of ozone nanobubbles coupled with hydrogen peroxide advanced oxidation and chemical precipitation with a complimentary reagent to prepare the water for a pressure driven membrane process (NF and/or RO).

Field Scale Pilot Study

The pilot study was conducted at the #1 Gallo Canyon gas well located approximately 2 miles northeast of Counselors, NM. M&M Production and Operations, Inc. (M&M) own and operate the natural gas well identified as API #30-039-23391. Figure 3 is a process flow diagram (PFD) for the pre-treatment pilot system. Produced water to be treated is gathered directly from the oil/water separator unit and/or the water storage tank. Next, the produced water was gravity fed into a settling tank where solids settle out of suspension. Water was decanted, a coagulant was added as needed, pumped through a bag filter (5 and 20 *u*m removal size were used separately with no noticeable difference), then into the proprietary ozone (O_3) columns (two 4" diameter columns were used for the pilot to expedite system set up in the field). Hydrogen peroxide (30% H_2O_2) was metered into the process as needed. Water and O_3 flowed co-current to maximize contact time and reaction kinetics. The oxidation-reduction potential (ORP) of the solution was monitored to determine ozone, and H_2O_2 flowrates. Next the water flowed through another 5 *u*m bag filter, a carbon polishing column and finally into a clean saline water storage tank. At that point the water was free of organic materials, only containing mono- and divalent salts. In an actual field operation, the next step would be removal of the salts using a membrane process such as RO or other method dependent on the salinity. Figure 4 is a view of the actual field site.

