PRODUCED WATER RECLAMATION IN THE PERMIAN BASIN USING CHLORINE DIOXIDE

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ABSTRACT

High disposal costs and a limited availability of freshwater have led many industry players in the Permian Basin to reclaim produced water and use it in subsequent well fracturing. This reclamation process typically involves pumping produced water from numerous production batteries to a central location where it is placed in storage in large surface impoundments until such time that it is needed in fracturing operations. Unfortunately, a natural process referred to in the oil and gas industry as "souring" can occur within these impoundments during the time period when the produced water is being stored. Souring can occur quickly and render produced water completely unsuitable for subsequent use in fracturing without extensive and costly *in situ* chemical and/or physical treatment, thereby negating all incentives the industry has for recycling this water. Produced water also typically contains a high concentration of dissolved ferrous iron (Fe^{2+}), which has the potential to cause significant operational issues downhole if used in fracturing without some form of pretreatment.

This paper describes in detail how constituents present in produced water cause surface impoundment souring to occur, and demonstrates, with supporting field application data, how chlorine dioxide (ClO_2) can facilitate economical reclamation by simultaneously treating both problematic aspects of produced water prior to its subsequent storage in surface impoundments. First, ClO_2 readily oxidizes undesirable soluble ferrous iron present in produced water to the insoluble ferric form (Fe^{3+}). Second, ClO_2 helps break the natural "chain of causation" that leads to impoundment souring by destroying bacterial emulsions, which in turn allows entrained oil to effectively separate from the water, and suspended solids, including precipitated ferric iron, to drop out via gravitational settling and/or mechanical filtration. Finally, because ClO_2 is a highly penetrating gas, it quickly pervades any volume of produced water requiring treatment, thereby allowing for process adaptation to virtually unlimited flowrates.

INTRODUCTION

High disposal costs, as well as a limited availability of freshwater, have led many oil and gas producers to reclaim produced water and use it in subsequent well fracturing operations, either alone or in a blend with some percentage of freshwater. This reclamation process typically involves pumping produced water from numerous production batteries in a given area to a central location where it is placed in storage in large surface impoundments, typically ranging in capacity from around 300,000 to over 1,000,000 barrels, until such time that it is needed for use in fracturing operations, often weeks or months later.

Unfortunately, a natural process commonly referred to in the oil and gas industry as "souring," can occur within these impoundments during the time frame when the produced water is being stored. Souring can occur quickly and render produced water completely unsuitable for subsequent use in fracturing without extensive and costly physical and/or chemical treatment, thereby negating all incentives the industry has for recycling this water. Produced water typically also contains high concentrations of dissolved ferrous iron (Fe^{2+}), which have the potential to cause significant operational issues downhole if used in fracturing without some form of pretreatment.

THE SOURING PROCESS

The cause of produced water souring in surface storage impoundments is well understood [1-3]. Three key environmental factors work together to create this problem, particularly during the summer and early fall months when surface water temperatures are highly conducive to mesophilic-range bacterial growth (i.e. 25-45^{o}C). These three factors are: **1.** a heavy loading of putrescible organic matter (i.e. bacteria "food" source); **2.** an ample supply of sulfate ion (SO_4^{2-}); and **3.** development of anaerobic conditions within the system.

When water entering a surface impoundment contains a substantial amount of putrescible organic matter, aerobic bacteria, via their respiration process, rapidly deplete all available dissolved "free" molecular oxygen (O_2) present in the system in their collective attempt to metabolize this incoming matter [2]. All free molecular O_2 gets quickly depleted because the natural solubility of O_2 in water is quite low, for example only 9.2 mg/L at 20^{o}C and 760 mm Hg in freshwater [4]. The solubility of O_2 in water further decreases with increasing salt concentration. Once all free molecular O_2 has been used up, large portions of the system turn anaerobic. When this occurs, aerobic bacteria go dormant and anaerobic bacteria begin growing and reproducing, utilizing whatever "combined" sources of oxygen are present they are capable of using to complete their respective metabolic cycles, most notably nitrate (NO_3^-) or SO_4^{2-} [2-3, 5-9].

