"ELECTROCHEMICAL BIOCIDES" – ENVIRONMENTALLY RESPONSIBLE ALTERNATIVES TO HAZARDOUS AND LESS EFFECTIVE PRODUCTS

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ABSTRACT

Unlike traditional oilfield biocides, those created using Electro-Chemical Activation (ECA) technology, do not interfere with gel additives, do not increase TDS levels, leave no residual toxic chemicals, are cost competitive and are extremely effective killing bacteria without the microorganisms becoming resistant to the natural biocide solutions. This paper discusses the results of treating water with ECA technology generated solutions of anolyte at several operating sites in Colorado and field-trial and lab data collected from sites in southeastern New Mexico and Texas. Experience over the past year with stimulation treatment water has shown that a loading rate of 0.5 – 1.5 gallons per thousand gallons eliminates bacteria in most waters. Also covered are the advantages of using ECA solutions for treating produced water and down-hole shock treatments.

INTRODUCTION

The oil industry, like many industries, can experience an upset or disruption in fracturing operations without knowing or being able to see why. Biocide use is common practice in downhole fracturing applications to alleviate nuisance bacterial activity which interferes with chemical additives or plugs off the formation. Most fracturing fluids consist of gelling polymers, gel breakers, surfactants, scale inhibitors, and friction reducers, etc.

Typical biocides on the market today will save time and money, however, it is common to use twice the amount necessary and hazardous remnants are left downhole, which may produce by-products and strip other chemical additives of their functionality. Pilot testing of a technology, called Electro-Chemical Activation (ECA) FEM-3 produced biocides, in the Dayton Field of southeastern New Mexico and the Piceance Basin of western Colorado is underway to remove bacterial corrosion from downhole tubing and to pre-treat stimulation water. This technology is safe, generated on-site, non-hazardous, and highly effective. It will cost pennies per gallon versus dollars per gallon for conventional biocides, after capital equipment costs are amortized over some specific time period.

ELECTROCHEMICAL ACTIVATION

A mechanism for generating electrochemical biocide agents from saline solutions used for different well treatment applications has been developed for addressing the issues previously described. ECA technology was developed in the 1970's in the drilling fluids used in the former Soviet Union, and allows for the modification of the functional properties of water. The process utilizes a unique patented device for passing water or saline solution through a specially designed electrolytic cell called a flow-through electrolytic module, (FEM). See Figure 1. The cell is composed of an extruded titanium tube separated from a titanium rod which is plated with precious metals by a ceramic membrane.

ECA FEM-3 produced biocide equipment is protected in a stainless steel NEMA 4X enclosure and operated with a touch screen interface connection to the internal central processing unit. Remote operation is available with an IP address and an Ethernet connection. For an example of 8-FEM Specifications and a typical ECA unit see Figure 2 and Table 1& 2.

The solutions generated in the negatively charged chamber (catholyte) and/or positively charged chamber (anolyte) can be used separately or in combination to destroy microorganisms, neutralize chemical agents, or clean and degrease surfaces. The anolyte fluids are strong oxidants for use as germicidal agents to kill viruses, fungi and bacteria. The catholyte solutions are anti-oxidizing, mildly alkaline solutions that can be used as mild detergents and degreasers.

Anolyte and Catholyte solutions are:

- Environmentally responsible
- Nontoxic
- Not required to have special handling
- Hypoallergenic
- Safely disposed in most municipal sewage systems
- Fast acting

-Anolyte: Powerful oxidizing biocide agents
- Used during all stages of disinfection and cleaning
-Catholyte: Alkaline antioxidant
- Applied in liquid, aerosol or frozen forms
- Chemical residue free
- Generated on-site or off-site for imminent use, eliminating handling and storage issues
-Produced from water, R.O, or softened water and salt

GELLING ADDITIVES

Given the correct media, water, and living conditions, microorganisms quickly procreate in a well or in formations. Bacteria can affect the viscosity yield of gelling additives (i.e. guar, HPG, etc.) in the water which is used to mix the fracturing fluids. Commonly, enzyme or oxidizing gel breakers are used to reduce the viscosity of gelled water after the proppant has been placed in the created fracture system. Breakers enable the base fracturing fluid water to be recovered as a lower viscosity fluid (< 10 cps). Most water based fracture fluids are composed of a polysaccharide gel (i.e. guar etc.) which serves as an excellent nutrient media for bacterial growth. These bacteria multiply, thrive and interfere with other chemical additives making them less efficient or less functional with time.

