SUCCESSFUL SALTWATER SOURCED BIOCIDE AND/OR ALKALINE WATER REMEDIATIONS IN BOTH LEGACY AND NEW WELLS

David L. Holcomb
Pentagon Technical Services, Inc.

WHAT IS ECA PRODUCED ANOLYTE?

Electrochemically activated (ECA) saltwater produces environmentally friendly anolyte (Hydrolyte®), an oxidizing biocide for controlling or eliminating harmful bacteria such as sulfate reducers (SRB) and mitigating H2S in wellbores.

ECA or electrochemical activation is a process that uses membrane cell electrolysis of water or saline solutions to produce effective oxidizers (anolytes) for disinfecting and sanitizing surfaces or aqueous systems, and/ or produce antioxidants (catholytes) for degreasing, cleaning and oil recovery improvement. These solutions are 99.5 % water and are transported as a non-chemical with no strict Hazmat requirements. Anolyte is a product for biocidal use and is hypochlorous acid (HOCl or HCLO).

It is derived from performing electrolysis of water containing electrolytes (NaCL, K_2CO_3, KCL) which produces predominately HOCl as the anolyte and a small amount of Catholyte as sodium (NaOH) or potassium hydroxide (KOH), which is used as an effective cleaner, degreaser, surfactant replacement and for enhanced oil recovery applications. The process can now be tuned to produce either all anolyte or all catholyte depending on treatment requirements. The anolyte can be manufactured for several pH levels with the most common being 6.5-6.7. although lower pH levels may be produced for specific applications. Concentration levels of between 400 and 900 ppm can be prepared and higher concentrations if necessary although most applications can be successful at these levels.

BIOCIDAL EFFICACY OF ECA ANOLYTE:

Numerous certified studies have been published validating the effectiveness of HOCl for killing and controlling growths of numerous bacterial, viral, mold and complex biofilms at economical rates of addition. The results meet or exceed the efficacy of most of the hazardous biocides on the market today. It has been adopted by numerous hospitals for sanitizing operating theaters, equipment and rooms. It has also been used for meat processing hygiene and fruit treatment. Microbiological testing efficacy test data was validated by third party laboratory, Intertek, in Houston, Texas.

The measurement of anolyte activity is called Oxidation Reduction Potential (ORP) and that coupled with measuring the FAC (free available chlorine) to validate concentrations at or near the manufacturing site. The anolyte should be manufactured and used within a two-week period and stored in a low light and cool environment for maximum performance.

H2S mitigation can be accomplished using Hydrolyte® anolyte in producing wells, newly drilled wells, and sour water storage facilities. The HOCl combines with H2S to form sulfur, hydrochloric acid and water.

Oil and gas wells have been treated successfully with electrochemically activated (ECA) oxidizers. Twenty-five well treatments in New Mexico, Oklahoma and Utah. Remediation treatment volumes usually consists of between 500 and 5000 gallons per well or zone of Hydrolyte® applied in a variety of methods including placing ("dumping") down the backside(annulus) or pumping into wells down the tubing or casing annulus using a "kill" truck.

H2S treatments can be as simple as dumping a drum down the backside of a producing well or adding the product to treat frac tanks or ponds or in post drilling completions drill outs, etc.

ECA ANOLYTE (HOCl) DESCRIPTION:

ECA manufactured Hypochlorous acid (HOCl) as anolyte at 600-1200 ppmand 900 ORP.

It is 80x-200x Stronger Disinfectant than Bleach and 1,5 x Stronger than Chlorine Dioxide

It kills all dangerous pathogens and bacteria, viruses on contact with lasting protection on surfaces and in liquid solutions when properly dosed.

It is 100% non-toxic on or around humans, pets, animals, plants and marine life

It is EPA registered as a “Safe and Powerful” disinfectant.

It is relatively inexpensive ($3.50- $4.50 /gal.) as delivered or made on or near the operation site to use within a two-week window for maximum efficacy

It is successfully being used today and has been used in several oilfields for over twenty years and some applications were even done in the 1970’s starting in Russian oilfields.