The amount of putrescible organic material entering a system can be quantified with a surrogate measure called Biological Oxygen Demand (BOD). The BOD of a system is the amount of free molecular O_2 that must be introduced into the water, in mg/L, in order for all degradable organic matter present to be metabolized solely by the action of aerobic bacteria. If free molecular O_2 is not introduced into the water at a rate equivalent to or greater than a system's BOD loading, any free O_2 that is present will be depleted quickly by aerobes and the system will turn anaerobic [10].

This natural process is problematic in oilfield surface impoundments because many anaerobic species common to the oilfield, in particular species from the genus *Desulfovibrio*, are also sulfate-reducing bacteria (SRB) that create undesirable byproducts when they utilize their preferred combined oxygen source, which is SO_4^{2-} [11]. Specifically, when SRB utilize SO_4^{2-} as their oxygen source, they form a variety of very noxious reduced sulfur compounds including sulfide (S^{2-}), bisulfide (HS^-) and hydrogen sulfide (H_2S), depending on system pH [12]. When these various sulfide species are formed in an impoundment and they encounter iron, which is common due to the near-ubiquitous presence of rust in pipes, tanks, equipment, etc., iron sulfide (FeS) is also formed [1, 13]. When this natural cycle completes itself in the oilfield environment, it is generically referred to as souring.

Data from Permian Basin production batteries shows that produced water typically contains all necessary "ingredients" to create souring conditions if stored untreated in a surface impoundment for any substantial length of time [14]. Tables 1-3 summarize BOD, SO_4^{2-} and dissolved O_2 levels observed during a random sampling of effluent water from 14 different Permian Basin batteries. BOD levels were found to range from a low of 115 to a high of 647 mg/L, with an average of 249 mg/L. The magnitude of these BOD levels is very similar to that commonly observed in domestic raw sewage [10]. Concentrations of SO_4^{2-} showed a mean value of 370 mg/L and a range of 33 to 869 mg/L. Levels above 70 mg/L are generally considered sufficient for SRB to reduce SO_4^{2-} to sulfides, and levels as low as 15 mg/L may be adequate, if other requisite conditions for souring are also present [15]. All 14 water samples showed a dissolved O_2 concentration of 0.0 mg/L.

It has historically been difficult to predict when a given surface impoundment will transform itself from desirable aerobic to undesirable anaerobic conditions due to an excessive BOD loading in the presence of an ample SO_4^{2-} supply, unless dissolved O_2 levels are being routinely monitored [14]. This point in time is critical because the overall quality of water being stored in an impoundment rapidly deteriorates in terms of its suitability for use in fracturing as soon as all dissolved free molecular O_2 present within the system is depleted and previously-dormant SRB "come to life" and start metabolizing the excessive BOD loading, converting available SO_4^{2-} to sulfides in the process.

Once all requisite conditions are in place and the souring process begins, SRB quickly enter an “exponential growth phase” during which their numbers double every few hours or less. With every doubling in SRB population comes an increase in the rate at which new sulfides are created and added to the previously formed compounds already present in the impoundment. Once started, this exponential growth pattern in SRB populations, and corresponding sulfide formation rates, continues unfettered until such time that either remedial action is taken to break the souring cycle or environmental conditions within the impoundment somehow become self-limiting, for example if all BOD is completely decomposed or all SO_4^{2-} gets consumed **[1-3]**. Neither of these self-limiting scenarios is likely to occur in Permian Basin produced water impoundments because BOD loadings tend to be both substantial and ongoing, and high SO_4^{2-} concentrations tend to be ubiquitous throughout the region **[14]**.

IN SITU TREATMENT OF SOUR IMPOUNDMENTS

Since the souring cycle is rarely, if ever, self-limiting in Permian Basin produced water impoundments, remedial treatment measures must normally be instituted at some point to break this cycle and destroy accumulated sulfides so that the water can again be made suitable for use in fracturing operations. A number of potential issues and pitfalls can, however, accompany implementation of such treatment measures.

First, treatment of sulfides throughout an entire surface impoundment can be extremely expensive. The presence of mean sulfide levels of only 15 to 30 ppm, which are commonly observed within a period of three to four weeks after a produced water impoundment first turns sour, can result in treatment costs of $0.50 to $1.00 per barrel or more, excluding labor and equipment charges **[16]**.

