Aegis Tech Line

Aegis Chemical Solutions

Technical Newsletter

Volume 05, January 2018

AEGIS ClO_2 WATER TREATING DIVISION

HISTORICAL PERSPECTIVE

Chlorine dioxide (ClO_2) has long served an important niche role in the oilfield water treatment market due to several highly unique oxidative and biocidal properties that differentiate it from all other available treatment options. Aegis recognized early on that these unique properties also had the potential to make ClO_2 the product of choice in the ever-expanding hydraulic fracturing water treatment market, including both freshwater and recycled produced water, as well as in other non-traditional oilfield applications.

WHY ClO_2?

First, ClO_2 has the lowest oxidation strength of any conventional oxidant, meaning it's both less corrosive and less likely to engage in undesirable side reactions with other substances present in water. Second, ClO_2 has the highest oxidation capacity, meaning that it is the most efficient of all conventional oxidants per unit volume. Third, ClO_2 has by far the highest biocidal efficacy rating per unit volume of any oxidant that can be applied on a large scale by a mobile system. Fourth, ClO_2 is a highly-penetrating non-ionic gas that can quickly pervade and treat virtually any volume of water needed. Finally, ClO_2 is a leading "green" technology that creates no harmful byproducts during use and decays rapidly to ordinary sodium chloride (i.e. table salt) following application.

AEGIS BEGINS ClO_2 BUSINESS

Based on its early recognition of chlorine dioxide's untapped potential, Aegis took first steps toward forming a specialized ClO_2 Water Treatment Division in late 2012 to augment its existing array of successful Production Chemical offerings.

The strategy Aegis followed in creating a dedicated ClO_2 Water Treating Division was to recruit both leading academic experts and highly experienced field application specialists to work together to develop innovative and cost-effective ClO_2 treatment options for the oilfield. This group concurrently trained a new generation of field operations personnel who could introduce the application technology to the market on a broad scale. Aegis also formed an exclusive arrangement with Evoqua Water Technologies (formerly Siemens AG) to supply all the Aegis oilfield ClO_2 generation equipment. Evoqua is widely recognized throughout the industry as the premier manufacturer of safe, durable, high-quality ClO_2 generation systems.

AEGIS LAUNCHES THE ClO_2 WATER TREATMENT DIVISION

When the Aegis' ClO_2 Water Treatment Division launched its first product offering in early 2013, its field operations staff was comprised of three experienced Senior Operators and five newly-trained Operator's Helpers. Equipment available to this new team consisted of five small ClO_2 generation systems ranging in production capacity from a low of 500 pounds per day (PPD) to a high of 2,000 PPD. All personnel and equipment were based in Midland, TX.

RAPID GROWTH

In the short time since its inception, Aegis' ClO_2 Water Treatment Division has grown exponentially in terms of all key metrics, including number of field personnel, equipment capabilities and service territory. As 2018 begins, Aegis currently has more than 100 Senior Operators, Operators and Operator's Helpers staged across a wide geographic region, including Midland, TX, Jourdanton, TX, Kilgore, TX, Freer, TX, Carlsbad, NM, El Reno/Hennessey, OK and Shreveport, LA. Aegis' fleet of ClO_2 generation equipment has grown to include 25 large generators ranging in production capacity from 2,000 PPD to 12,000 PPD. Aegis also has 21 smaller 500 PPD units.

TYPES OF TREATMENT

Larger ClO_2 generation systems are typically used in freshwater fracturing applications where volumetric flowrates requiring "on-the-fly" treatment can range from 80-120 barrels per minute (BPM) or more.

The 500 PPD units are normally used at produced water recycling sites where volumetric flowrates are usually much lower, i.e., 5-15 BPM. This is because produced water is often not treated on-the-fly, but rather is placed in large storage tanks or surface impoundments (ponds) for lengthy periods of time after treatment before being used in fracturing.

CUSTOMER BASE AND TREATMENT HISTORY

Aegis' ClO_2 Water Treatment Division customer base includes numerous large and mid-size oil and gas producers throughout Texas, New Mexico, Oklahoma and Louisiana. On the freshwater treatment side of the business, Aegis has completed around 2,565 fracturing projects during its five years of operation, with approximately 543,734,000, barrels of water treated. On the produced water recycling side, roughly 9,500,000 barrels have been treated at a variety of both transient and fixed customer recycling sites. Produced water recycling metrics tend to be lower than those for freshwater for several reasons. Smaller volumes of water are typically treated per unit of time, projects tend to be ongoing rather than discreet and produced water reuse has only recently become popular among customers. Because produced water recycling has now become very popular, however, it is among the fastest increasing areas of Aegis' ClO_2 Water Treatment business.

TREATMENT OBJECTIVES FOR DIFFERENT APPLICATIONS

Although treatment objectives are quite different, data from both freshwater and produced water fracturing projects demonstrate that ClO_2 is highly effective in both types of applications. In on-the-fly freshwater treatment, the principal aim is to inactivate (kill) all species of bacteria that might cause subsurface problems should they survive the fracturing fluid blender and be injected downhole into the formation. In produced water recycling, the primary objective is not to eradicate all bacterial growth, but rather to oxidize soluble ferrous iron (Fe^{2+}) to insoluble ferric iron (Fe^{3+}) and break apart bacterial emulsions so that residual oil and solids fractions, including precipitated ferric iron, can be separated from the water before it is placed in storage for subsequent reuse.

