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Hybrid reactor based on combined cavitation and ozonation: From concept to practical reality

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ABSTRACT

The present work gives an in depth discussion related to the development of a hybrid advanced oxidation reactor, which can be effectively used for the treatment of various types of water. The reactor is based on the principle of intensifying degradation/disinfection using a combination of hydrodynamic cavitation, acoustic cavitation, ozone injection and electrochemical oxidation/precipitation. Theoretical studies have been presented to highlight the uniform distribution of the cavitational activity and enhanced generation of hydroxyl radicals in the cavitation zone, as well as higher turbulence in the main reactor zone. The combination of these different oxidation technologies have been shown to result in enhanced water treatment ability, which can be attributed to the enhanced generation of hydroxyl radicals, enhanced contact of ozone and contaminants, and the elimination of mass transfer resistances during electrochemical oxidation/precipitation. Compared to the use of individual approaches, the hybrid reactor is expected to intensify the treatment process by 5–20 times, depending on the application in question, which can be confirmed based on the literature illustrations. Also, the use of Ozonix® has been successfully proven while processing recycled fluids at commercial sites on over 750 oil and natural gas wells during hydraulic operations around the United States. The superiority of the hybrid process over conventional chemical treatments in terms of bacteria and scale reduction as well as increased water flowability and better chemical compatibility, which is a key requirement for oil and gas applications, has been established.

1. Introduction

Generally, water treatment takes place by various chemical and physical means [1,2], but the drawbacks of all these techniques outweigh their efficacy [3–5]. The chemical methods, involving the use of chlorine, hydrogen peroxide etc. are limited by severe mass transfer limitations resulting in lower disinfection rates. Also, some of the chemical methods produce non-acceptable residual components [6]. For example, chlorine, which is widely used in water treatments, results in the formation of mutagenic and carcinogenic agents in water and wastewater effluents. Also, chlorine dioxide, which is gaining popularity in the oil and gas business and other industries as an alternative to chlorine or ozone, suffers from disadvantages such as: requirement of onsite generation, stability issues and limited applicability especially in the case of microorganisms producing colonies and spores, which agglomerate in spherical or large clusters. Chemical treatment of such clusters may destroy microorganisms on the surface leaving the innermost organisms intact. Furthermore, the efficacy of any disinfection method depends on a number of factors, including solution conditions (e.g., temperature, turbidity) and variable microorganism resistance to inactivation and hence the treatment strategy cannot be generalized. The potency of certain physical techniques, such as ultraviolet light, is limited by light scattering [7], absorbing solutions [8], or when microorganisms are capable of photo-reactivation (self-repair). Another disadvantage of the chemical methods is limited effectiveness when chemical flocculation is used as a pretreatment stage. The removal of fine particles such as clays from water is usually achieved by flocculation using chemicals such as aluminum sulfate. The flocs can entrap bacteria and their spores protecting them from chlorination. The vast majority of floc particles are removed, but one or two may pass through the system unaffected by the final disinfection stage. Thus, there is a need for developing some alternate techniques for water disinfection. Another important requirement of the alternative water treatment is that the treatment approach should be able to reduce the scale formation, which possibly will avoid the use of any external scale inhibitors in the process giving a superior treatment approach.

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Studies have shown that the combination of two or more advanced oxidation treatment technologies leads to better disinfection rates [9]. This is equally applicable for the industrial wastewater treatment where a complex load of pollutants is expected to be present. The efficacy of conventional methods will be decreased for these high loading effluents, which also contain some of the bio-refractory compounds. In the case of industrial wastewater treatment, the efficacy of the treatment process depends strongly on the rate of generation of free radicals along with the extent of contact of the generated radicals with the contaminant molecules. Therefore, the reactor and the overall process should be designed efficiently to maximize both of these parameters. The similarity between the mechanism of destruction among different advanced oxidation techniques and some of their common optimum operating conditions point towards the synergism between these methods and the fact that the combination of different advanced oxidation processes should give better results as compared to the individual techniques. Moreover, combining individual techniques with other techniques can eliminate drawbacks of the stand-alone technology. Considering the enhanced effectiveness of the hybrid techniques and, in coherence with the policy of developing non-chemical based treatment schemes, a novel combinative treatment process has been developed and commercialized. The patented technology, described as **Ozonix**®, utilizes the synergistic effects of ozone, hydrodynamic cavitation, acoustic cavitation and electrochemical oxidation/precipitation. The main mechanism for intensification is expected to be generation of additional oxidation mechanisms and elimination of the mass transfer resistances due to the turbulence generated under cavitating conditions. The Ozonix® process employs a powerful, liquid chemical-free combination that provide very high rate treatment for bacteria, scale, organics (oil, grease, volatiles) and hydrogen sulfide while producing a fluid that is more compatible with other processing requirements. Ozonix® treatment also reduces Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) by fully oxidizing hydrocarbon compounds and some real time operations have shown reductions of 400 mg/L of hydrocarbon compounds down to less than 40 mg/L with one pass. The Ozonix® solution is scalable, modular and can be customized to fit a particular water treatment need.

The main focus of the present work is to describe the technology and its operation on an industrial scale supported with actual commercial scale data. The purpose of giving the results for disinfection and variations in the water quality is to demonstrate effectiveness of the technology based on the combined oxidation treatment in treating contaminated water. The work is very important considered that such depictions of successful applications of cavitation based reactors at commercial scale are very scarce. A recent work by Abramov et al. [10] also focused similar description of ultrasound based technology for enhancement of oil recovery from failing wells. The described technology involves lowering a source of power ultrasound to the bottom of the well either for a short treatment before removal or as a permanent placement for intermittent use. It has been reported that an average productivity increase of nearly 3-fold can be achieved for this type of production well using the combined ultrasound with chemical treatment technology.