Second, *in-situ* treatment of sulfides only brings about a temporary improvement in water quality when an impoundment still has in place all requisite conditions for souring to occur, in particular excess BOD loading and an ample supply of SO_4^{2-}. Any water treated in such a scenario must be utilized promptly following completion of treatment. The souring cycle tends to reestablish itself very quickly after treatment ceases, usually within a period of only a few short days. Once souring begins anew, water quality again deteriorates very quickly.

Finally, some sulfide treatment products actually exacerbate longer-term sulfide formation problems within an impoundment due to their inherent composition. Peracetic acid (PAA), for example, is sometimes used to treat sulfides by oxidizing them back to SO_4^{2-}. Although PAA will oxidize sulfides *in situ* if rapidly and thoroughly mixed throughout an impoundment, it quickly breaks down to its component molecules, which are acetic acid and hydrogen peroxide. Unfortunately, acetic acid is an organic molecule which, itself, adds a substantial amount of BOD to the impoundment ecosystem, thereby providing an additional source of bacteria food for SRB to utilize when the souring cycle naturally reasserts itself in short order **[17]**.

These factors, taken together, typically make *in situ* impoundment treatment highly uneconomical. A much more cost-effective approach is to pretreat produced water prior to placing it in an impoundment in a manner that eliminates or greatly minimizes its souring potential. It should be noted that the souring process can also be forestalled or limited in scope by continuous introduction of free molecular O_2 into the impoundment to maintain aerobic conditions, usually by installation of a mechanical aeration system **[1-3]**. Unfortunately, however, when BOD levels are in the range of domestic sewage, which they typically are in produced water, the capital equipment cost and operational expense of an aeration system sufficient to prevent souring conditions from developing is often far greater than the corresponding cost of simply pretreating the water to eliminate or minimize its souring potential before it reaches the impoundment in the first place.

IMPOUNDMENT SOURING PREVENTION

Of the three key environmental variables that play a role in impoundment souring (i.e. high BOD loading, ample SO_4^{2-} supply and development of anaerobic conditions), BOD loading is the parameter most easily and economically controlled prior to impoundment storage.

Traditional oil and solids separation systems of the type already in common use at produced water reclamation sites, consisting of a gunbarrel followed by a series of gravitational settling tanks, will typically remove some amount of BOD because it usually resides mostly in the oil and solids fractions of the fluid. Unfortunately, however, anaerobic bacteria present in produced water often create emulsions that interfere with effective separation. Emulsions form at the oil/water interface within the fluid due to the accumulation of biomass, FeS and other suspended particulate matter. Ineffective physical separation, in turn, leads to excessive oil and solids carryover, and thus a high BOD loading in system effluent headed for impoundment storage.

The efficacy of a traditional oil and solids separation system in reducing impoundment BOD loading can often be greatly enhanced by adding a ClO_2 treatment step immediately prior to the point where produced water enters the system gunbarrel. The addition of a ClO_2 treatment step at this point in the process also facilitates the simultaneous, effective removal of iron contamination from the water before it is subsequently reused in fracturing.

CHLORINE DIOXIDE

Chlorine dioxide has long been recognized as a unique and versatile oxidative microbiocide. It is registered (i.e. EPA-approved) under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) for a variety of uses including drinking water disinfection, wastewater disinfection, food plant sanitation, biomedical waste treatment, cooling water system treatment and oilfield water system treatment [18-19].

Chlorine dioxide is a small, highly-reactive “free-radical” molecule that reacts with other substances primarily by means of oxidation rather than substitution. It does not chlorinate organic substances to make hazardous trihalomethanes, haloacetic acids, etc. the way free-chlorine compounds do. The reaction of ClO_2 with microorganisms or other oxidizable substances takes place in two steps. In the first stage of the reaction, the ClO_2 molecule accepts a single electron to form chlorite ion (ClO_2^-). In the second stage, ClO_2^- accepts four additional electrons to become chloride ion (Cl^-) [20-22].

