ELECTROLYTIC BIOCIDES: GREEN ALTERNATIVES FOR STIMULATION FLUID PROTECTION AND FORMATION BIOMASS REMEDIATION

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Using a novel, small sized, flow-through electrolytic module, (FEM), and a cost-effective saline solution, nascent oxidant biocides (i.e. hypochlorous acid) can be produced for preventing and/or controlling micro-organisms that may plague aqueous polymer solutions in surface or downhole oil or gas well operations. The technology involves the use of electric current applied to the FEM while saline water is flowed through the two chambers of the FEM. A titanium tube plated with precious metals and a titanium rod are separated by a ceramic membrane to create the anode and cathode chambers. The flow is electrolyticly charged to produce both anolyte (anode solution) which has oxidizing biocidal properties and catholyte (cathode solution) with antioxidant cleaning properties. These may be used separately or in conjunction with one another to treat various surface and/or downhole issues relative to the protection of water used, for example, for preparing fracturing polymer gels. Those same gels, or other polymers that have been injected into reservoirs, may become food for biomass growth which may in turn impede production, fluid recovery or injection operations. Application of anolyte solution can provide remediation of that condition using relatively small, accurately placed volumes.

The system produces solutions which provide optimum concentration levels for the function required and then reverts to safe aqueous saline dilutions. The technology has been employed in Russian oilfields, as well as in water treatment applications in Canada, Europe, Asia, Africa, and the U.K.

INTRODUCTION

An ongoing challenge in today's petroleum industry is the presence and rapid growth of bacterial related problems and their effect on a variety of aqueous handling situations in well production, disposal, stimulation and remediation, as well as on surface water handling operations. Highly resistant strains of bacteria have evolved which now resist many previously as well as currently used solutions for their control or eradication.

In hydraulic fracturing operations problems with prematurely broken gels, H2S corrosion and personnel safety concerns, contaminated formations, frac tank residues, and conventional biocide environmental, transportation and container disposal issues area few of the problems which plague the success of stimulation and production of oil and gas wells. Bacteria are present in water used for fracturing fluids and in the residue left in frac tanks from previous jobs. Left untreated, bacteria multiply at an alarming rate, especially in the presence of nutrients such as guar, guar derivatives or other polymers used in fracturing gel preparation. When the bacteria ingest these polymers, they release enzymes which break down the polymer structures and block crosslinker sites, which in turn make the fracturing fluid less capable of adequate proppant transport. In addition, when the bacteria die more enzymes are released that accentuate polymer degradation even more. Once bacteria are pumped downhole, they may create hydrogen sulfide which corrodes subsurface equipment and/or plugs off an entire producing interval.

Biocides used to control these bacteria are designed to kill living organisms and are considered potentially hazardous to humans and animals. With increased environmental attention, biocide container handling and disposal has become increasingly difficult.

Biocide improvements in controlling damaging enzymes have been made, but there are still the many other issues as mentioned above, with which the industry is left to deal.

Numerous producing and disposal wells have been contaminated by bacteria introduction and attempts at remediation with several other hazardous chemicals have been made over the years. Treatments where dangerous free chlorine gas or potentially harmful chlorine compounds are used have had some success, but still leave many of the issues of safety and environmental impact unaddressed. They may also adversely alter the chemistry in the reservoir or wellbore to pose corrosion and pH issues which must also be addressed with other treatments or control methods.

Aqueous fluid flowback, storage and disposal after well treatment operations is also a source for breeding and growth of harmful bacteria under many conditions, particularly in warmer climates or in artificially heated water. Treatment of these aqueous fluids which often contain residual polymers and nutrients is often inadequate or nonexistent.

The treatment is often left up to the qualitative addition of chemical biocides to large volumes of aqueous fluid before storage and/or disposal. This may or may not be an adequate treatment, and often scarce and valuable disposal wells are fouled with bacterial biomass and are difficult to treat once this condition is flushed and aged deep into the reservoir.

ELECTROCHEMICAL ACTIVATION

A mechanism for generating electrochemical biocide agents from saline solutions for use as required has been developed for addressing the issues described above. Electrochemical activation (ECA) technology was developed in the 1970's in the Soviet Union and allows for the modification of the functional properties of water. The process provides a unique method and a unique patented device for passing water or saline solution through a specially designed electrolytic cell called a flow-through electrolytic module, (FEM). The cell is composed of an extruded titanium tube which is plated with precious metals and separated from a titanium rod by a ceramic membrane. The solutions generated from the negative output and/or positive output can be used separately or combined to destroy microorganisms, neutralize chemical agents, purify water or clean and degrease surfaces. The anolyte fluids produced are strong oxidants for use as germicidal agents to kill viruses, fungi and bacteria. Catholytes are antioxidizing, mildly alkaline solutions that can be used as detergents and degreasers.

Both anolyte and catholyte solutions are:

- Environmentally friendly
- Nontoxic
- Not required to have special handling
- Hypoallergenic
- Safely disposed in municipal sewage systems
- Fast acting
- Powerful biocide agents
- Used during all stages of disinfection and cleaning
- Applied in liquid, aerosol or frozen forms
- Chemical residue free
- Generated on-site or in concentrated amounts for imminent use, eliminating handling and storage issues
- Produced from municipal tap water and salt

MECHANISM FOR BIOCIDE GENERATION

Electrochemical activation is a technology for generating meta-stable substances from water and compounds dissolved in it through electrochemical exposure the weak saline solution is altered temporarily to produce meta-stable solutions without the addition of chemical reagents. As a physical and chemical process, electrochemical activation is a combination of electrochemical and electrophysical influences on water containing ions and molecules of dissolved substances on the surface of the electrode (either anode or cathode) and in conditions of non-equilibrium transfer of a charge by electrons through the "electrode-electrolyte" ceramic membrane.