CASE STUDY # 1; S.E. NEW MEXICO

A New Mexico operator was experiencing frequent rod, pump and tubing failures in an older field containing 120 pumping wells, most of which were 30 to 35 years old. The wells were 1800' to 3500' deep, typically yielded 1 to 2 barrels per day and had low bottom-hole pressures due to the age of the wells.
The Operator typically had to repair wells after 2 to 4 months of operation and it was not uncommon for 8 to 10 months to pass before a work-over rig was available to pull the string and repair the tubing. The holes in the tubing and damage to the string was usually caused by corrosion from sulfate reducing bacteria (SRB), which was also responsible for hydrogen sulfide gas, black water and extra effort by the pumper to clean the oil up to sell it.
The Operator learned about a process called Electro-Chemical Activation (ECA) technology, which allows for a powerful, but environmentally responsible, biocide to be produced from salt, water and electricity. Not wanting to further contaminate the formation, the Operator purchased a device which uses ECA technology to produce electrolyzed oxidizing (Anolyte) water, (ECA Anolyte Biocide @ 90% HOCl, for H2S Mitigation) that could be placed down-hole to reduce tubing failures due to corrosion by destroying the microorganisms that were causing the failures.

APPLICATION:

The Operator began producing anolyte water which contained hypochlorous acid as the predominant active chlorine species and which is more efficacious and faster acting than the hypochlorite ion, bleach.
With low formation pressures and flow, the Anolyte water could be pumped down the well annulus and applied directly to the desired treatment area as the wells were kept pumped off to the perf.
Typical treatment regimens were to pump 10 barrels of the water into the well, followed with a 100-to-200-barrel water "push" that forced the anolyte water into the formation and in contact with the bacteria causing the problem.
and bacterial induced corrosion in rods, pumps, and tubing. The formation pressures and low flow rates allow for simple well treatment regimens with EO water which can reduce tubing failures, improve well quality and increase profits.

ECA water was used to reduce the external bacterial induced corrosion and by the end of 2007, only 26 tubing failures occurred during that 24-month period. The combination of poly-lined tubing and well treatment with ECA Anolyte (HOCL) water dramatically reduced tubing failures caused by SRB sourced H2S corrosion. Improved fluid quality and eliminated H2S in the wells.

CASE STUDY #1; CONCLUSIONS:

Many older producing fields are in formations which harbor SRB bacteria. The bacterium creates hydrogen sulfide gas, black water, lower quality fluids, and subsequent bacterial corrosion in rods, pumps, and tubing. The lower formation

pressures and low flow rates allow for simple well treatment regimens with ECA anolyte water which reduces tubing failures, improves well quality, and increases profitability.

WHAT IS ECA PRODUCED CATHOLYTE?

The catholyte created from ECA of salt water is the chemical equivalent of a caustic soda or potash, except for the fact that it is a product of electrochemical activation (ECA) of various salt solutions (NaCl, K2CO3, KCl) . It has a pH around 10.5-12.5. It can frequently replace other alkaline agents, where caustic soda is found to be allegedly more effective, efficient and affordable.

The process known as ECA changes the condition of the electrolyte salt solution into a metastable state. (The anolyte solution has high positive redox (oxidizing) value and has microbiocidal capabilities whereas the catholyte has a negative ORP and excellent surface energy and cleaning properties.

A catholyte solution with a negative ion charge develops detergent properties, at pH of 10.5-12.5, and can contain ECA products such as sodium hydroxide (NaOH), potassium hydroxide (KOH) or a blend of the two in a highly excited state. The unique electroactive ions (-800 to -900 ORP), and high concentrations (1200-2800 ppm) as “SUPER” catholytes, which have a relatively long, maximum efficacy, shelf-life (thirty days).

The high concentration KOH catholyte may be used in most hydrocarbon reservoir types as an alternative to some conventional stimulation, well remediation, EOR or wellbore cleanout products / fluids and may result in higher and more effective recovery of crude oil, and to effectively neutralize H2S in water, , and prevent or abate Scale, Iron, emulsion issues , etc. using highly cost-effective as well as eco-friendly chemical ingredients i.e. NaCl or K2CO3 salt(s) in water. These products will have between 20 and 100 times more efficacy than non-ECA products.