The mechanism by which ClO_2 inactivates microorganisms is not completely well understood. As a general matter, however, it is known that ClO_2 destroys microbes by attacking their cell walls (or viral envelopes in the case of viruses) and interfering with essential protein formation. Because ClO_2 is an oxidative biocide, microorganisms cannot develop a resistance to it [23-24].

Chlorine dioxide is unique among conventional oxidative biocides in terms of both its physical/chemical properties and its reaction capabilities.

First, ClO_2 has the lowest oxidative strength of any conventional biocide, yet has the greatest oxidative capacity. Oxidation strength is measured in electron volts (eV) and describes how strongly an oxidizer will react with an oxidizable (i.e. reducing) substance with which it comes in contact. At 0.95 eV, ClO_2 has a lower oxidative strength than ozone (2.07 eV), paracetic acid (1.81 eV), hydrogen peroxide (1.80 eV), hypochlorous acid (1.49 eV), chlorine (1.36 eV) or hypobromous acid (1.33 eV).

Because ClO_2 has a lower oxidation strength, it is considered a more selective oxidant. Typically, ClO_2 only reacts with compounds that have activated carbon bonds such as phenols, or with other active compounds like sulfides, cyanides, and reduced iron and manganese compounds. More powerful oxidative biocides than ClO_2 will react with a wider variety of chemicals. This property can limit their overall cost-effectiveness because significant amounts of these products get used up in unhelpful side reactions. Corrosivity is also closely associated with oxidative strength. As a general rule, ClO_2 is far less corrosive than any other oxidative biocide at the low residual concentrations typically remaining after application [25-27].

Oxidative strength does not correlate well with the biocidal efficacy of a given compound. Although ClO_2 has the lowest oxidative strength, it nonetheless has among the highest efficacy ratings on a “concentration x contact time” (CT) basis of any conventional oxidative biocide **[28]**.

Oxidation capacity, as opposed to oxidation strength, refers to the number of electrons transferred during an oxidation reaction. The greater the oxidation capacity of a substance, the less of it that will be required to achieve the same biocidal treatment objective. Chlorine dioxide accepts five electrons when reacting with oxidizable substances it encounters in the environment whereas other conventional oxidants, including ozone, paracetic acid, hydrogen peroxide, hypochlorous acid, chlorine and hypobromous acid only accept two electrons. Because ClO_2 has more oxidative capacity than competing products, less is required to obtain an active residual concentration when used as a biocide **[22, 25-28]**.

Second, ClO_2 is a gaseous molecule that is highly soluble in water (e.g. roughly 3,000 mg/L at standard temperature and pressure) as well as in a wide variety of organic materials, including petroleum components. When dissolved in water, ClO_2 exists as a non-ionic gas, meaning that it retains its distinct chemical structure and biocidal properties across a wide 2 to 10 pH range. In contrast, for example, Cl_2 is only one-tenth as soluble as ClO_2 and quickly dissociates to form hypochlorous acid and hydrochloric acid when placed in water. These two ionic chlorine species are both more corrosive and less effective as biocides than the original chlorine gas **[29]**.

The high solubility of ClO_2 has important implications for biocidal treatment efficacy. Because it is extremely soluble in both water and organic substances, ClO_2 is very effective at penetrating through biofilm layers that help protect underlying microorganisms in contaminated systems from other oxidative and non-oxidative biocides. This extreme solubility and penetrability often make ClO_2 the biocide of choice for controlling stubborn biofilms in industrial cooling water systems and oilfield water systems, both downhole and on the surface **[30-32]**.

There are numerous reaction pathways through which ClO_2 can be created **[19, 22, 33-34]**. A very popular option in the oilfield environment is the molecular chlorine/chlorite process, which first pre-reacts sodium hypochlorite (NaOCl) with hydrochloric acid (HCl), then reacts the resultant Cl_2 gas with sodium chlorite ($NaOCl^-$) to form ClO_2.

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

The molecular chlorine/chlorite process has certain advantages over competing generation methods. First, ClO_2 generated by this process is extremely pure (100% theoretical generation efficiency), meaning no potentially harmful byproducts are formed during the reaction process. Second, the molecular chlorine/chlorite process provides virtually unlimited ClO_2 production capacity per unit time because the reaction occurs almost instantaneously (e.g. 120,000 pounds per day or more). Finally, this process generates a solution with near-neutral pH, which makes it less corrosive than ClO_2 solutions generated with other methods.

