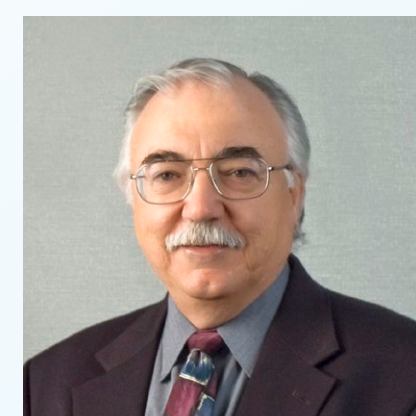


Metastable Hypochlorous Acid (HOCl) As An Oilfield Biocide

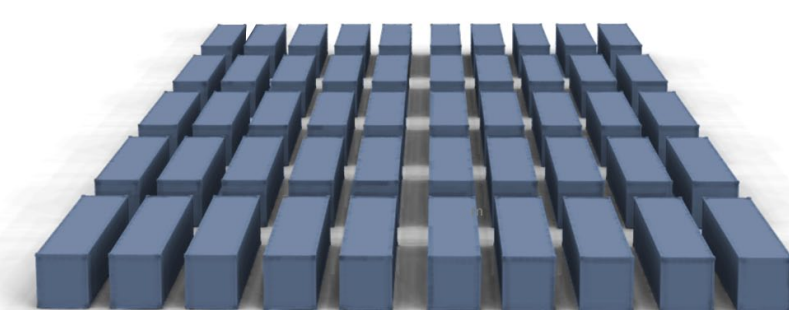


By **David N. Harry**
Chief Technical Officer
Benchmark Performance Group, Houston, Texas

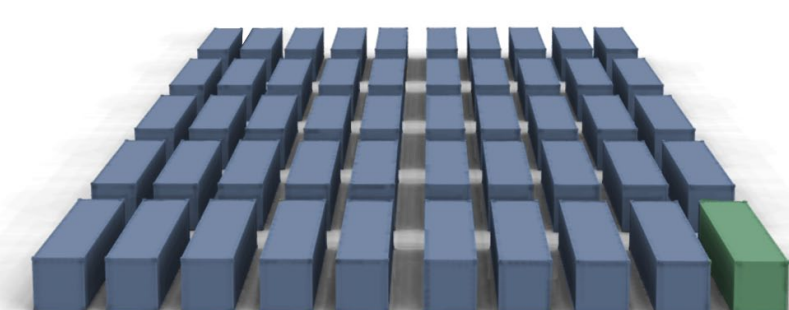
ABSTRACT

A metastable form of hypochlorous acid (HOCl) has been registered with the USEPA as a biocide suitable for use in oilfield applications. It is registered for use in 49 states, and is pending registration in the 50th (California). More than 500,000 gallons of the biocide have been used to treat water for hydraulic fracturing treatments in Pennsylvania, Louisiana, Oklahoma, and Texas. The USEPA registered product is trademarked by Integrated Environmental Technology, Ltd., the entity which manufactures the EcaFlo® devices to make the USEPA registered biocide, as EcaFlo® Anolyte. For oilfield applications, the biocide is sub-registered as Excelyte® and is patent pending for this application. The metastable form of hypochlorous acid, hereinafter referred to as ms-HOCl, is up to 100 times more effective as a biocide than hypochlorites (i.e., bleach, NaOCl), and is not DOT Corrosive, as is the case with bleach.