2. Background of selecting different oxidation mechanisms in the hybrid reactor

Ozone is a very powerful oxidizing agent (E° = + 2.07 V) that can react with most species containing multiple bonds (e.g., C=C, C=N, N=N, etc.) at high rates and also result in a significant degree of disinfection. These oxidations are simple and the process only requires contact of ozone with the chemical constituents. Ozone is nonselective and it usually reacts with multiple compounds simultaneously; this is because the mechanism of degradation by ozone is often dependent on how it reacts with contaminants, hence an appropriate reaction pathway must exist for ozone to react with a substrate. In other words, although the thermodynamics for ozone-induced oxidation may be favorable (due to ozone's high reduction potential), kinetic factors will most often dictate whether ozone will give the required degree of treatment in a reasonable time frame. Thus, a combination of ozone with other advanced oxidation techniques, such as hydrodynamic and acoustic cavitation, can result in better contact and mass transfer rates, which result in a significant degree of process intensification [9]. Also, once an ozone molecule oxidizes a bacteria cell it leaves behind oxygen (O_2) in the water. This oxygen then passes through an electrical and ultrasonic field in the reactor creating other very powerful oxidizing agents such as hydroxyl radicals (E° = +2.80 V). Hydroxyl radicals continue to react with organic material in the water.

Cavitation is defined as the phenomena of the formation, growth and subsequent collapse of micro-bubbles or cavities occurring in extremely small timeframes (milliseconds) while releasing large magnitudes of energy [11–13]. It should be also noted that though the release of energy is over a very small pocket (i.e., micro-bubble size), cavitation events occur at multiple locations simultaneously and hence increase the overall effect. Some of the effects of cavitation include the generation of hot spots, production of highly reactive free radicals, continuous cleaning as well as increase in the surface area of the solid catalysts, enhancement in the mass transfer rates due to turbulence generated as a result of acoustic streaming, etc. Two main types of cavitation phenomena have been shown to produce the desired intensities for water and wastewater treatment. These are described as acoustic cavitation, which is based on the use of ultrasonic irradiations; and hydrodynamic cavitation, which is based on the use of alterations in the fluid flow for the generation of cavities [14]. The mechanism of water treatment due to cavitation has been mainly attributed to the mechanical (e.g., generation of turbulence, liquid circulation currents and shear stresses), chemical (generation of active free radicals) and heat effects (generation of local hot spots i.e., condition of very high temperature and pressure locally).

Electrochemical oxidation/precipitation has been found to be an environmentally benign technology able to completely mineralize non-biodegradable organic matter and eliminate nitrogen species and hence can be effectively applied to the water treatment [15]. The inherent advantage is its environmental compatibility as it uses a clean reagent, the electron, and there is little or no need for the addition of chemicals. The Ozonix® process inhibits scale through electrochemical oxidation/precipitation. The oxidation reaction takes place at the anode, which is positively charged, and the reduction reaction takes place at the cathode, which is negatively charged. Divalent cations combine with CO_2 and SO_2 generated from the oxidation of organic material. These precipitated hardness salts are then broken into smaller suspended particles in the process and passed through the system. These salt particles are chemically inert, suspended in solution, and will no longer contribute to scale deposition or interfere with other chemical additives used during fracturing operations (such as gels or friction reducers). Electrochemical oxidation/precipitation is generally characterized by simple equipment, easy operation and brief residence time of the effluents. Electrochemical processes often have lower temperature and pressure requirements than those of equivalent non-electrochemical counterparts such as incineration and supercritical oxidation. As a consequence, volatilization and discharge of unreacted wastes is avoided. However, there are some drawbacks such as mass transfer limitations and high-energy requirements, which make the application of electrochemical oxidation/precipitation alone in water treatment facilities uneconomical. The efficacy of electrochemical oxidation/precipitation can be further enhanced if it is effectively combined with cavitation (eliminates mass transfer resistances). There have indeed been some recent literature studies reporting the beneficial effects of combining the electrochemical oxidation/precipitation with sonochemical reactors where cavitation is generated using ultrasonic irradiation [16,17].

Overall, the efficacy of the electrochemical process, if applied individually for water treatment, is limited as it depends strongly on the rate of generation of the oxidizing agents along with the extent of contact of the generated radicals/oxidants with the contaminants. Based on the principle of using combined oxidation, the Ozonix® reactor utilizes the combination of ozone, cavitation and electrochemical oxidation/precipitation. The main benefits of this broad spectrum advanced oxidation process are expected enhanced treatment rates attributed to the generation of hydroxyl radicals, enhanced contact of ozone molecules with the contaminants due to the turbulence generated in the reactor and elimination of mass transfer resistances in the electrochemical oxidation/precipitation cell that facilitates the contact of the contaminants with the electrodes. The combined effect of all these factors should result in intensified treatment process with reduction in the treatment time of the process and lower energy consumption. Though the exact benefits are dependent on the process stream, specifically the constituents and the average physicochemical properties of the medium, it is expected that the intensification in the treatment rates using the hybrid cavitational reactor as described using the combination of the specific oxidation processes outlined above would be in the range of 5–20 times than that which would have been obtained using individual oxidation processes.

3. General specifications of the reactor

The hybrid mobile Ozonix® reactor is a completely self contained 53 ft long mobile trailer with an onboard diesel generator and fully automatic PLC controls. The unit can be operated at variable flow rates, and mainly operates on the combination of hydrodynamic cavitation, acoustic cavitation, ozone and electrochemical oxidation/precipitation. Fig. 1 shows a pictorial view of the reactor and also a block diagram showing different zones in the reactor which are effective in wastewater treatment. The reactor first uses static mixing elements to generate hydrodynamic cavitation. Static mixers are a series of proprietary geometric mixing elements fixed within a pipe (tube) with multiple orifices which use the energy of the flow stream to create mixing between two or more fluids. The optimized design of static mixers achieves the greatest amount of mixing with the lowest pressure loss possible. The multiple holes in the static mixers act as localized orifices, dropping the pressure of the fluid locally and allowing the formation of cavitation bubbles. As these cavitation bubbles are carried away with the flow, they collapse or implode in the zone of higher pressure. The collapse of these cavitation bubbles at multiple locations produces localized high energy conditions such as shear, high pressure, heat, light, mechanical vibration, etc. The generation of hydrodynamic cavitating conditions in the reactor is expected to increase the overall oxidation capacity of the reactor [18] and acts synergistically with acoustic cavitation occurring later in the treatment stage.