ELECTROCHEMICALLY ACTIVATED (ECA) ALKALINE WATER; CATHOLYTE AS KOH, VERSUS CHEMICALLY DRY DISSOLVED IN AQUEOUS SOLUTIONS

While the mechanisms that make anolyte (acidic- neutral pH electrolyzed water) such a powerful sanitizer are well documented, the understanding of why the catholyte (alkaline electrolyzed water) is such an effective cleaner is must less understood. Very little research had gone into the catholyte side of the electrolysis reaction.

One very significant difference is that the ECA (electrolyzed alkaline water will have a negative 900 mv ORP, and non-electrolyzed or routine chemically mixed NaOH will have a positive ORP. It is known that a negative ORP helps the catholyte attract and retain oils, fine particulates and oils, as well as facilitating their transport into, through, and out of or from even low permeability porous media. The surface tension is also significantly lower with ECA produced catholyte than chemically blended caustic soda

(NaOH or KOH) at equivalent or even lower concentrations. Finally, the handling, safety, environmental and skin contact effects at equivalent pH (11-12.5) are much more benign with ECA due to effectiveness at such.

Studies have been done using specialized scanning electron microscopy and atomic force microscopy that suggests that structural changes (molecular water clusters) are occurring produced catholyte than ordinary caustic soda (NaOH - sodium hydroxide) or potash (KOH) solutions.

While the mechanisms that make anolyte (acidic or neutral electrolyzed water) such a powerful sanitizer are well documented, the understanding of why the catholyte (alkaline electrolyzed water) is such an effective cleaner was less understood. With more recent research having gone into the catholyte side of the electrolysis reaction its increased efficacy has now been validated by third party testing at Intertek Labs in Houston, Texas.

High pH NaOH and KOH based cleaners are widely used. Sydansk, et.al. at Marathon Oil has published and patented applications and production improvement benefits from non-ECA KOH. The active ingredients in catholyte are also NaOH or KOH created when the sodium or potassium ion in the anolyte chamber crosses the membrane to contact the cathode (negatively charged electrode). The catholyte pH can be between 10.5 and12.5. These properties are common with many cleaners. What is now understood is why the electrolyzed catholyte has proven to be much more effective than standard chemical solutions generated by mixing alkaline reducers and water to reach an equivalent NaOH/ KOH ppm. The difference involves a very unique, and effective coated membrane that will allow production of a unique arrangement of charged (ionized) water molecules once the catholyte is produced via the electrolysis of specialized brine solutions. In addition to NaOH, the very effective cleaner KOH (potassium chloride) can be produced as well from either KCL (potassium chloride or more desirably from K_2CO_3 (potassium carbonate). in catholyte water, illustrating parameters that were not routinely measured in the past. These nanosized structures have been shown to aid in separating oil from typical sandstone or carbonate reservoir surfaces via disjoining pressure, droplet removal, coalescence and dispersion into, across and through a more effectively produced water wet substrate. More efficient flow capacity is created using the surface chemistry benefits available from the unique electro-ionized, reducing agents, especially as KOH + 2e.

In 3rd Party Lab tests, the ECA catholyte has been reused up to five times, removing high percentage oils from the wall of processing tanks and flow lines. The catholyte keeps cleaning well long after the ORP had been neutralized, so ORP alone does not explain why it cleans so well.

CASE STUDY # 2:

ALKALINE ECA KOH CATHOLYTE NEW WELLTREATMENT # 1:

In November 2022, Fairview completed the NWSOCU #18. Initial production was 5 bopd with no water. We then treated the well with 3,000 gallons of KOH-high concentration KOH Catholyte solution. After a 3-day soaking period, the well was returned to production on December 2, 2022. Production rate increased to 30 bopd with no water visible. Note: This production level had not been seen in any of the previous 20+ wells in the field.

FIELD HISTORY:

Since 2005, Fairview Production Co. LLC has owned and operated the NW Sulphur Oil Creek Unit in Murray County Oklahoma. Our producing formation is the Basal Oil Creek which tops at 1500' and is on average 40' thick across the 140-acre lease. This formation produces 17 API gravity crude via 30% porosity and 4 darcy permeability. Over the years, Fairview's plan has been to drill new wells to the top of the Oil Creek, set casing, then drill out the last 10' into the pay zone (open hole completion). Fairview uses progressive cavity pumps to lift production to the surface. Initially, the new wells were all oil but very slow to fill the wellbore, thus only about 5 bopd could be achieved. To increase production rates, Fairview started using cyclic steam injections (huff and puff) treatments on each new well with good results. However, the cost, maintenance, and invasive process of steam generation became prohibitive. Last year, researching other treatment methods, Fairview discovered the 21st Century Energy, Inc. website. Fairview inquired about the ECA products, specifically KOH-Catholyte. The supplier responded quickly, and we had many discussions and visits to the lease. It was agreed that the lease formation (Oil Creek) could be a viable candidate to increase production rates via wettability alteration, reduction in surface and interfacial tensions, multi-ion exchanges, etc.