Identical Footprint



1,000,000 gallons of untreated frac water



1,000,000 gallons of frac water treated with 20 gallons per thousand of Excelyte® (ms-HOCl 500)

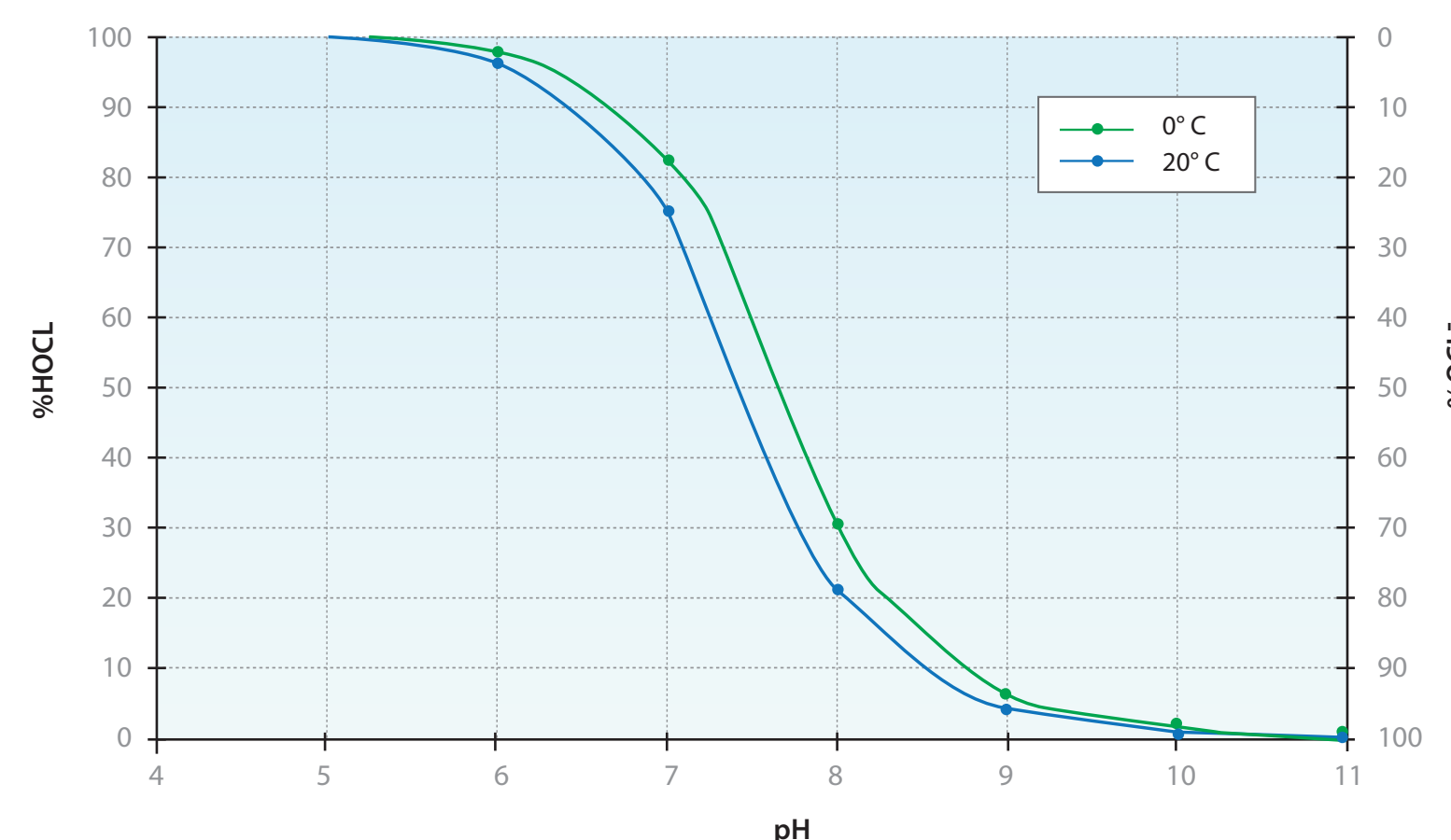
OVERVIEW

A metastable form of hypochlorous acid (HOCl) has been registered with the U.S. Environmental Protection Agency and most US States as a biocide suitable for use in treating water for oilfield applications. Registration in California is pending. The biocide provides an effective “double-edged” weapon against oilfield bacteria, combining both oxidation/reduction potential and chlorination to achieve an easily and quickly measured effectiveness.