Next in the system is the ozone injection zone followed by the acoustic cavitation zone. Acoustic cavitation is achieved by using multiple transducers attached to the tubular cross-section of the main reactor. In order to achieve uniform mixing of ozone with the effluent stream and enhance treatment rates, the Ozonix® reactor is equipped with multiple transducers attached to the wall

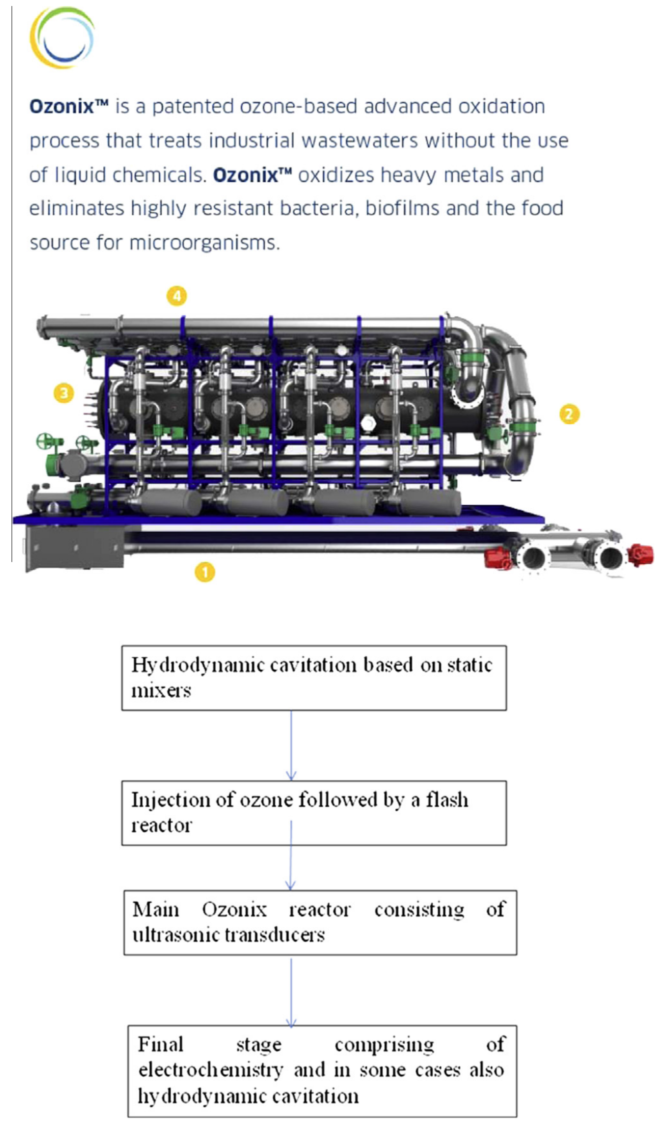

Fig. 1. Schematic representation of the Ozonix® reactor (1: Hydrodynamic cavitation; 2: Ozone injection zone, 3: Main reactor vessel with ultrasound 4: Final stage based on electrochemistry) and block diagram showing the zones encountered by the flowing effluent.

of the reactor. Kumar et al. [19] showed that the cavitational activity distribution is much better in a reactor with multiple transducers (total of 18 transducers with 3 each on six sides of the hexagon as described in the published work) as compared to a reactor with a single transducer where it is just concentrated near the horn surface. The turbulence created by the acoustic streaming is also expected to eliminate ozone mass transfer limitations.

The combined operation of ozone and cavitation ensures that in addition to direct attack by ozone, contaminants also get degraded by hydroxyl radicals thereby increasing the efficacy of the treatment. The release of free radicals during ultrasonic irradiation in the presence of ozone is actually a two-step process [20,21] taking place in the cavitating bubble due to the conditions of very high temperatures. Additionally, hydrogen peroxide formed by the recombination of hydroxyl radicals reacts with ozone via Peroxone process. The reaction takes place at a significant rate at high pH values ($pH > 8$) and results in the additional production of hydroxyl radicals.

The final process in the Ozonix® reactor is electrochemical oxidation/precipitation taking place on multiple electrodes. These

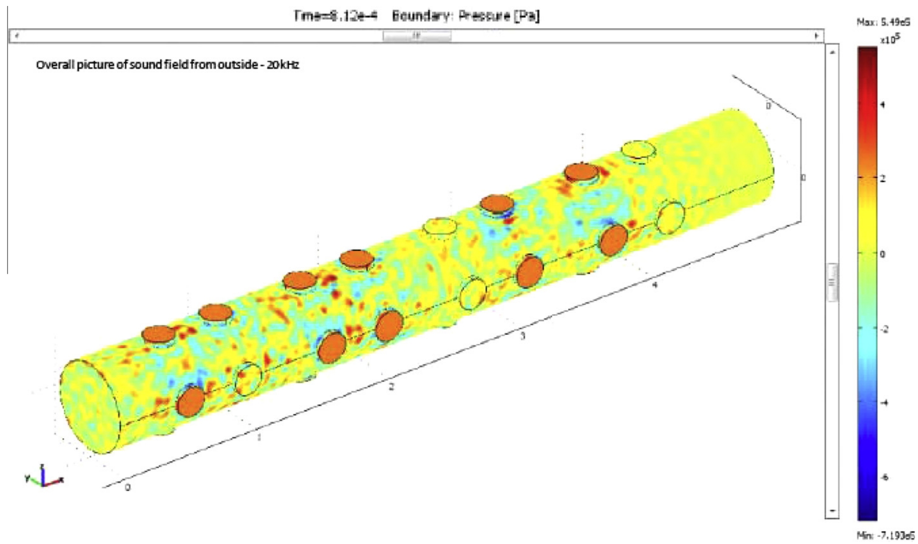

Fig. 2. The distribution of the cavitational activity in the main Ozonix® reactor as obtained using theoretical simulations.

electrodes are non-active and hydroxyl radicals generated at the electrode surface assist the oxidation. The turbulence generated by acoustic cavitation helps in eliminating the mass transfer resistances associated with electrochemical oxidation/precipitation.