Because the gel is prone to support bacterial growth, typical practice is to apply biocides to prevent gel degradation and formation contamination. In order to preserve the gelling polymer, bacteria must be eliminated. In order to eliminate a living microorganism or bacteria, the enzymes, which are excreted by the microorganism must also be denatured. Bacteria can exist as both anaerobic (oxygen-hating) and aerobic (oxygen-loving) bacteria. Biocides used must be compatible with the fracture base fluid and the rest of the fracturing additives. When enzymes are used as low temperature breakers, biocides that denature are not recommended. Furthermore, biocides that chelate cannot be used with crosslinked fluids. Most biocides in use today, and those in use over the last 100 years, are harsh, corrosive, and unstable. Many biocides that have been used for many years, have reduced performance due to the bacteria becoming resistant to the chemical formulation.

A single fracture job usually involves the injection of thousands of pounds or more of proppant mixed with large volumes of water based fluids, often containing hazardous materials that include an appropriate quantity of biocide (i.e. 6 gallons per 1000 gallons). There are an estimated 25,000 fracturing jobs performed each year in the United States, further magnifying the potential hazard from using non-environmentally friendly biocides.

Further, the Safe Drinking Water Act requires that individual states or the U.S. Environmental Protection Agency (EPA) regulate "underground injection" activities to ensure the protection of "underground sources of drinking water." ECA technology produces environmentally "green" biocidal solutions which are not considered hazardous and do not interfere with gelling additives downhole.

COMPARISON OF BIOCIDE TECHNOLOGIES

In comparison to other commonly used disinfectants or biocides, bactericides produced using ECA technology do not increase TDS levels, leave no residual, and are cost-competitive over the life of the equipment. See Table 3. This particular ECA equipment (based on patented FEM-3, or "Flow-Through Electrolytic Module" technology) does not require Department of Transportation (DOT) registration and are not subject to cradle-to-grave compliance regulations. ECA anolytic biocide solutions produced in a pH range of pH 6.5-7.0, contain 75-95% of the solution's free available chlorine as hypochlorous acid. Hypochlorous acid is up to 100 times more effective as a biocide than commonly used sodium hypochlorite (bleach) solutions and is produced at a neutral pH. The initial capital cost of ECA/ FEM-3 equipment may seem high, however, there are minimal maintenance issues and no special disposal requirements associated with daily use.

A common biocide such as DBNPA is often used during fracturing operations. This biocide is available as a liquid, powder, or pellet form. The product is highly corrosive at a pH of 2.0-3.5. Special disposal requirements apply to the DBNPA biocide to rid it of its hazardous properties. Most commonly used biocides' MSDS forms declare that DBNPA is "toxic to fish and aquatic life". Additionally, the effects of DBNPA overexposure can be fatal to humans. The special disposal requirements increase the cost of the biocide, and the risk for fines for surface and ground water contamination. There are hidden costs associated with maintaining an inventory of biocides and providing labor to store, keep records, handle and apply regulated chemical biocides. High concentration requirements are also required for control of oilfield bacteria (i.e. 10-20 ppm for DBNPA) as described in common technical product guides. Further, there is uncertainty as to the effectiveness of biocides used for long periods of time as they become ineffective due to mutation and development of resistant strains.

Sodium Hypochlorite (NaOCl) (bleach) is an alternative water treatment biocide in use today. It is considered corrosive and leaves a hazardous residual behind thereby increasing the total dissolved solids (TDS). Although NaOCl and other chlorine forms (Chlorine dioxide) are effective at bacterial kill there are several disadvantages to its use:

- At an acid pH dangerous gases are liberated.
- Corrosion-resistant equipment preferably 316 stainless steel (not 304 stainless steel) is necessary.
- The chemical strength is affected by ultraviolet rays, extreme heat or extreme cold; therefore, the storage life is very short. Titration for bleach strength of sodium hypochlorite needs to be conducted each shift and dosages adjusted accordingly.
- Chlorine dioxide is a very unstable substance; when it comes in contact with sunlight, it decomposes. During chlorine dioxide production processes, large amounts of chlorine are formed.
- Leaves a die if not completely neutralized.
- Chlorine dioxide creates disinfection byproducts chlorite and chlorate. Free chlorine reacts with organic matter to form halogenated disinfection byproducts.
- Harmful to skin in concentrated form.
- It is less effective for the deactivation of rotaviruses and E. coli bacteria.