Another common means of generating ClO_2 in the oilfield involves use of the mineral acid/chlorite process, with either HCl or sulfuric acid (H_2SO_4) serving as the mineral acid:

HCl/Chlorite Process

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

H_2SO_4 /Chlorite process

$$\mathbf{4NaClO_2 + 2H_2SO_4 \rightarrow 2ClO_2 + HClO_3 + 2Na_2SO_4 + H_2O + HCl}$$

The mineral acid/chlorite process has several disadvantages compared to the molecular chlorine/chlorite process. First, the maximum ClO_2 generation efficiency that can be achieved is far lower. When HCl is used as the mineral acid, the maximum theoretical process efficiency is only 80 percent. When H_2SO_4 is used, the maximum theoretical efficiency drops to only 50 percent. This reduced generation efficiency results in significant chlorite being wasted or converted into potentially harmful byproducts, such as free-chlorine compounds, which can chlorinate organic materials. Second, the mineral acid/chlorite reaction to form ClO_2 occurs very slowly (i.e. several minutes). This slow reaction speed inherently limits the amount of ClO_2 that can be generated per unit time (e.g. 1,000 pounds per day or less). Finally, because the acid/chlorite reaction is extremely slow, excess acid is typically added to increase reaction speed. Excess acid favors free-chlorine compound formation and lowers the pH of generated solution to the point where it can become highly corrosive (i.e. < 2.5).

$$\mathbf{NaClO_2 + 4HCl \rightarrow 2Cl_2 + 2H_2O + NaCl}$$

A third common means of generating ClO_2 involves the use of sodium chlorate ($NaClO_3$) (as opposed to chlorite, hydrogen peroxide (H_2O_2) and H_2SO_4:

$$\mathbf{NaClO_3 + {}^{1}/_{2}H_2O_2 + {}^{1}/_{2}H_2SO_4 \rightarrow ClO_2 + {}^{1}/_{2}O_2 + {}^{1}/_{2}Na_2SO_4 + H_2O}$$

This chlorate-based process is capable of generating ClO_2 solutions with purity levels equivalent to the molecular chlorine/chlorite process (i.e. 100% theoretical efficiency). This technology is, however, generally viewed as being inappropriate for the oilfield environment because its generation byproducts include substantial amounts of both free molecular O_2 and SO_4^{2-}, neither of which is desirable in the oilfield due to their relationships to either corrosion or sulfide formation.

There are several reasons why, once generated, ClO_2 is highly effective in reducing BOD levels and removing iron from produced water prior to impoundment storage. First, because ClO_2 is a highly soluble and penetrating gas, it quickly and thoroughly pervades nearly any volume of produced water that requires treatment. Second, as a potent oxidant and microbiocide, ClO_2 rapidly converts soluble ferrous to insoluble ferric iron, breaks apart emulsions upon contact by oxidizing both biomass and sulfides, and inactivates bacteria that cause emulsions to form in the first place, thereby allowing oil to effectively separate from water, and solids, including precipitated ferric iron, to drop out quickly via gravitational settling. Third, ClO_2 technology is readily adaptable to automation, which makes unmanned, around-the-clock treatment both feasible and economical.

In addition to reducing BOD loading through enhanced oil and solids separation, ClO_2 also raises the oxidation-reduction potential (ORP) of treated water, which in turn helps prevent SRB from utilizing SO_4^{2-} to create sulfides, even in the absence of free molecular O_2. It is believed that SRB are normally unable to complete their metabolic cycle when the ORP of water is higher than -100 millivolts (mV) **[35-38]**. An ORP value of +350 mV or higher is typically targeted when treating produced water with ClO_2.

FIELD APPLICATION DATA

The efficacy of treating produced water with ClO_2 prior to impoundment storage was studied at an existing Permian Basin reclamation site for approximately 40 days during the summer of 2017. This facility was interested in trying ClO_2 largely because the technology then in use at the site, PAA and sodium hypochlorite oxidation followed by dissolved air flotation and walnut shell filtration, was unable to treat the large volumes of produced water needed by the facility on a timely basis. This site's treatment needs were highly variable, and ranged from a low of roughly 2,500 barrels per day (BPD) to a high of well over 20,000 BPD.