STIMULATION PROJECT SUMMARY: FAIRVIEW PRODUCTION COMPANY

Formation: Oil Creek; API Oil Gravity:16- 19; Location: Murray Co, Oklahoma

Formation Geology: ARDMORE-SHERMAN - Limestone, gray to tan, granular, with greenish-gray shale and brown fine- to medium-grained sandstone thickness 600 to 1,100 feet, decreasing eastward. (Simpson Group)

Lease Reference: NW Sulphur Oil Creek (NWSOC); Well data: NWSOCU #18 (API 09920673)

Total depth: 1535 ft. Casing depth 1522' with 13' open hole. PC pump set at 1450'.
Lease Holder: Fairview Production Company

Fairview has operated this lease since 2007. They have 22 producing wells and a small number of older wells are shut in as they had turned to water.

OVERALL PRODUCTION HISTORY AND SUMMARY

Generally, it has been Fairview's practice to expand production by drilling one new well per year. The history of production has had a consistent pattern. New wells come in producing 5 bbl./day after completion. That 5 bbls/d has been consistent with little variation. The average primary recovery production period will last, on average, about a year and a half before they go to water over the course of about three months. Importantly, the fluid level in the wellbore remained nearly half full during production. After 15 months This well continues to produce over 25 bopd with no visible water today. See Fig.1 for early time comparison in five wells!

POST TREATMENT HISTORIES PLUS FIG.1 COMPARATIVE PLOT

Daily Updates after treatment: (See Fig. 1 for early comparison to previous wells)

11/29/2022: 24 hours after treatment, no pressure on annulus and fluid level at 150' from surface.

12/1/2022: Well returned to production.

12/2/2022: Water/oil mixture carrying excessive sand causing pump to torque-up and drive head stopping with overload fault.

12/3/2022: Used hot-oiler truck to pump heated produced crude down the annulus to help clear downhole pump. Well back on production.

12/4/2022: Produced 15 BO and 15 BW.

12/5/2022: Produced 30 BO and no water seen. Fluid level at 960' from surface

12/6-12/2022: Produced 30 BO and no water seen. Fluid level at 900' from surface.

Weekly Updates:

12/16/2022: Daily production near 30 bopd with no water seen. Fluid level steady at 1000' from surface.

12/23/2022: Extreme cold conditions. Daily production near 30 bopd with no water visible. Fluid level steady at ~1000' from surface.

12/30/2022: Daily production near 30 bopd with no water visible. Fluid level rose 30' to 970' from surface. OBJ

1/6/2023: Daily production near 30 bopd with no water visible. Fluid level 970' from surface.

3/31323: Daily production near 30 bopd with no water visible. Fluid level steady at 975' from surface.

Monthly: April '23 Through December'23, Consistent daily production near 25-30 bopd with no water visible. Fluid level steady at 975' from surface

RETURN ON INVESTMENT

Fairview eclipsed their prior annual production 58 days after reopening NWSOC #18. NWSOCU #18 treated 11 months ago with KOH-catholyte producing 20-30 bopd with no visible water. Fluid level 500' above the pump = 600' into wellbore. In addition, Fairview Production Co. LLC has completed another new well NWSOCU #19. After observing the expected initial production of nearly 5 bopd, Fairview treated this well with the KOH-Catholyte solution in the same manner as the prior well. See table 1 for general economics summary.

CASE STUDY # 2:

WELL DATA: SECOND NEW WELL TREATMENT #2 , NWSOCU #19 (API 09920677)

Total depth: 1523 ft. 5 1/2" Casing depth 1510' with 13' open hole. PC pump set at 1360'.