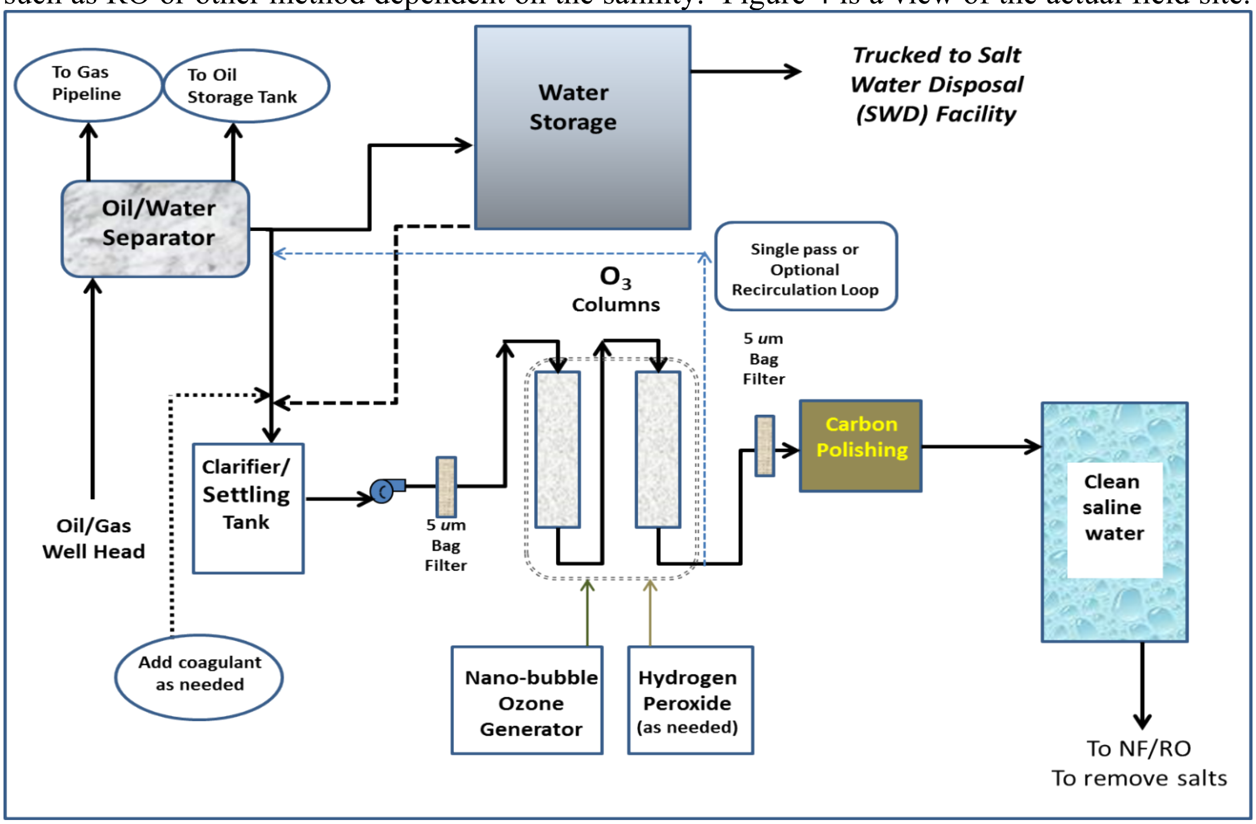

Figure 3. Pilot system process flow diagram.

Figure 4. Pilot test field site.


Figure 5. Oil/water separator.

The oil/water separator divides water and hydrocarbons based on varying density. Separated water is then transferred on-site to a water storage tank (refer to Figure 4). M&M's current standard operating procedure is to transfer the stored water to a tanker truck and transport off-site for disposal in a permitted SWD (salt water disposal) well resulting in a significant cost to overall operations. During the pilot, water was drained via gravity to the pilot makeup storage tank (Figure 7A).

A very small amount of coagulant was added and mixed into the makeup water to flocculate the relatively high levels of iron and manganeese which had been oxidized and precipitated by the ozone to facilitate removal in the cartidge filter. In a full scale system, failure to remove iron and manganese would negatively impact the RO membranes.

The iron appeared to complex with the sulfate forming ferric sulfate flocs. Ferric sulfate precipitation flocs are visible in Figures 7a and 7b. The water was pumped through the filter cartridge where precipitated material was removed. Figures 8 and 9 show pre and post filtration cartidges respectively. Following the filter cartidge water entered the top of Column 1 flowing downward through the packing media. The columns are packed with inert, non-reactive media balls that act to increase surface contact area between the ozone and water (Refer to Figure 6). Ozone nanobubbles were pumped into the the columns flowing downward (co- current) with the water. Water then exits the bottom of Column 1 and enters the top of Column 2 again flowing downward. Hydrogen peroxide was metered in through an injection port (refer to Figures 10 and 11) as needed to enhance the chemical oxidation of the organic materials in the produced water. A proprietary element of the pilot treatment process that was critical to the organic destruction success is the very small size of the ozone bubbles

Figure 6. Ozone generator and columns

Figure 7A. Water treatment makeup storage

Figure 7B. Ferric sulfate floc

Figures 8 and 9 exhibit pre and post filter cartidges. The filters are 20 *u*m pore size. That means they are designed to remove particles larger than 20 *u*m.

Figure 8. Filtration cartridge prior to filtration.

Figure 9. Filtrati
filtration.

The clear PVC columns (Figures 10 and 11) allow viewing of the inert media balls and the reaction dynamics during water processing.

Figure 10. Ozone packed bed columns.