A conventional oil and solids separation system consisting of a 750-barrel gunbarrel followed by a series of four 500-barrel settling tanks was already in use at the facility when ClO_2 treatment was instituted. A 500 pound-per-day molecular chlorine/chlorite ClO_2 generation system was installed at the facility in early July and plumbed to inject ClO_2 into the incoming produced water stream at a point just prior to where the water first entered the gunbarrel. Unfortunately, this conventional system was so small relative to the flowrate passing through it that it simply couldn't provide adequate retention time for natural separation and gravitational settling to occur post ClO_2 treatment before being discharged to the surface impoundment (i.e. an average retention time of less than five hours). As such, a mobile mechanical filtration system employing

25 micron filters was also added at the tail end of the system to help catch solids, including precipitated ferric iron, that otherwise would have fallen out in the system's settling tanks had they been properly sized for the produced water flowrates needed at the facility.

The chemical composition of produced water entering the system varied significantly over time. The ClO_2 concentration required for effective treatment therefore varied significantly as well. To insure effective treatment occurred at all times regardless of variations in incoming produced water composition, a treatment regimen was employed whereby the injected ClO_2 concentration was adjusted continually to achieve a steady-state oxidation-reduction potential (ORP) value between +350 mV to +450 mV at the point of system discharge from the last settling tank to the impoundment.

Several parameters were used to assess treatment process performance. First, the volume of water treated each day with ClO_2 was measured via installed system flowmeters. Second, concentrations of iron (total) and residual oil present in produced water entering and leaving the system, as well as in the post-treatment surface impoundment, were measured on a weekly basis to evaluate the effectiveness of ClO_2 in removing these problematic constituents. Finally, BOD levels present in the surface impoundment were measured monthly to assess the efficacy of ClO_2 in reducing a heightened souring potential observed before ClO_2 use began at the facility.

The respective volumes of produced water treated each day with ClO_2 are shown in Table 4, along with a summary of the lowest, highest and average daily volumes. Average concentrations of iron and oil measured in system influent, system effluent and the post-treatment surface impoundment, both before and after implementation of the ClO_2 treatment process, are shown in Table 5. Iron concentrations measured in the post-treatment surface impoundment during weekly sampling events while ClO_2 treatment was in use are shown in Table 6. Average BOD concentrations measured in the post-treatment surface impoundment during three monthly sampling events prior to implementation of the ClO_2 treatment process and two months during process implementation, are presented in Table 7.

Results demonstrated that the ClO_2 treatment process satisfied all facility requirements in terms of both the quantity and quality of produced water needed for fracturing operations.

With respect to water quantity, the data showed there were no practical lower or upper limits on the volume of produced water that could be treated successfully with ClO_2 in a given 24-hour period. Treated produced water volumes ranged from a low of 2,473 BPD to a high of 23,661 BPD. The treated volume exceeded 10,000 barrels on 63% of study period days. The average daily treated volume was 14,184 barrels.

With regard to water quality, the data showed the ClO_2 treatment process greatly reduced concentrations of all three constituents of concern (i.e. total iron, residual oil and BOD) present in the surface impoundment where treated produced water was stored prior to its subsequent reuse in fracturing.

Before ClO_2 use, iron concentrations in the surface impoundment were measured to be in the 15 mg/L range. With ClO_2 use, iron concentrations in the impoundment fell to an average of only 5.7 mg/L, an approximate 62% reduction. Even more notable, iron levels measured in the impoundment fell progressively from the initial 15 mg/L level throughout the study period to a low of only 2 mg/L during the final sampling event, an 87% overall reduction. Had the conventional oil and solids separation system in use at the site been properly sized to provide adequate retention time, it is likely that the iron concentration could have been reduced further, or eliminated entirely.