As a result of chemical activation, water becomes meta-stable (activated) for several hours, possessing increased reactivity which can be used in different physiochemical processes. Water activated at the cathode electrode (catholyte) demonstrates high electron activity and antioxidant properties. Correspondingly, water activated at the anode (anolyte) possesses low electron activity and oxidizing properties.

Electrochemical activation allows for an enhanced alteration of the dissolved gases, acidic, basic and oxidizing properties of water without the addition of chemical regulation, and to synthesize meta-stable chemicals (oxidants and anti-oxidants) from water and substances dissolved in it. The effect of water meta-stability from the ECA process is the basis for its use in conditioning, purification, and decontamination, as well as for transforming water, or diluted electrolyte solutions, into environmentally friendly, anti-microbial, detergent, extractive and other solutions which may be synthesized on-site by special ECA devices.

For the electrochemical transformation of water and substances dissolved in it, FEMs are used as either independent electrochemical devices or in high capacity devices where multiple FEMs share a common manifold. A unique characteristic of the FEM is its functional combination, of ideal longitudinal replacement and transverse mixing of solution in the reactor. The FEM is also capable of regulating the artificially induced ion-selective conductivity of the internal ceramic oxide-zirconium diaphragm. Maximum solution meta-stability can be achieved with low power consumption.

ECA PROCEDURE

ECA uses 0.001-1.0 % saline solutions, or ordinary tap water, to generate environmentally friendly, highly active solutions of oxidizing anolyte and/or anti-oxidizing catholyte solutions. Anolyte oxidizing solutions have a pH range of 3.5 – 8.5 and an oxidation- reduction potential (ORP) of + 600 to +1200 mV. The most common application of anolyte is as a biocide at concentrations as low as one ppm to free available chlorine (FAC). Anolyte can be generated on-site for the treatment of small to extremely large volumes of water which may be injected, produced or stored during oil and gas field operations. Almost all bacteria, or biological species that occur as contaminants in petroleum field or facility operations, can be destroyed or controlled with a relatively low FAC concentration. Competitively priced anolyte solutions may be produced at the site on a mobile unit, or transported to the work site in bulk after being produced at a central generation facility. The pH of produced solutions may be regulated without the need for acid or caustic buffers, descalers and corrosion inhibitors.

A catholyte solution can be produced and used in a variety of concentrations as a mild cleaning and/or degreasing additive, and it may have applications in wellbore cleaning along with the biocidal properties of anolyte solutions. This may also help in the application of these solutions as near wellbore, reservoir cleaning treatments, after the formations' becoming damaged from previous injection, drilling or other treatment techniques.

BIBLIOGRAPHY

1. Technical Brochures ; Larry Jones; Integrated Environmental Technologies, Ltd.; 4235 Commerce Street; Little River , South Carolina 27909; USA

2. U.S Patent Numbers, 6,004,439 ; 1999 : "Apparatus for Obtaining Products by Anode Oxidation of Dissolved Chlorides of Alkaline or Alkaline-Earth Metals"

EXAMPLE SPECIFICATIONS & PERFORMANCE STANDARDS

The EcaFlo™ Model 080 contains 8 FEMs that produce anolytes and catholytes. Both anolytes and catholytes are non-toxic, environmentally friendly and yet very effective solutions for the control of unwanted micro-organisms.

Table 1
Specifications

Overall Cabinet Dimensions	34" L x 28" D x 52" H
Weight (Dry)	100 lbs.
Cabinet Enclosure	Stainless Steel, NEMA 4X
Portability	Yes, Wheel Mounted w/ Locking Capability
Power Requirements	110V AC, Dedicated 20 Amp Circuit, Standard Wall Receptacle
Water Source	Minimum 30 psi w/ Std. Garden Hose Connection
Controller	Touch Screen HMI Interface w/ CPU for Automatic Operation, Remote Operation w/ Ethernet Connection
Brine Tank	10 gal w/ Agitation Pump

Table 2
Performance Standards

Production Capacity	20 Gallons per Hour
FAC Concentrations	400-600 ppm
Current Consumption	6-8 Amps, 75 Watts per FEM
Brine Concentration	5-10 Grams per Liter
Production Run Times	12 Hours Max per 24 Hour Period, 4 Hours Max Continuous Duty Cycle

Table 3
Models and Production Capacities

EcaFlo™ Model #	**# FEMs**	**Gal/Hr**	**Gallons Per 12 Hr Day**	**Water Treated @ 50 ppm**	**Water Treated @ 5 ppm**
080 (Figs. 1& 2)	8	20	240	2,400	24,000
160	16	40	480	4,800	48,000
240	24	60	720	7,200	72,000
400	40	100	1200	12,000	120,000
800	80	200	2400	24,000	240,000

Note: Fresh solution has been shown to be an effective biocide in water at concentrations as low as 1.0 ppm FAC.

Figure 1 - 8 FEM ECA Unit Exterior

Figure 2 - 8 FEM ECA Unit, Interior

Figure 3 - An Individual FEM