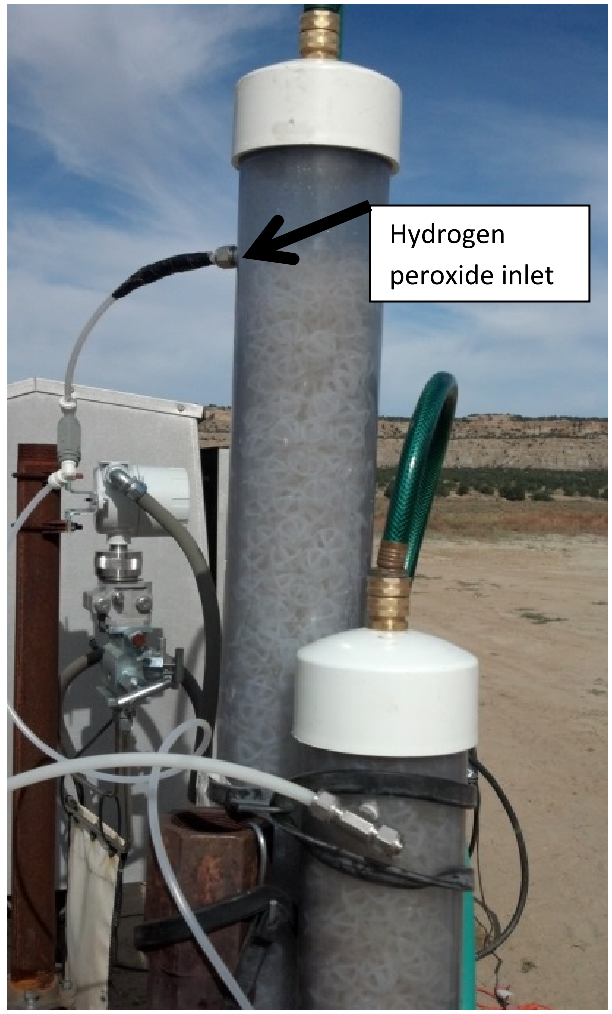

Figure 11. Hydrogen peroxide inlet tube on ozone columns.

Pilot System Performance

Table 2 contains the analytical data from two separate sampling events during the pilot system operation. Pre-1 and Pre-2 were samples collected from the raw produced water prior to any

Table 2. #1 Gallo Canyon pre and post water analysis results.

		Sample ID					
	Analytes	Pre-1	Post-1	% Removal	Pre-2	Post-2	% Removal
	N-Hexane Extractable Material	18	N/D	100	320	N/D	100
	TOC (Total Organic Carbon)	17	5.1	70	19	5.3	72
	BOD (Biochemical Oxygen Demand)	69	< 2	97	29	3	90
	TDS (Total Dissolved Solids)	28,100	28,100	-	25,600	27,500	-
	pH	7.23	7.44	-	7.28	7.55	-
	Conductivity (*u*mhos/cm)	45,300	45,300	-	44,700	44,200	-
Volatiles	Benzene	4500	1.3	99.97	4100	1.0	99.98
	Toluene	3200	ND	100	2500	ND	100
	Ethylbenzene	150	ND	100	77	ND	100
	Xylenes, Total	1000	ND	100	600	ND	100
Metals	Aluminum	3.8	0.051	98.7	4.6	0.036	99.2
	Calcium	220	250	-	240	250	-
	Copper	ND	0.012	↑	D	0.009	↑
	Iron	20	ND	100	17	ND	100
	Magnesium	47	46	-	47	47	-
	Manganese	0.33	0.74	124 ↑	0.34	0.78	129 ↑
	Potassium	90	93	-	88	90	-
	Sodium	9600	10000	-	9500	9800	-
Anions	Fluoride	ND	ND	-	ND	ND	-
	Chloride	17000	18000	-	16000	17000	-
	Phosphorus, Ortho-P as P	ND	ND	-	ND	ND	-
	Sulfate	ND	ND	-	ND	ND	-
	Nitrate+Nitrite as N	ND	ND	-	ND	ND	-
Alkalinity	Bicarbonate (as CaCO3)	232.1	196.8	15	232.8	193.9	17
	Carbonate (as CaCO3)	ND	ND		ND	ND	
	Total Alkalinity (as CaCO3)	232.1	196.8	15	232.8	193.9	17
	Hydrogen Sulfide	ND	ND		ND	ND	
	Sulfide Dissolved	*ND*	*ND*		*ND*	*ND*	
	COD (Chemical Oxygen Demand)	689	730		890	605	
	Volatile Solids (% of Total Solids)	3.88	5.36		3.97	5.19	

* All units are mg/L unless otherwise noted.

treatment. Post-1 and Post-2 samples were collected from the clean water storage tank at the end of the treatment process. Figure 12 displays the difference in visual appearance of the pre and post treatment water. The pre-treatment sample is on the left, the post-treatment on the right.

Figure 12. Pre and post produced water samples.