EFFECTIVENESS OF ClO_2 WATER TREATMENT

The efficacious nature of ClO_2 in treating both freshwater and produced water has been well documented through rigorous data collection and reporting procedures Aegis follows at both types of projects. Case studies which demonstrate the effectiveness of ClO_2 in both treatment scenarios have been prepared by Aegis and are available to potential customers seeking more information about ClO_2.

INNOVATION IN APPLICATION OF ClO_2

In addition to fracturing water treatment, Aegis has also extended the application profile of ClO_2 to include other oilfield uses where it's unique properties make it the treatment option of choice. Among these innovative applications are increasing the effectiveness and longevity of downhole acidizing jobs, increasing physical separation and injectivity of fluids at salt water disposal wells and production batteries, enhancing oil recovery from waterfloods and *in situ* treatment of sessile bacteria and sulfidic sludge in pipelines, storage vessels, etc.

KEY DIFFERENCES IN ClO_2 GENERATION PROCESSES

AEGIS GENERATOR DESIGN (THREE PRECURSOR PROCESS)

Aegis generators (Evoqua Water Technologies) produce a very dilute ClO_2 solution with very high purity (i.e., ≥ 95%) through the controlled reaction of three common industrial chemicals. Aegis ClO_2 generators incorporate what is known as the "gaseous chlorine/chlorite" process. This process is a two-step reaction and the precursor chemicals are sodium hypochlorite (bleach - 12.5%), hydrochloric acid (HCl - 15%), and sodium chlorite (25%).

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In the first step of the process, HCl and bleach are reacted to form chlorine (Cl_2) gas:

$$NaOCl + 2HCl \rightarrow Cl_2 + NaCl + H_2O$$

In the second step of the process, newly formed Cl_2 gas is reacted with sodium chlorite to form ClO_2 gas:

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl$$

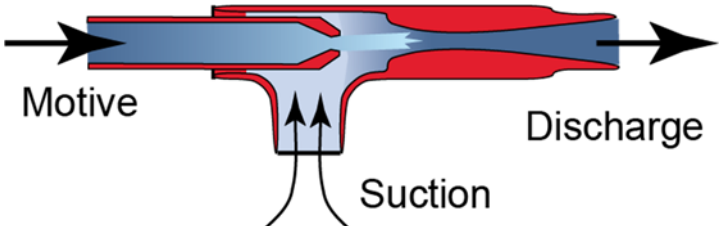
The complete reaction of the three precursor chemicals to form ClO_2 gas can be summarized as follows:

$$2NaClO_2 + NaOCl + 2HCl \rightarrow 2ClO_2 + 3NaCl + H_2O$$

These two reaction steps occur inside a small reaction **column** or chamber within the generator. The three precursor chemicals are suctioned into the reaction column or chamber by a vacuum created via the steady flow of a stream of **motive water** through an **eductor** at a defined flow rate and pressure.

The ClO_2 gas that is formed nearly instantaneously within the small reaction column or chamber is then immediately suctioned into the flowing water stream through the eductor, where it becomes a dissolved gas in water at a very low concentration level.

Eductor Illustration



ClO_2 gas leaving reaction column

The **chlorine/chlorite process** is used extensively in municipal drinking water disinfection and other industrial applications where high purity ClO_2 solutions (i.e. > 95%) are required.

The **chlorine/chlorite process** has a very rapid reaction time (i.e. milliseconds) and the process effluent is pH neutral (i.e. 2 or less units below influent pH). Because reaction times are so fast, production volumes are virtually unlimited (120,000 pounds per day or more).

ACID/CHLORITE PROCESS (TWO-PRECURSOR PROCESS)

Another commonly used ClO_2 generation process in the oilfield is known as the "**acid/chlorite" process.**

The **acid/chlorite process** generates ClO_2 using a three-step reaction process as follows:

$$NaClO_2 + HCl \rightarrow HClO_2 + NaCl \quad (1)$$

$$HClO_2 + HCl \rightarrow 2HOCl \quad (2)$$

$$2HOCl + 4HClO_2 \rightarrow 4ClO_2 + 2HCl + 2H_2O \quad (3)$$

It is chlorous acid ($HClO_2$) and not chlorite ion that is oxidized to ClO_2 in this process. No ClO_2 is produced until hypochlorous acid (HOCl) is formed. **HOCl forms relatively slowly from $HClO_2$ (i.e. several minutes).**

The **acid/chlorite process** has a maximum theoretical ClO_2 yield and efficiency of only 80% (< 80% practical efficiency) as follows:

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 2H_2O + 5NaCl$$

Because of the inherent slowness of this reaction, excess acid (i.e. several times theoretical) is typically added to drive the reaction speed.

Excess acid favors chlorine (Cl_2) formation rather than chlorous acid. In the presence of excess acid, chlorite can get converted to Cl_2 instead of chlorous acid as follows:

$$NaClO_2 + 4HCl \rightarrow 2Cl_2 + 2H_2O + NaCl$$

The use of excess acid in the **acid/chlorite process** can reduce ClO_2 yield and reaction efficiency far below 80%, and results in a product with a very low pH (<2.5) and high Cl_2 impurity.

Because the acid/chlorite reaction process is inherently slow, production volumes are also typically very limited (i.e. few hundred pounds per day maximum).

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