More than 500,000 gallons of the biocide have been used to treat water for hydraulic fracturing treatments in Pennsylvania, Louisiana, Oklahoma, and Texas. The USEPA registered product is trademarked by Integrated Environmental Technology, Ltd. (IET), the entity which manufactures the EcaFlo® devices to make the registered biocide, as EcaFlo® Anolyte. For oilfield applications, the biocide is sub-registered as Excelyte® and is patent pending for use in fracturing.

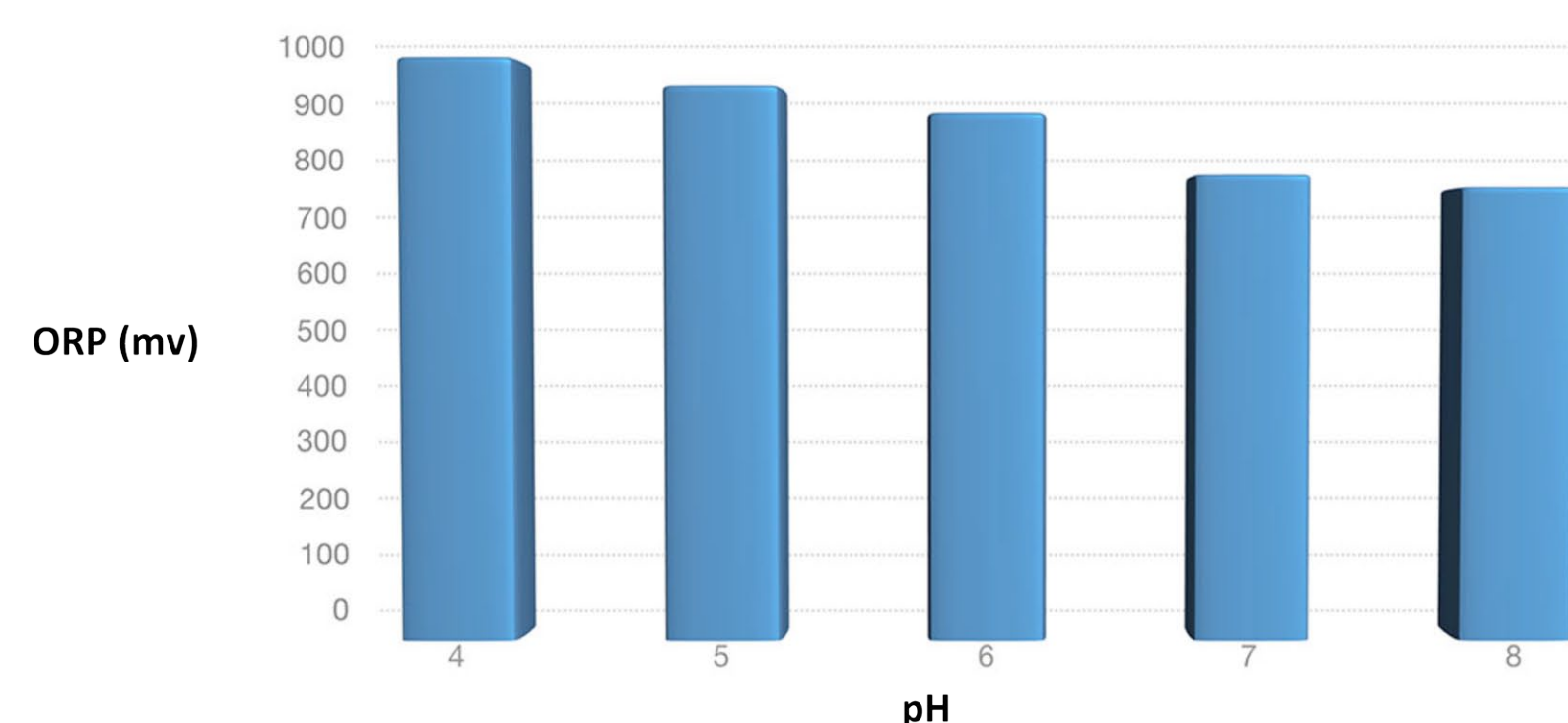
The metastable form of hypochlorous acid (ms-HOCl) is up to 100 times more effective as a biocide than hypochlorites (i.e., bleach, NaOCl), and is not USDOT Corrosive, as is the case with industrial bleach solutions. For oilfield applications, the biocide is typically provided as a pH circumneutral product possessing a minimum free-available chlorine content of 500 ppm. A method to determine the biocide requirement, called the Free-Available Chlorine (FAC) Demand test, is available. The test provides for a method to quickly determine the necessary biocide dosage without having to wait two to four weeks for the more-accepted microbiological test method results.