CONCLUSIONS

Produced water from the #1 Gallo Canyon gas well was treated at pilot scale using ozone and hydrogen peroxide. The objective of the pilot study was to evaluate the effectiveness of the O_3/H_2O_2 system as a pre-treatment method for removal of the petroleum hydrocarbons, paraffin wax, microorganisms and other volatile components present in typical coal bed methane gas produced waters. Sample analysis indicated that 100% of the total petroleum hydrocarbons were removed in both samples collected as indicated by the removal below detection limits of the N-Hexane extractable materials. The volatiles (benzene, toluene, xylene were 98.7% removed or greater. The BOD (biochemical oxygen demand) was lowered by 97 and 90% respectively. Biochemical oxygen demand (BOD) is the amount of dissolved oxygen needed (i. e., demanded) by aerobic biological organisms to break down organic material present in a given water sample at a certain temperature over a specific time period. Biochemical oxygen demand is the amount of oxygen required for microbial metabolism of organic compounds in water. [6] The high removal of BOD means that the oxygen necessary for microorganisms to thrive has been removed. This is ideal for a pre-treatment prior to a secondary treatment with membranes because the possibility of membrane fouling due to organisms is limited.

The COD (chemical oxygen demand) values were largely unchanged. Chemical oxygen demand (COD) testing is commonly used to indirectly measure the amount of organic compounds in water and as such the COD values should have declined as the organic material was destroyed. However, when a water contains high enough levels of oxidizable inorganic materials (chloride) which may interfere with the determination of COD then the value will not go down. Because of the high concentration of chloride in most produced waters, COD is not an ideal measure of organic constituent removal. The test for COD uses potassium dichromate ($Cr_2O_7^{2-}$). The following is the stoichiometric equation for the reaction with chloride.

$$6Cl^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 3Cl_2 + 2Cr^{3+} + 7H_2O \quad [7]$$

Another concern with produced water is the presence of iron and manganese. The ozone process removes these constituents from the water through oxidative precipitation to ferric sulfate or iron oxide and manganese oxide followed by subsequent coagulation and filtration. In this pilot a coagulant was added once the oxidation of the iron to ferric sulfate was visually observed. This resulted in ferric sulfate precipitant (flocs) formation, which was easily removed using the paper cartridge filters as shown in Figure 9. A full scale system might require a larger scale filtration press or similar system to remove large amounts of flocculated metals prior to the secondary treatment. The TOC was removed by 70 and 72% respectively. If a larger TOC removal was required prior to secondary treatment, the reaction kinetics could be adjusted by modifying the water and O_3/H_2O_2 flow rates.

The water exiting the pre-treatment pilot system was brackish water free of organic constituents. This water chemistry is ideal for secondary treatment such as RO designed to remove the remaining salt minerals.

FUTURE RECOMMENDATIONS

As produced water treatment expands nationwide it is anticipated that many of the responsible parties will use proven membrane technologies such as RO or ED as the primary treatment. The principal challenge then becomes protection of the membranes by ensuring an adequate pre-treatment to remove potential membrane damaging constituents. The pre-treatment systems will need to be adaptable to the fundamentally different demineralization processes. The fundamental categories of preprocessing that will need to be considered include:

- flow equalization
- deoiling
- suspended solids removal
- soluble organics removal for biological growth control [5]

Some or all of these categories may be required depending on the produced water chemistry.

In addition, the testing and results from this pilot study for a produced water will have direct applicability to a flowback water from hydraulic fracture wells.

REFERENCES

[1] Energy-Water Nexus. Information on the Quantity, Quality, and Management of Water Produced during Oil and Gas Production. United States Government Accountability Office – Report to the Ranking Member, Committee on Science, Space, and Technology, House of Representatives. January 2012. GAO-12-156. http://www.gao.gov/assets/590/587522.pdf

[2] http://aqwatec.mines.edu/produced_water/treat/docs/Tech_Assessment_PW_Treatment_Tech.pdf

[3] "Evaluation of Impacts to Underground Sources of Drinking Water by Hydraulic Fracturing of Coalbed Methane Reservoirs". US EPA 816-R-04-003. June 2004.

[4] Title 19, Chapter 15, Part 34 of the New Mexico Administrative Code.

[5] Hayes, Tom and Arthur, Dan. "Overview of Emerging Produced Water Treatment Technologies". 11th Annual International Petroleum Environmental Conference, Albuquerque Hilton Hotel, Albuquerque, NM. October 12-15, 2004.

[6] https://en.wikipedia.org/wiki/Biochemical_oxygen_demand

[7] https://en.wikipedia.org/wiki/Chemical_oxygen_demand

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