4. Theoretical simulations for understanding the cavitational activity distribution and the mixing conditions in the Ozonix® reactor zone

The cavitational activity is not uniformly distributed in all the conventional designs of sonochemical reactors and is mostly concentrated close to the transducers, especially in the case of low frequency reactors [22]. To predict cavitational activity in the main reactor in terms of sound pressure field distribution, the wave equation was solved using the finite element simulation of the sound field. The wave equation is given as:

$$\nabla\left(\frac{1}{\rho}\nabla P\right) - \frac{1}{\rho c^2}\frac{\partial^2 P}{\partial t^2} = 0 \quad (1)$$

where ρ is the density of the liquid medium and c is the speed of the sound in liquid medium.

The acoustic pressure P is a function of frequency of irradiation as follows:

$$P = p_0 sin(\omega t \pm kx) \quad (2)$$

where ω is angular frequency and k is wave number.

When applying the wave equation to the propagation of an ultrasonic wave in the liquid medium, the following assumptions can be made:

(1) Linear propagation of the sound wave through the medium.
(2) Shear stress is negligible.
(3) Density and compressibility of liquid medium are constant.
(4) Pressure is time harmonic i.e., $p(r,t) = p(r)e^{i\omega t}$.

These assumptions were used to derive the Helmholtz equation:

$$\frac{\nabla^2 P}{\rho} - \frac{\omega^2}{\rho c^2} p = 0 \quad (3)$$

Eq. (3) was solved by using a three dimensional acoustic module in the Comsol Multiphysics software, which considers the finite element method. The solution of this equation gives the spatial variation of the acoustic pressure in the reactor. The transient analysis gives the real time sound pressure field in the reactor without making the assumption of harmonic pressure variation. In solving the equation, the following boundary conditions were applied:

(1) At the tip of the transducer, $p = p_0$ (entire ultrasound energy is entering into the reactor through the tip of transducer). For time harmonic analysis, P_0 is the initial amplitude of the harmonic source.
(2) At the wall of reactor, $p = 0$ (pressure amplitude vanishes near the wall).

The obtained result, when all the transducers were assumed to be vibrating at the resonating frequency and maximum amplitude based on the rated power dissipation levels, is depicted in Fig. 2 from which it is clearly visible that the sound field is very well developed in the region in front of the ultrasound irradiating faces of the transducers. Because of the presence of the transducers on four sides, the ultrasonic field is developed from all four sides caus-

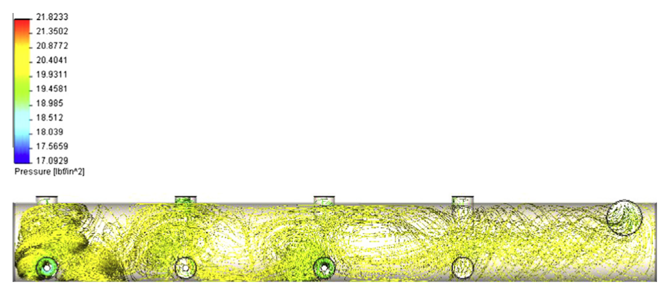

Fig. 3. Pressure distribution in the main Ozonix® reactor.

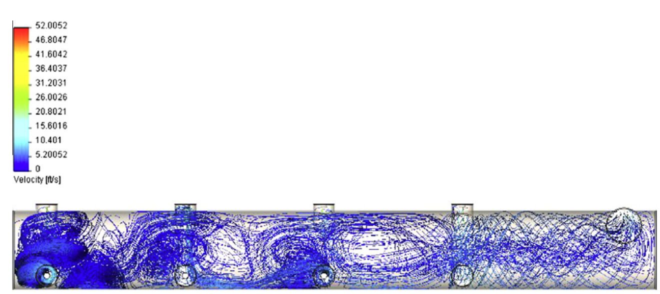

Fig. 4. The velocity pattern in the main reactor.

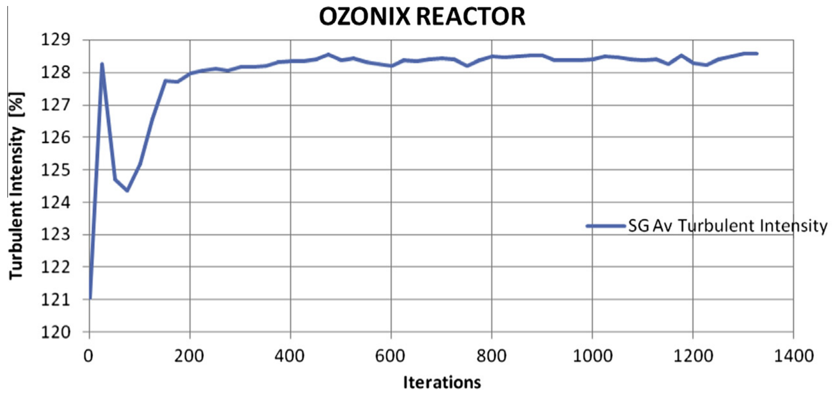

Fig. 5. The level of turbulence in the main reactor as predicted using flow simulations.

ing uniform distribution inside the reactor. The central region where ultrasonic waves from all the transducers in that layer meet has higher intensities as represented by very dark blue or red regions.

Table 1
Reactions used in the model (M is a third body representing the pollutant).