Fairview drilled and completed the NWSOCU #19 in October 2022. The well had an initial production rate of 5 bopd with no water in the Oil Creek formation.

On 10/11/2023, Fairview treated the new well with 2750 gallons of high concentration KOH catholyte fluid. Produced water was used to displace the KOH catholyte fluid into the formation. Hot-oiler vessel was used to heat (120F) and pump the catholyte fluid down the annulus. The injection pressure gradually increased to 1700 psi and broke back to near 1100 psi and the catholyte was injected at around 1 barrel a minute. After treatment, the well was shut-in for 4 days.

10/14/2023: 72 hours after treatment, no pressure on annulus and fluid level at 150' from surface.

10/16/2023: well, was returned to production. Pumped up in 30 minutes. Pumping mostly water initially.

10/17/2023: well, turned to oil with no visible water. Well pumping fast enough to pump off the well. Slowed the pump down.

10/18/2023: pumping oil with no visible water. Fluid level 50' above the pump. Oil production calculated at 10-15 barrels.

10/19/2023: pumping oil with no visible water. Fluid level 50' above the pump, about 250' into the wellbore. Oil production calculated at 10-15 barrels.

10/22/2023: pumping oil with no visible water. Fluid level 50' above the pump = 250' into wellbore. Oil production calculated at 10-15 barrels.

10/25-27/2023: pumping oil with no visible water. Fluid level 200' above the pump = 350' into wellbore. Oil production calculated at 10-15 barrels.

10/29-31/2023: pumping oil with no visible water. Fluid level 150' above the pump = 300' into wellbore. Oil production calculated at 10-15 barrels.

11/7/2023: pumping oil with no visible water. Fluid level 150' above the pump = 300' into wellbore. Flow line 50 psia. Oil production calculated at 10-12 barrels.