In addition to the disadvantages described above, chlorine dioxide is explosive under pressure. It is difficult to transport and is usually manufactured on site. Chlorine dioxide is usually produced as an aqueous solution for biocide applications.

FIELD PILOT STUDIES

To date, field trials and lab testing have been performed in the Permian Basin of Southeastern New Mexico and the Piceance Basin of Western Colorado. One specific case study is currently under way near Artesia, New Mexico where downhole bacterial related tubing corrosion evidence has been seen. See Figure 3.

Field Pilot Study No. 1: Yates Petroleum is conducting the study, and has set up a 7' X 7' housing facility near their gas plant in the Dayton Field, Southeastern New Mexico which supplies RO water. The gas plant supplies water and electricity to the housing facility and a space heater prevents the housing facility from freezing. An ECA unit, operating using a timer, runs up to 12 hours "on" and 12 hours "off" during a 24 hour period producing primarily anolyte solution which is stored a 700 gallon container. A 225 gallon container stores alkaline catholyte. A 250 gallon container stores brine solution at a 50% higher than recommended concentration (recommendation 5-10 g/l). This concentration is higher to adjust for salt reduction and allows the operator to generate a 500-700 ppm FAC solution of anolyte with an ORP of 900. When anolyte is injected into a well downhole, it is diluted with water and other fluids resulting in an effective 5 ppm solution.

Typical water treatment concentrations of anolyte fall between 1 and 2 ppm FAC so that the bacteria experience a shock-treatment downhole. Concentrations can be adjusted appropriately, based on the size of the storage tank and a starting anolyte concentration of FAC. See Table 4.

Unfortunately, any analysis of bacteria on or around the tubing downhole is qualitative rather than quantitative. There is no easy way to retrieve a representative anaerobic bacterial downhole sample and perform a culture analysis since they have been exposed to oxygen. Bacteria are trapped in a stagnant area under the pump so all treatment must be performed at the external surface that where injected fluids such as ECA anolyte solutions can reach.

There is a need to treat over 100 wells in the Dayton Field with ECA analytic biocide. Yates Petroleum is treating 8 wells per week or 8-10 barrels per week. Each well receives 1-2 drums (55-110 gal). Early into this study, ECA technology has been proven to be quite effective at killing bacteria in lab tests and during the pilot study. Tubing will be pulled periodically and inspected for reduced signs or absence of bacterial by-product corrosion.

Field Pilot Study No. 2: In a separate field pilot study being conducted in the Piceance basin of Rifle, Colorado by Antero Resources, fracture water has been treated with ECA FEM-3 technology. There are three wells under observation, each with different stages associated to them. These wells include the Island Park B-2 (Stages 1-7), Island Park B-3 (Stages 1-5) and Lundgren A-1 (Stages 1-6) wells.

An ECA unit has been installed at Antero's Rifle, Colorado office where it is protected from the outer elements. See Figure 4. Anolyte solution is produced at a concentration of 700 ppm FAC, ORP of 875, and pH of 6.5-6.7. The final treating concentration results is a "typical" loading rate of 0.5 – 1.5 GPT. The solution is stored in 275 gallon totes on-site where the ECA unit is operated. See Figure 5. Catholyte solution is stored in 500 gallon HDPE containers in the same area as the anolyte. The unit is operated both locally and remotely by an assigned IP address dedicated to the unit. Operation includes a series of auto-cycles through at least one (1) four hour period without interruption. After the four (4) hour rest period immediately following the production phase, the unit starts automatically for a period long enough to produce an additional fifty (50) gallons of product for a grand total of 250 gallons per tote. The ECA unit is virtually maintenance free because it automatically goes through a wash cycle after twelve (12) hours of production.

Antero Resources is currently conducting kill studies to assess the effective anolyte concentration required to destroy bacteria in their wells. Previous lab testing has proven effective at killing bacteria within 0.5 to 2 ppm. Results will be available in early February 2006 for review.