Ratio of HOCl to OCl- as a function of pH



Metastable hypochlorous acid has been demonstrated to be a powerful, fast acting biocide compatible with Slickwater Fracturing additives such as polyacrylamide friction reducers, microemulsions, and surfactants, and with Crosslinked Polymer fracturing fluids, such as borate crosslinked guar and zirconium crosslinked CMHPG. As a fast-acting biocide, metastable hypochlorous acid performs its function under surface conditions eliminating the need to evaluate the efficacy of the product under down-hole environments.

Relationship of ORP changes in pH

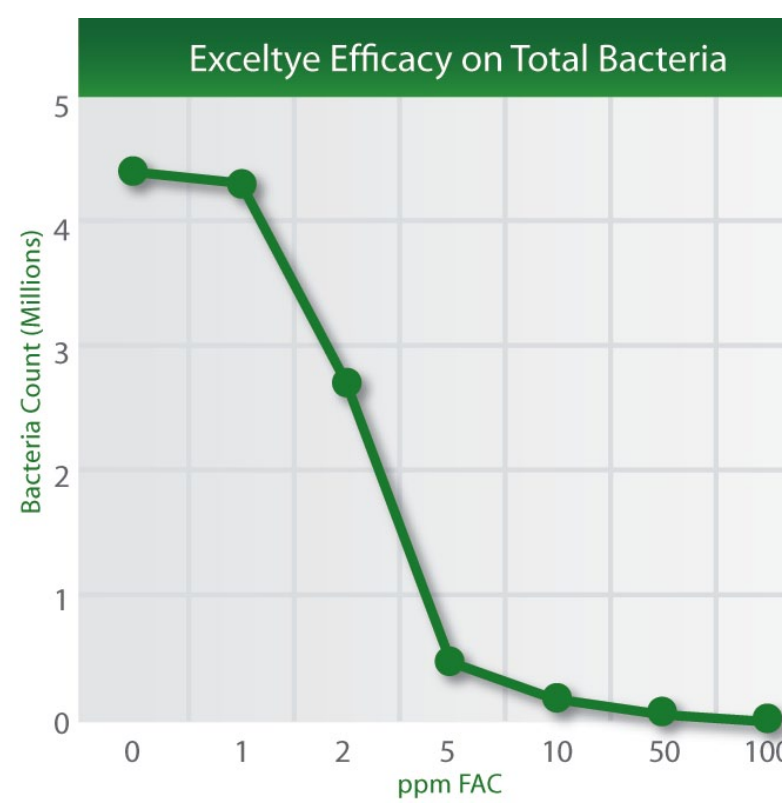


Hypochlorous acid is a mild acid which decomposes very rapidly to a very dilute sodium chloride solution. Metastable hypochlorous acid (ms-HOCl), as represented by Excelyte® manufactured by IET's EcaFlo® units, decomposes much more slowly while still responding very quickly to any bacteria present, and to oxidizable molecules such as hydrogen sulfide, providing for an active product which can be delivered to drill-sites, well-sites, or other field locations to act quickly upon iron-, sulfate-, and/or sulfate-reducing bacteria in water.