A substantial reduction in residual oil concentration was also observed while ClO_2 was in use at the facility. Residual oil levels present in influent produced water were typically measured to be in the range of approximately 200 mg/L (i.e. 196 mg/L average). Prior to ClO_2 use, much of this entrained oil appears to have been passing straight through the facility into the surface impoundment, where a concentration of 172 mg/L was still measured. After ClO_2 use began, the average residual oil concentration measured in both system effluent and the surface impoundment fell to the approximate 40 mg/L range, an 80% mean reduction. Again, had the conventional oil and solids separation system been properly sized to provide adequate retention time, it is likely the residual oil concentration could have been reduced further, or eliminated entirely.

Finally, an average BOD reduction of similar magnitude was also observed in the impoundment while ClO_2 was being used, from 250 mg/L before use to 68 mg/L after (i.e. a reduction of roughly 73%). This BOD level decrease was likely attributable to both the reduced amount of residual oil making its way into the impoundment, and the facility's decision to terminate PAA use at the site, which was adding supplemental BOD to the system above and beyond that already present in the residual oil.

All data collected during the approximate 40-day study period showed ClO_2 to be a viable option for treating produced water destined for reuse in fracturing. The process proved capable of treating almost unlimited volumes of produced water on a daily basis to a very high standard of quality. Concentrations of all three constituents of concern present in treated produced water were reduced dramatically from levels observed before ClO_2 use began at the site. Iron concentrations were reduced 87%, residual oil concentrations an average of 80% and BOD concentrations an average of 73%. The ClO_2 treatment process also proved economical, while still satisfying all facility expectations.

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Table 1

Typical Produced Water BOD Levels

Production Battery	BOD (mg/L)	Production Battery	BOD (mg/L)
1	121	8	233
2	271	9	296
3	226	10	164
4	263	11	220
5	248	12	172
6	115	13	147
7	360	14	647

Table 2

Typical Produced Water SO_4^{2-} Levels

Production Battery	SO_4^{2-} (mg/L)	Production Battery	$SO4^{2-}$ (mg/L)
1	396	8	33
2	459	9	686
3	712	10	315
4	242	11	132
5	117	12	712
6	169	13	81
7	869	14	260

Table 3

Typical Produced Water Dissolved O_2 Levels

Production Battery	O_2 (mg/L)	Production Battery	O_2 (mg/L)
1	0.0	8	0.0
2	0.0	9	0.0
3	0.0	10	0.0
4	0.0	11	0.0
5	0.0	12	0.0
6	0.0	13	0.0
7	0.0	14	0.0

Table 4

Daily Treated Water Volumes

Date	BPD Treated	Date	BPD Treated	Date	BPD Treated	Date	BPD Treated
7/13	8,255	7/24	11,805	8/04	10,180	8/15	13,525
7/14	2,473	7/25	13,555	8/05	10,547	8/16	13,536
7/15	2,769	7/26	19,594	8/06	7,826	8/17	13,146
7/16	4,699	7/27	19,194	8/07	9,064	8/18	11,003
7/17	8,784	7/28	12,136	8/08	11,981	8/19	11,905
7/18	8,158	7/29	9,054	8/09	13,133	8/20	11,271
7/19	8,033	7/30	9,485	8/10	19,280	8/21	11,561
7/20	9,316	7/31	6,193	8/11	23,407	8/22	5,567
7/21	10,070	8/01	10,699	8/12	18,398	**Low**	**2,473**
7/22	9,810	8/02	10,505	8/13	23,661	**High**	**23,661**
7/23	10,506	8/03	11,898	8/14	15,632	**Avg.**	**14,184**

Table 5

Mean Iron and Oil Concentrations

Sample Location	Before ClO_2		With ClO_2	
	Total Iron (mg/L)	Oil (mg/L)	Total Iron (mg/L)	Oil (mg/L)
System Influent	59	235	84	196
System Effluent	-	-	8.2	40
Impoundment	15	172	5.7	41

Table 6

Impoundment Iron Concentrations

Sample Location	Sample Date	Total Iron (mg/L)
Impoundment	7/14	14
Impoundment	7/24	4
Impoundment	7/31	3
Impoundment	8/07	-
Impoundment	8/14	2

Table 7

Mean Impoundment BOD Concentrations

Sample Location	Before ClO_2	With ClO_2
Impoundment	250 mg/L	68 mg/L