LABORATORY STUDIES

Lab Study No. 1: Laboratory testing performed in October 2006, at a gas refinery plant in Seminole, Texas, indicates that cooling tower water contaminated with aerobic bacteria in the form of a biofilm (composed of scale and biomass) can be reduced to significant levels depending on the concentration of ECA FEM-3 anolyte solution used. The company experiencing these biofilm issues is not able to remove enough bacteria at the inlet or production stream using chlorine gas and liquid chlorine. Therefore, a biofilm has formed at the outlet of their production water operations creating high maintenance costs associated with routine physical removal of the biomass.

Upon performing microbial laboratory tests using the natural biocide produced using the ECA FEM-3 technology, bacteria was reduced from 171,000 colony forming units (CFUs) to 23,000 CFUs with a anolyte concentration of 2 ppm FAC. These numbers were further reduced to 114 CFUs using an anolyte concentration of 5 ppm. To accomplish a total kill of bacteria, a concentration of 30 ppm FAC is required. Based on the laboratory data, as little as 2 ppm FAC anolyte solution is necessary to reduce bacteria in the cooling tower water sample by 86.6%.

Lab Study No. 2: Laboratory testing performed in October 2006, for a oil and gas company in Rifle, Colorado, indicates typical fracture water in the Western Colorado region can be treated with ECA-FEM -3 biocide technology using very little anolyte solution. Fracture water was evaluated for efficacy using a 545 ppm FAC concentration of the natural biocide produced using the ECA FEM-3 technology. The microbial testing results are listed below:

100	ppm	Anolyte	19 CFU/100ml
50	ppm	Anolyte	13 CFU/100ml
30	ppm	Anolyte	44 CFU/100ml
20	ppm	Anolyte	31 CFU/100ml
10	ppm	Anolyte	31 CFU/100ml
5	ppm	Anolyte	113 CFU/100ml
3	ppm	Anolyte	3940 CFU/100ml

No-Anolyte Added (control) 106000 CFU/100ml

Based on the laboratory data, as little as 3 ppm FAC anolyte solution is necessary to reduce bacteria in the fracture water sample by 96.3%. See Chart 1.

PRODUCED WATER "SHOCK" TREATMENT

Produced water accounts for the largest single waste stream in the oil field production chain. It is "produced" with gas or oil during the extraction process. In the United States, almost 7 barrels of water are produced for each barrel of oil and in some gas plays such as coalbed methane, the rates are higher per MCF of gas produced. The level of bacterial contamination in produced water can depend on location, and whether it's from an oil or gas well, the type of formation, the reservoir's age, and primarily, what was injected into the well during the production process. There are numerous publications which describe produced waters' complexity and the subsequent impact on oil production and subsequently reduced monetary returns from both mature and new wells. These waters consist of dispersed oil, salts (TDS), organic compounds, treatment chemicals, produced fine and solids, scale, bacteria, metals, sulfates, and radioactive material. Treatment can be quite expensive if attempting the removal of two or more of these contaminants at the same time. There are, however, alternative treatments and beneficial uses (i.e. reuse) for the large quantities of produced water depending on the level of treatment required. Businesses are now beginning to realize the value of managing produced water economically.

There are two ways to address produced water contaminated with bacteria. First is identify and quantify the bacterial type and potential quantity, and then treat the produced water as it is removed from the well. The second is to treat the water downhole with slugs of diluted analytic biocide, which creates a "shock" effect for killing the harmful bacteria. Both methods serve different applications, one is surface treatment after removal of contaminated fluids from the formation, while the other is meant to rid the near wellbore region of harmful bacteria during production operations.

Produced water removed from a formation with gas or oil can be treated for bacterial control with ECA/ FEM-3 biocide technology by first collecting the water in an approved, lined lagoon or storage tank and then generating and adding enough anolyte solution directly to the produced water. The anolyte solution is generated on or off-site and applied to the produced water as a biocide. Depending on the concentration and presence of other contaminants in the water, ECA technology serves best to be applied as post-treatment, much as a disinfectant would be in drinking water treatment.