Reaction	Rate constant ($m^{3n}s^{-1}$, n = 0,1,2)	Temp. range (K)
$H_2O + H_2O \rightarrow H + OH + H_2O$	5.8×10^{-9} exp(−440,000/(RT))	2000–6000
$H + OH + H_2O \rightarrow H_2O + H_2O$	1.48×10^{-30} $(T/298)^{-1.18}$ exp(−2580/(RT))	200–6000
$H + H_2O \rightarrow OH + H_2$	1.58×10^{-11} $(T/298)^{1.2}$ exp(−79,900/(RT))	250–3000
$OH + H_2 \rightarrow H + H_2O$	$3.01 \times 10^{1.3}$ $(T/298)^{1.3}$ exp(15,300/(RT))	250–3000
$H + H + H_2O \rightarrow H_2 + H_2O$	8.85×10^{-33} $(T/298)^{-0.60}$	100–5000
$H_2 + H_2O \rightarrow H + H + HO$	1.88×10^{-8} $(T/298)^{-1.10}$ exp(437,000/(RT))	600–5000
$O + O + H_2O \rightarrow O_2 + H_2O$	9.26×10^{-34} $(T/298)^{-1.0}$	300–5000
$O_2 + H_2O \rightarrow O + O + H_2O$	1.99×10^{-10} exp(451,000/(RT))	300–10,000
$OH + OH \rightarrow O + H_2O$	1.65×10^{-12} $(T/298)^{1.14}$	300–2500
$O + H_2 O \rightarrow OH + OH$	1.25×10^{-11} $(T/298)^{1.30}$ exp(71,500/(RT))	300–2500
$OH + M \rightarrow O + H + M$	4.09×10^{-9} exp(416,000/RT))	300–2500
$O + H + M \rightarrow OH + M$	4.36×10^{-32} $(T/298)^{-1.0}$	300–2500
$OH + O \rightarrow O_2 + H$	4.55×10^{-12} $(T/298)^{0.4}$ exp(3090/(RT))	250–5000
$O_2 + H \rightarrow OH + O$	1.62×10^{-10} $(T/298)^{0.4}$ exp(62,110/(RT))	300–5000
$O + H_2 \rightarrow OH + H$	3.44×10^{-13} $(T/298)^{2.67}$ exp(26,270/(RT))	300–2500
$H + OH \rightarrow H_2 + O$	6.86×10^{-14} $(T/298)^{2.8}$ exp(16,210/(RT))	300–2500
$O_2 + H + M \rightarrow HO_2 + M$	1.05×10^{-31} $(T/298)^{-1.73}$ exp(2240/(RT))	300–3000
$HO_2 + M \rightarrow O_2 + H + M$	2.41×10^{-8} $(T/298)^{-1.18}$ exp(203,000/(RT))	200–2200
$HO_2 + O \rightarrow OH + O_2$	2.91×10^{-11} exp(−1660/RT))	300–2500
$O_2 + OH \rightarrow HO_2 + O$	3.71×10^{-11} exp(−2,220,000/ RT))	300–2500
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	7.01×10^{-10} exp(−50,140/RT))	850–1250
$H_2O_2 + O_2 \rightarrow {}_2HO_2$	9.01×10^{-11} exp(−166,000/RT))	300–2500
$OH + OH \rightarrow H_2O_2$	1.51×10^{-11} $(T/298)$	200–1500
$OH + OH + M \rightarrow H_2O_2 + M$	6.04×10^{-31} $(T/298)$	500–2500
$H_2O_2 + H \rightarrow OH + H_2O$	4.01×10^{-11} exp(16,630/RT))	300–2500
$H_2O_2 + H \rightarrow HO_2 + H_2$	8×10^{-11} exp(33,260/RT))	300–2500
$HO_2 + H_2 \rightarrow H_2 O_2 + H$	5×10^{-11} exp(109,000/RT))	300–2500
$H_2 O_2 + O \rightarrow HO_2 + OH$	1.42×10^{-12} $(T/298)^{2.0}$ exp(16,630/(RT))	300–2500
$HO_2 + OH \rightarrow H_2O + O_2$	4.8×10^{-11} exp(2080/(RT))	300–2500
$H_2O_2 + OH \rightarrow HO_2 + H_2O$	2.91×10^{-12} exp(−1330/(RT))	300–2500
$HO_2 + H_2O \rightarrow H_2 O_2 + OH$	4.65×10^{-11} exp(−137,000/ (RT))	300–1000
$HO_2 + H \rightarrow 2OH$	2.81×10^{-10} exp(−3660/(RT))	300–2500
$HO_2 + H \rightarrow H_2 + O_2$	2.66×10^{-12} $(T/298)^{1.77}$ exp(2380/(RT))	200–3000
$HO_2 + H \rightarrow H_2O + O$	6.55×10^{-12} $(T/298)^{1.47}$ exp(−58,100/(RT))	200–3000

In addition to the confirmation of uniform cavitational activity in the reactor, we also predicted the pressure profiles and the flow patterns. The objective was to quantify the effectiveness of the cavitating conditions and also establish the patterns for energy dissipation with expected level of turbulence in different operating zones. This would help in establishing the extent of enhancements that can be obtained in the mass transfer rates of the reacting species to the gaseous oxidants such as ozone. In order to predict the turbulent flows, we used the Comsol's Flow Simulation which employs the Favre-averaged Navier–Stokes equations as well as transport equations for the turbulent kinetic energy and its dissipation rate (i.e., k-ε model).

Numerical results shown in Fig. 3 reveal that the pressure distribution is quite uniform throughout the reactor and that the entry through each nozzle creates the turbulence, which is expected to enhance the extent of ozone mixing in the reactor leading to beneficial effects. The velocity pattern shown in Fig. 4 also indicates that uniform mixing is likely to occur throughout the reactor. Furthermore, the flow has dominant components in all the three directions in the stream. Fig. 5 shows the percentage change in turbulent intensity in the flow. It should be noted that the variation in the intensity of 5% and more is considered as high degree of turbulence and as can be seen from the predictions, indeed significant degree of turbulence exists in the main reactor. The predictions allows confirmation of hypothesis that due to the combined operation of cavitation and ozone, the ozone dissolution and subsequent mass transfer will indeed be enhanced so as to get beneficial results in the actual application.