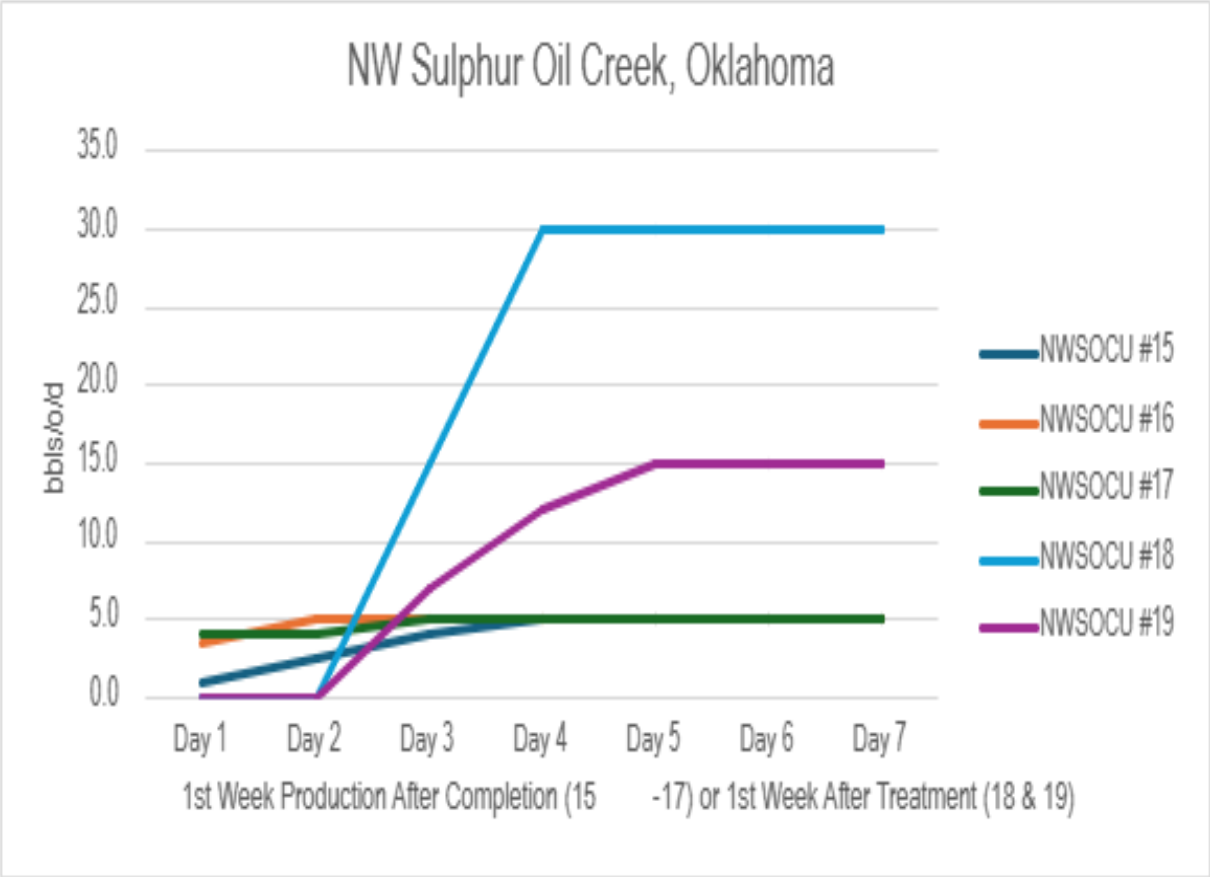


FIG 1: EARLY TIME PRODUCTION DATA FOR TWO FAIRVIEW CASE HISTORIES AND ADJACENT WELLS

Table 1. GENERAL ECONOMICS FOR FAIRVIEW WELL:

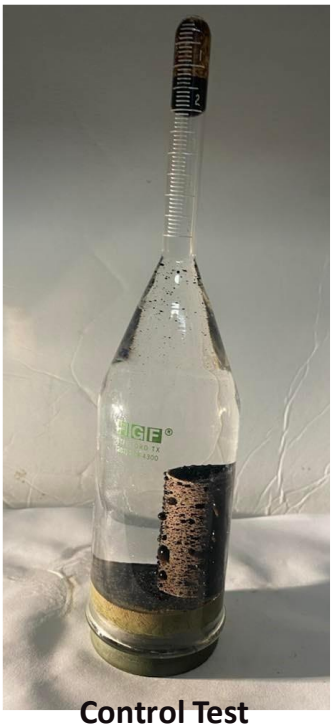
NWSOCU # 18

REVENUE CATEGORY	2022	2023

Gross Oil Prod. BBL	**10,400**	**14,700**	
Gross Sold Prod. BBl	**9414**	**14,640**	
Avg Mo. Oil Prod. BBL	**785**	**1225**	
Gross Revenue $$	**841,568**	**1,024,800**	
Net Monthly Revenue $$	**48,742**	**59,353**	
Net Annual Income $$	**388,374**	**469,836**	
Net Monthly Income $$	**32,365**	**39,153**	**-**

AMOTT CELL TEST AT TEMPERATURE OF 120F

After 7 Days



Control Test

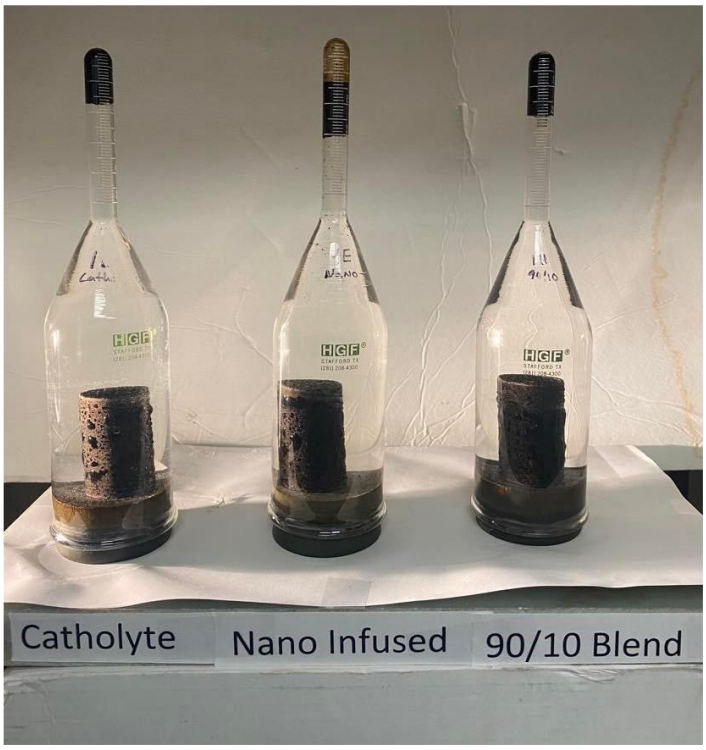


FIG 2: AMOTT CELL COMPARATIVE COUNTERCURRENT IMBIBITION TESTS ILLUSTRATING 19 GRAVITY OIL RECOVERY USING A KCL BRINE CONTROL VERSUS KOH CATHOLYTE, NANOGAS INFUSED KOH CATHOLYTE, AND A 90/10 BLEND.