"Shock" treatment of bacteria downhole in the Yates Petroleum Dayton Field pilot studies now being conducted near Artesia, New Mexico, can be easily accomplished by simply generating an anolyte solution in a suitable storage tank or drum, and adding the solution directly into to the well. The solution can either be applied at a concentrated strength (500-700 ppm FAC anolyte), or mixed with other fluids and placed downhole. Compatibility with the other fluids which do not exhibit any significant biological oxygen demand properties that can interfere with the anolyte's efficiency is necessary. An ideal method for "shock treating" a well is to add an optimum concentration of anolyte downhole to effectively reduce or eliminate the bacteria while avoiding any significant disruption of well operations. Unfortunately, there is no convenient way to collect a representative or consistent water sample for analysis every time. Such is the case of the Yates Petroleum Corporation, Artesia pilot project in Artesia, New Mexico where the bacteria have been verified to be anaerobic but virtually non-detectable by the time a sample reaches the surface.

Conservatively, produced water costs between 10 and 50 cents a barrel to process and either dispose or reuse. This is an annual cost of $5 billion to $25 billion a year in the US alone. Many producing companies report that they are paying anywhere from $0.30/bbl to $4.50/bbl for off-site disposal of oil field waste/ water.

The highest costs come primarily from disposal well injection. The least costly method is to re-inject the water back into the formation to help maintain reservoir pressure. However, the Worldwatch and many other environmental research organizations are reporting, the world is running out of freshwater. The water tables are falling everywhere. Produced water reuse, if possible, is on the forefront of almost everyone's efforts in the oil and gas industry today.

More than 200 million barrels of produced water are generated worldwide each day, or more than 75 billion barrels each year. While most companies opt for injection well disposal as a primary solution, the most economical way to assess how to evaluate produced water handling is first, compare treatment costs including chemical biocides, and then choose an effective treatment method which may help reduce costs for power requirements, as well as corrosion and scale mitigation, etc. Technologies which apply point-of-use biocide generation, versus paying for a product or piece of equipment, are recommended. ECA-FEM-3 anolyte generator systems produce biocidal solutions that ultimately cost pennies per gallon to generate. Savings add up quickly over the cost of traditional chemical biocides..

CONCLUSIONS

In conclusion, lab testing and initial field pilot studies have demonstrated that ECA produced biocides are effective at destroying bacteria within the laboratory and are showing promise at killing bacteria in the filed as expected. Testing within the New Mexico, Texas, and Colorado oilfield formations as well as surface waters have proven that:

1) ECA biocides using FEM 3 technology are produced by equipment designed and assembled with a rigid titanium and ceramic frame, which has allowed companies to produce anolyte solutions in the field or while mounted onto a truck. This is an added benefit which other ECA technologies or biocide generators have not shown.

2) ECA FEM-3 biocide technology performs mineralization of treated solutions. Because the conductivity of the biocidal solution has proven to be lower during application in field case studies, there has been lower corrosion activity experienced by using generated solutions, thereby allowing greater biocidal activity.

3) Studies in the New Mexico and Colorado regions are using ECA , anolyte biocides at pH ranges of 6.5-7.0 with 75-95% of the available chlorine produced as hypochlorous acid. This is 25-30 times more effective as a biocide than free available chlorine (FAC) containing solutions at pH 7.5-8.5 where FAC is present in the form of hypochlorite ions (bleach).

4) Laboratories studies in Texas and Colorado reveal that very little FAC from anolyte solution is necessary to reduce bacterial counts in cooling tower water and fracture water. The typical bacteria counts in both water sources are in the thousands per 100 ml of sample making bacteria manageable.

5) The ECA produced biocide’s salt concentration has been reduced by both Yates Petroleum and Antero Resources thereby reducing corrosive rates even further. As a result, there is less chance of interfering with pH, which interferes with fracture fluid and friction reducer performance.

6) The ECA produced biocides have proven to be truly "Green". Both Yates Petroleum and Antero Resources have not had any handling, transportation, disposal, or hazardous issues to deal with during installation, production or transportation of anolyte solutions.