Comsol was also used to quantify hydroxyl radicals in the entry zone and also in the cavitation zone. Chemical reactions used in the simulation are shown in Table 1 [23–26]. The result which is given in Fig. 6 reveals that the concentration of hydroxyl radicals is significantly enhanced in the cavitation zone which should ensure that enhanced oxidation capacity is obtained in the presence of cavitating conditions.

5. Literature illustrations for confirming the suitability of hybrid approach

Compared to ozone or acoustic/hydrodynamic cavitation alone, it has been shown that the combination of the two processes increases the degradation of fulvic acid [27], nitrobenzene, 4-nitrophenol and 4-chlorophenol [28], pentachlorophenol [29], *p*-aminophenol [30], and aniline [31]. Interestingly, the synergism between the techniques has only been observed at lower operating frequencies i.e., 20 kHz. The enhanced suitability of the low frequency operation was attributed to the fact that the extent of

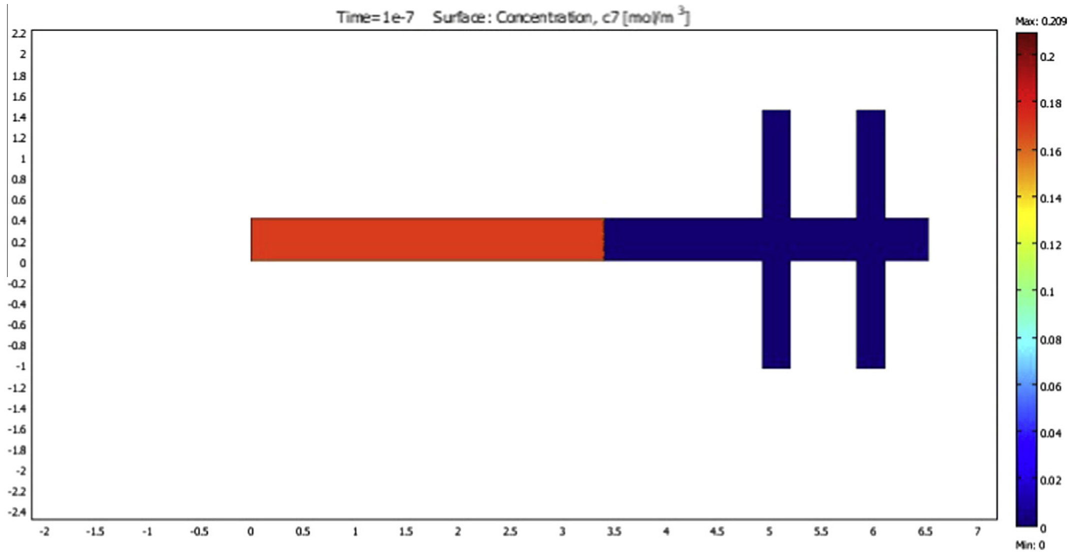

Fig. 6. Concentration of hydroxyl radicals at the entry and in the cavitation zone.

turbulence and the physical effects of cavitation phenomena are significantly higher at lower frequency as compared to the high frequency operation (>300 kHz).

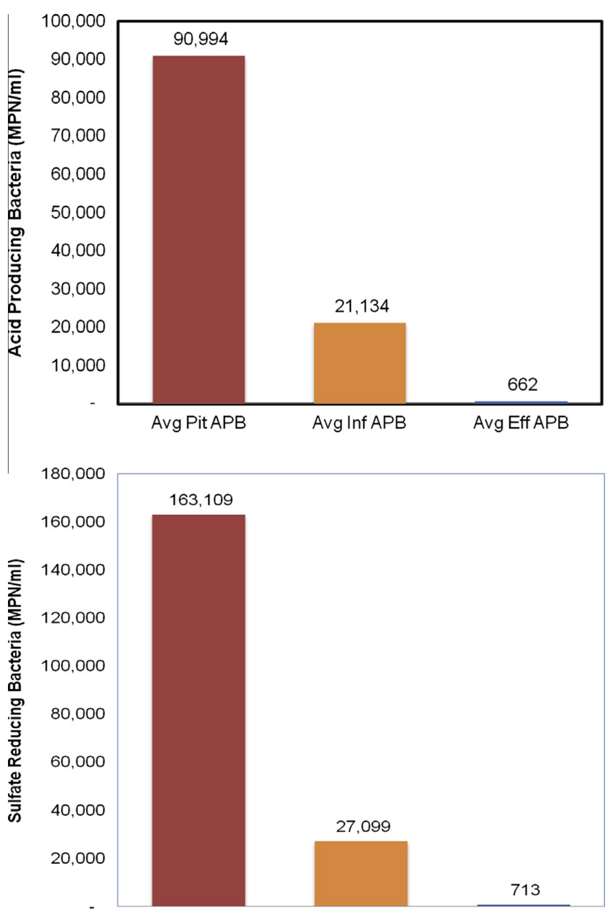

Fig. 7. The extent of disinfection obtained on 776 samples using the hybrid reactor technology in the Fayetteville Shale (APB: Acid Producing Bacteria; SRB: Sulphate reducing bacteria, Avg Pit: Average concentration of pit containing the polluted water, Avg Inf: Average concentration entering Ozonix, Avg Eff: Average concentration coming out from Ozonix).

The hybrid approach has also been shown to inactivate microorganisms [32–36]. The observed intensification in the combination of hydrodynamic cavitation with ozone or acoustic cavitation has been explained by three different mechanisms: (i) disaggregation of flocs of microorganisms which exposes inner microbes to the treatment, (ii) transient rupture of chemical bonds between molecular components of cellular membranes which, in general, results in an increase in permeability of substances and (iii) enhanced rates of diffusion allowing more rapid penetration of ozone into the microorganism thereby resulting in enhanced rates of disinfection.