This article is confined to discussing the use and benefits of metastable-hypochlorous acid (ms-HOCl) in well fracturing applications.

Microbiological Analysis - Planktonic Enumeration			
Sample Number	GHB (QW1522)	APB (QW1529)	SRB (QW1521)
Excelyte 50mL + FR pH 7.0 (0 mins)	4.5 X 10 ⁵ /ml	4.5 X 10 ⁵ /ml	4.5 X 10 ⁴ /ml
Excelyte 50mL + FR pH 7.0 (30 mins)	1.5 X 10 ¹ /ml	1.5 X 10 ¹ /ml	0.4 X 10 ⁰ /ml
Excelyte 50mL + FR pH 7.0 (24 hours)	2.5 X 10 ¹ /ml	2.5 X 10 ¹ /ml	<0.3 X 10 ⁰ /ml
Excelyte 50mL + FR pH 7.0 (7 days)	9.5 X 10 ⁰ /ml	9.5 X 10 ⁰ /ml	<0.3 X 10 ⁰ /ml

Excelyte® at 50 gallons per thousand (5 ppm FAC net); FR - Anionic Polyacrylamide Friction Reducer; APB - Acid producing bacteria; GHB - General Heterotrophic bacteria; SRB - Sulfate reducing bacteria



Properties	Bleach	Excelyte™
Disinfectant	Strong	Strong
Biocidal Property	Weaker	Stronger
Toxicity, mammalian	Yes	No
Ionic Charge	Anionic, Negative	Neutral
Corrosivity	Strong	None
DOT Hazardous	Yes	No
Protective Equipment	Yes	No
Environment Friendly	No	Yes
Frac Fluid Compatible	?	Yes

CONCLUSIONS

1. The metastable form of hypochlorous acid (ms-HOCl) is an effective and environmentally-acceptable biocide.
2. Metastable hypochlorous acid is available to most drill-site, well-site, and other field locations, as a USEPA registered biocide. (California pending)
3. Metastable hypochlorous acid is not DOT regulated.
4. An FAC-Demand Test is available to quickly determine ms-HOCl dosage for any quality water.
5. Metastable hypochlorous acid is compatible with additives such as polymers, crosslinkers, and friction reducers, typically used in well fracturing applications.
6. As a fast acting biocide, ms-HOCl is suitable for use in wells with BHST's from 85F to 450F.

REFERENCES

Benchmark Energy Products. *Excelyte® Technical Bulletin*. 10 Jun. 2010.

Benchmark Energy Products. *Excelyte® Material Safety Data Sheet*. 21 Jul. 2009.

Dunham, Dr. Val. *IET's Ecaflo: A Two-Edged Biocide*. Coastal Carolina University, Little River, SC, 2008.

Rimassa, Shawn M., et al. *Case Study: Evaluation of an Oxidative Biocide During and After a Hydraulic Fracturing Job in the Marcellus Shale*. Paper SPE 141211, from SPE International Symposium on Oilfield Chemistry in the Woodlands, TX, 11-13 Apr. 2011.

United States Environmental Protection Agency. *EcaFlo® Anolyte: Aqueous Solution of Sodium Chloride*. 19 Aug. 2010.

Johnson, Angela and Scott Campbell. *Evaluation of Excelyte for Microbiological Control*. Commercial Microbiology, Houston, TX, 11 Feb. 2011.

Emmons, Stewart A. *Aqueous Solution for Managing Microbes in Oil and Gas Production and Method for their Production*. US PTO Patent Application 20110030959, 10 Feb. 2011.

ACKNOWLEDGEMENTS

The author would like to thank Benchmark Performance Group management for the permission to publish this work. The author would also like to thank Dustin Brown with out whose assistance this poster would not exist.