REFERENCES

1. Biocides; Oil Gel Breakers; Nalco chemical Company.

2. “Hydraulic Fracturing Threatens Drinking Water”, OGAP, Perry Baycroft, Baker Oil Tools

3. Rohm Hass (Consumer and Industrial Products).

4. “Dryocide”, Adomite Well Stimulation and Drilling Fluids Additives; Sugar Land, TX, Nalco Chemical Company; © 1987

5. “Electrolytic Biocides: Green Alternatives for Stimulation Fluid Protection and Formation Biomass Remediation”; David L. Holcomb and Tandra L. Zitkus, Pentagon Technical Services, Inc.; Larry Jones, I.E.T., Ltd. © 2005

6. “Technology Promises New Solutions for Produced Water”, David Burnett and John A. Veil, Special Report: Health, Safety, and Environment, College Station, Texas.

7. “Less Water, More Oil Pays Dividends”, *Effective Produced Water Control Revives Returns*, Don Lyle, E &P, November 2005, pages 101-102.

8. “Coalbed Natural Gas Resources and Produced Water Management”, Dan Arthur and Bruce Langhus, ALL Consulting, and Viola Rawn-Schatzinger, RMC Consultants, GasTips, Part I, Summer 2003.

9. New Mexico Pilot Study, Dayton Field, Yates Petroleum Corporation, Artesia, New Mexico, 505-748-4240, Bruce Lanier, *Phone Interview* 1/5/2006

10. Clearwater, Inc, “Product Profiles”, “Biocides”, Page 5, June 1999.

11. Western Colorado Case Study, Piceance Basin, Antero Resources, Rifle, Colorado, 970-625-9922, Steve Fontenot, *Interview* 1/12/2006.

12. Chemical Technologies, LLC. “Advantages and Disadvantages of Bleaching with Sodium Hypochlorite”, http://www.chemicaltechnologiesllc.com

13. Lenntech, Disinfectants: Chlorine Dioxide, www.lenntech.com.

Table 1
8-FEM Specifications

Overall Cabinet Dimensions	35” W x 27” D x 65” H
Weight (Dry)	270 lbs.
Cabinet Enclosure	Stainless Steel, NEMA 4X
Portability	Locking Wheel Mounted
Power Requirements	120V AC, Dedicated 20 Amp Circuit, clean, reliable
Water Source	Minimum 35 psi w/ 3/4” dia. service line
Controller	Touch Screen HMI Interface with CPU for semi-automatic Operation, remote operation w/ Ethernet/IP Connection
Brine Tank	35 gal w/ Circulation Pump

Table 2
8-FEM Performance Standards:

Production Capacity	21 Gallons of Solutions per Hour, 250 gpd 17 Gallons Anolyte per Hour, 204 gpd 4 Gallons Catholyte per Hour, 48 gpd
FAC Concentrations	350-500 ppm
Current Consumption	5-8 Amps DC, 75 Watts per FEM
Brine Concentration	3-7 Grams per Liter
Production Run Times	12 Hours Max per 24 Hour Period, 4 Hours Max Continuous Duty Cycle

# FEMs	Gal/Hr Anolyte	Gallons Per 12 Hr Day @ 500 ppm FAC	Water Treated @ 50 ppm*	Water Treated @ 5 ppm*
4	8.5	100	1000	10,000
8	17	200	2000	20,000
24	50	600	6,000	60,000
48	100	1200	12,000	120,000
96	200	2400	24,000	240,000

*Note: Has been shown to be an effective biocide in water at concentrations as low as 1.0 ppm FAC.
**Note: The FEM 4 is a manually operated device and does not have HMI/CPU capabilities.

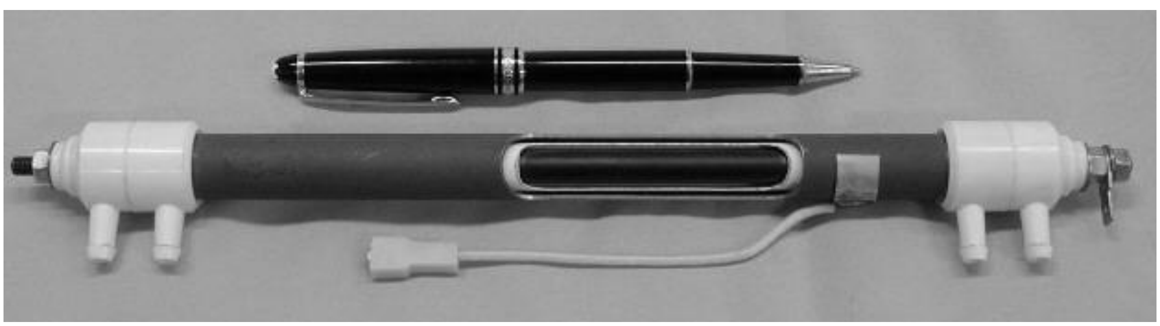

Figure 1 - ECA FEM-3 Technology (Flow-Through Electrolytic Module)