6. Overview of different applications for the hybrid reactor

The hybrid advanced oxidation Ozonix® reactor has a very good promise for water treatment and microbial disinfection in food processing industries, sludge control in biological oxidation processes, removal of sulfur in the case of coal washing and gold mining industries with an objective of increasing the recovery rates of valuable metals and prevention of biofouling in cooling water circuits.

The reactor can also be used in a ship to treat ship's ballast water that is being transported from one region to another. Translocation of organisms through ships (bio-invasion) is considered to

Influent (Before Treatment) Treated Effluent (After treatment)

Fig. 8. Pictures of the influent and treated effluent at the actual commercial site.

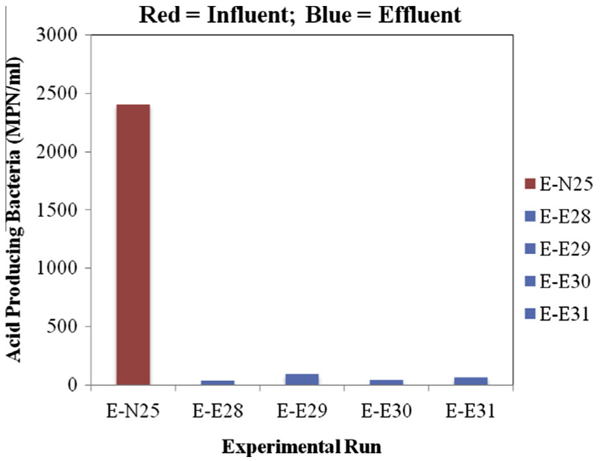

Fig. 9. The extent of disinfection obtained at a real commercial site using the hybrid reactor (E-E28, E-E29, E-E30 and E-E31 denotes different experimental runs where circulation was achieved through the reactor and measurements done at the outlet).

be one of the important issues that threaten naturally evolved biodiversity, the consequences of which are being realized increasingly in the recent years. The aim of this type of application is to make the process viable in a single pass as it is practically impossible to have multiple passes in the ballast water treatment considering the volume of the liquid to be treated and a typical piping network for the ballast water flow.

7. Experimental results

The hybrid advanced oxidation Ozonix® reactor has been tested, deployed, and commercialized in all major U.S. unconventional shale plays (Marcellus, Haynesville, Woodford, Fayetteville, Eagle Ford, and Permian Basin), treating more than 76 million barrels (3+ billion gallons) of fluid in a four-year period for various energy exploration and production customers. The Ozonix® process is proven to kill bacteria and inhibit scale "on the fly" in various types of completion fluids (flowback, produced, and shallow ground fluids) at very high rates. The oxidation of organics and heavy metals along with the precipitation of neutralized scale compounds results in a more compatible fluid for other frac chemicals and for the formation in which the fluid is being pumped. Operators can use the Ozonix® technology to increase the recycling rate of flowback, produced, and shallow ground fluids and completely eliminate liquid biocides and scale inhibitors from the completions process. The hybrid reactor is mounted on a tractor-trailer unit for portability. Flowback, produced, and/or shallow ground feed waters (in various proportions) are pumped into the hybrid reactor and are flash mixed with introduced ozone. Ultrasonic transducers induce cavitation inside the solution containing dissolved ozone, which results in the shearing of larger particles and a decrease in the particle flotation times. Electrodes present in the hybrid reactor facilitate precipitation of hard salts from the influent.

The effectiveness of the reactor was demonstrated on 776 bacteria sample sets taken from 282 wells in the Fayetteville Shale over a three-year period. The typical conditions for the operation was temperature of 85 °F and a maximum pumping rate of the frac water as 80 barrels/min on fracturing job using a single unit in operation. Further higher pumping rate is possible depending on the application by combining multiple Ozonix® trailers in tandem. Using the Most Probable Number per milliliter (MPN/mL) method, results showed that bacteria reduction extent was 96.5% for Acid Producing Bacteria (APB) samples and 97.5% for sulfate-reducing bacteria (SRB) samples (Fig. 7). The removal of sulfate reducing bacteria is an important requirement as the SRB converts sulfate ions to hydrogen sulfide, which in contact with steel results in the formation of iron sulfide. SRB proliferation may lead to considerable scaling, corrosion as well as formation of hydrogen sulfide gas, which is a huge safety issue.

Fig. 8 compares a typical influent (i.e., non-treated) and effluent (i.e., treated) sample. It can be clearly seen that the unit can successfully treat the black colored influent to the point of being almost colorless. These results demonstrate the superiority of the technology over other existing treatments; for example, the efficacy of UV based treatment is almost negligible for colored solutions due to very low depth of penetration of UV light.

Microbial analyses of the inlet and the outlet stream for four different experimental runs were also performed to check the reproducibility of the results. Fig. 9 gives the results for different experimental runs where same influent water was circulated through the reactor at 4 different instances. It can be clearly seen from the figure that the outlet stream of the hybrid reactor always

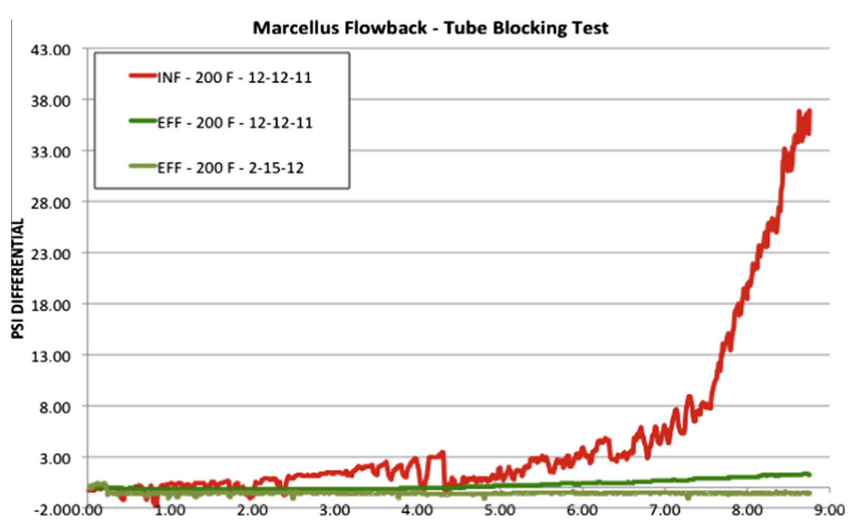

Fig. 10. Results of the Dynamic tube blocking tests (Source: Weatherford Labs; Houston, TX) (Inf -200 F means the influent sample at 200 F before passing through the reactor whereas Eff-200F means the treated sample at 200 F after passing through the reactor at two different time periods viz. one immediately after the run and other after some duration)