FIG.3
Test Fluids (Imbibed into 100 md Sandstone Core Saturated with 15 Degree API Oil Creek Crude)

% Oil Recovery	Sample #		PV, cc	Initial Oil Volume, cc	Produced Oil Volume, cc
41.6	1E	KOH catholyte alone	4.203	3.95	1.75
41.6	4E	KOH infused with N2 nanobubbles	4.574	4.33	1.8
15.9	4F	Control Test Chemical KOH	4.414	4.27	0.7

CONCLUSIONS AND PROJECTED DEVELOPMENT SUMMARY:

Electrochemically activated salt water derived Anolyte (HOCl) and Catholyte (KOH) has been demonstrated successfully in two applications as highlighted in this paper. Comparative economics indicates that these products will generally cost significantly less relative to performance as compared to other microbial mitigants or conventional H2S mitigation technologies or well stimulation / remediation surfactants.

1. Unique results for routine downhole HOCl anolyte applications proved to reduce rod failure over several years in a SE New Mexico field. The operator was sold and no new information is available from the new operator as of this publication.
2. Unique positive results were obtained over the past 2 ½ years using high concentration KOH Catholyte in two new wells in comparison to the previous 22 wells in their Murray County, Oklahoma field with relatively low (17-19) API gravity crude oil.
3. Recent projects include 4 recently pumped wells in the Permian Basin with the addition of high concentration nanobubble nitrogen spheres infused into the high concentration KOH Catholyte for improved surface area coverage and efficiency over shorter time periods. Results are being evaluated now and a follow-up paper will be given. The process is patented as per the reference in this paper.

REFERENCES:

1.Electrochemically Activated water as a non-polluting anti-fouling technology Cloete, Eugene. (2002) Corrosion 2002, NACE International Paper 02463.

2.Production report and summary: Fairview Production Co. LLC; Mr. John Elliot-Chief Engineer, Sulfur, Murray County, OK 73030

3.Treatment Report and summary: Mr. Bruce Lanier Retired from Yates Petroleum, Corrosion Technician, now resides in Amarillo, Texas.

3. Hydrolyte tm (ECA anolyte) as HOCl and Super KOH catholyte provided by Disruptive Oil and Gas Technologies Corporation, Myrtle Beach, South Carolina, Holdenville, Oklahoma.

4. Sydansk, Robert D. "Stabilizing Clays with Potassium Hydroxide." *J Pet Technol* 36 (1984): 1366–1374. doi: https://doi.org/10.2118/11721-PA; Marathon Research, Littleton, CO.

5. US PATENT # 11,896,938: Nanobubble Dispersions Generated in Electrochemically Activated Solutions; February 13, 2024

ACKNOWLEDGEMENTS:

The author would like to thank the following for their invaluable contributions to the preparation and presentation of this paper and allowing the opportunity to present it at the 2024 SWPSC:

Mr. John Elliott; Chief Engineer, Fairview Production Company, Muldrow, Oklahoma

Mr. Bruce Lanier; Retired, Former Corrosion Technician at Yates Petroleum, Amarillo Texas

Mr. Gary Grieco, CEO; Tom Kane, COO, 21st Century Energy Solutions, Inc., Disruptive Oil and Gas Corporation, Little River, South Carolina

Mr. Doug Humphries; President Disruptive Oil and Gas Corporation; Holdenville, Oklahoma

Mr. Len Bland; Mr. Jeff Hardin, Co-patentors, Developing nanobubble adaptations in ECA fluids; Nanogas Technologies.

Ms. Ronda Brewer, Program Manager -Southwestern Petroleum Short Course, Texas Tech University

SWPSC Program Committee and Board of Directors