Figure 2 - ECA FEM-3 Unit

ECA FEM-3 biocide solutions contain various flow-through electrolytic modules, or FEMs, that produce anolytes and catholytes. Anolytes are strong oxidizing agents that kill bacteria, fungus, mold, mildew, spores and other micro-organisms in very short contact times. Catholytes are anti-oxidant solutions that are highly effective degreasing and detergent agents. Both anolytes and catholytes are non-toxic, environmentally friendly and yet very effective solutions for the control of unwanted micro-organisms.

Figure 3 - Bacterial Degradation of Downhole Piping (Yates Petroleum Case Study)

Figure 4 - ECA FEM-3 Unit
(Antero Resources Case Study)

Figure 5 - Anolyte Storage Tanks
(Antero Resources Case Study)

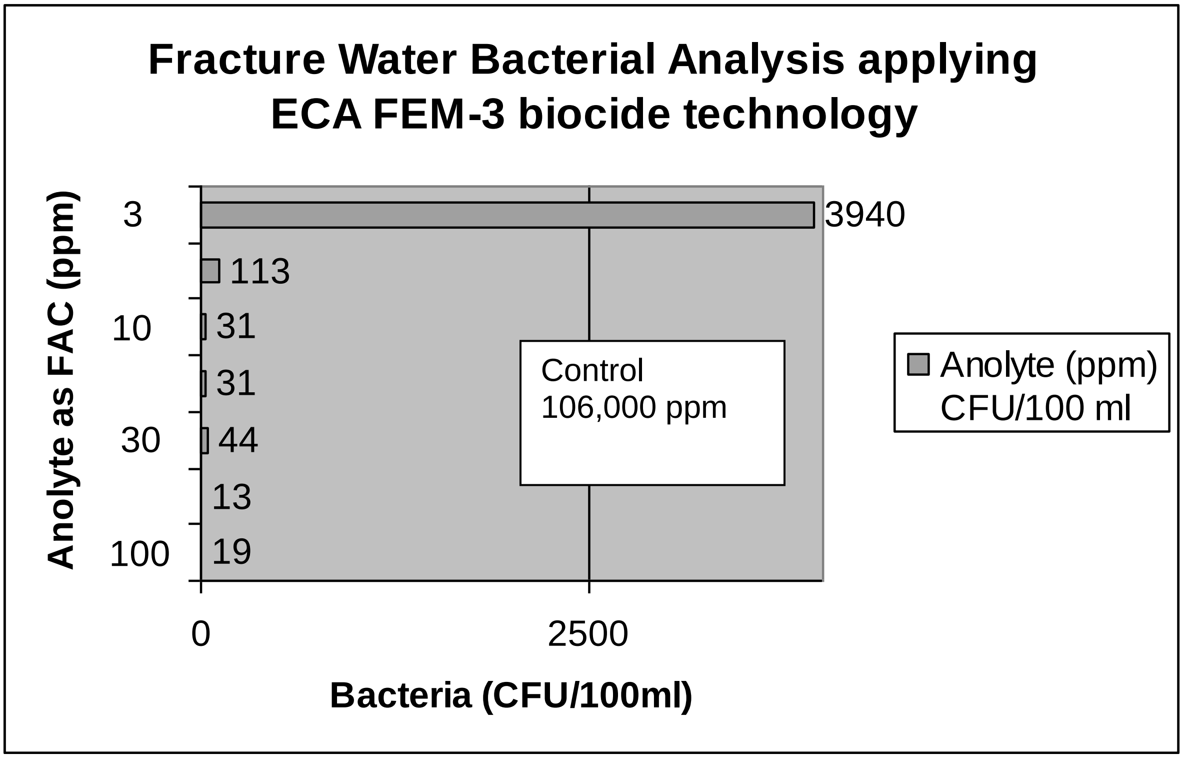

Chart 1 - Lab Study No. 2
(control and initial bacteria concentration without anolyte at 106,000 ppm)