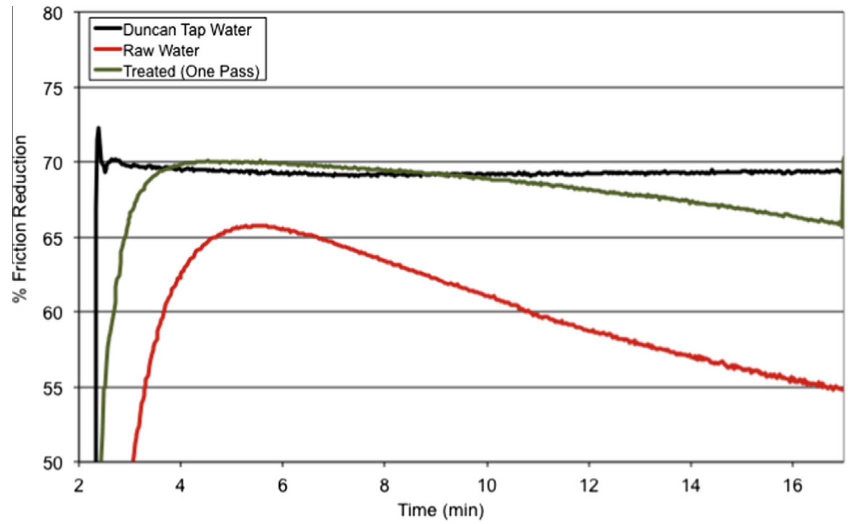

Fig. 11. Results of the Flow loop tests (Source: CoreLabs; Duncan, OK).

passed the norms required for the water quality and near complete disinfection has been achieved with the unit. The data given in the figures also confirms the reproducibility of the results which is important aspect considering the randomness of the cavitation phenomena. The extent of reduction in all the 4 runs (4 different circulations through the reactor) was observed to be varying by ±2% which can be considered as excellent reproducibility. The maximum extent of disinfection was 98.4% whereas minimum of the reported runs was 96.2%.

An additional benefit of the treatment is that it ensures zero scale deposition from water treated by the hybrid reactor. The dynamic tube blocking test method was used to examine the tendency of fluids to form scale. This test is used to screen brines and verify their tendency to form scale and to evaluate the effect of chemical additives and/or other remedial treatments on the scaling tendencies. The method consists of pumping a brine of known composition through a heated capillary tube and monitoring the time required to plug the tube due to scale formation and deposition. The results of the dynamic tube blocking test shown in Fig. 10 indicate superiority of the treated effluent (increased flowability) over the untreated influent. The combined action of ozone (chemical oxidation reaction with the precipitating salts) and ultrasound (mechanical action in terms of breaking the salts and eliminating the tendency of solid particles to settle on the surface) significantly reduces the scale formation in the system.

Another benefit of the treatment is that the fluid interacts notably better with other chemicals present in the fluid, particularly the friction reducer. The most common type of friction reducer is a negatively charged (anionic) polyacrylamide. Because of its negative charge, this friction reducer is adversely impacted by multivalent cations like calcium, barium and iron. Ozonix® oxidizes or precipitates iron and divalent cations that would otherwise interfere with the friction reducer. In essence, the same drivers that cause the Ozonix® process to inhibit scale also cause anionic friction reducers to interact more favorably with treated fluid. Certain biocides interfere with the efficacy of friction reducing chemicals. Since there is no need to add liquid chemical biocides to fluid treated by Ozonix®, there is no biocide to interfere with the friction reducer. The results in the friction loop test shown in Fig. 11 indicates a significant improvement in the Friction Reducer efficiency, starting at a 7% improvement at 5 min, leading to a 27% improvement at 30 min. The treated water behaves much more like Duncan tap water and shows much better characteristics as compared to the untreated frac water.

8. Conclusions

The present work has illustrated the basic concepts behind the design of a hybrid advanced oxidation reactor based on the combined use of ozone, acoustic cavitation, hydrodynamic cavitation and electrochemical oxidation/precipitation. The reactor is installed on a mobile platform which gives the flexibility of treatment at the client's site leading to an additional advantage of very low investment for the client.

The results of the flow simulations have clearly established the fact that the combined operation and the geometrical configuration used in the present hybrid reactor is likely to yield significant turbulence which should take care of any mass transfer related issues in the oxidation of contaminants by ozone.

The experimental results using the actual hybrid advanced oxidation reactor as obtained at a commercial site should increase the degree of confidence regarding the success for other applications such as industrial wastewater treatment, ballast water treatment, sludge control, etc. Based upon actual field results with commercial customers in the oil and gas business, it can be concluded that the hybrid advanced oxidation Ozonix® reactor resulted in a effective treatment of the frac water giving much better results as compared to the chemical treatments.

Overall, the patented Ozonix® technology is a chemical free process that can be used to manage the quality of the supply of raw water, flow-back water, produced and shallow ground fluids and petroleum industry wastewaters. The reactor has also been shown to completely eliminate the need of chemical biocides and scale inhibitors thereby eliminating the problems associated with residual chemicals in the process. The reactor also plays a major role in altering the flowability of the treated water giving a lower coefficient of friction, which results in lower pump pressure requirements for similar flow rates and also possibly reducing the requirement of traditional chemical friction reducers.

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