

Shale Gas Water

Introduction: Water Reuse

- Everyone and virtually every industry needs water
- Water will be a major driving force in all drilling and production in the future
- Water is not “just water”, it is a very complex component of industrial processes
- Supply of suitable water is finite, so competition for that water is intensifying
- Water reuse is the environmentally sound solution, but there are considerable economic and technical obstacles
- Diffused gas treatment shows potential to overcome these obstacles



Potential Oilfield Water Sources

Fresh water

- shallow well
- surface

Frac return water

Process water

Well water

- brackish
- sour
- saline
- high barium
- high sulphate
- high metals
- oily

Recycled Produced water



Produced Water

Treatment Methods

- Gas diffusion

- ozone
- oxygen
- CO₂
- sulphides
- hydrogen
- degassing

- Evaporation

- Filtration

IGF/DAF

- oil separation
- solids separation

Electro Coagulation

Membrane

- ultra-filtration
- reverse osmosis
- nano-filtration

TYPICAL CHALLENGES

- Technical effectiveness
- Capital cost
- Operating cost
- Energy consumption
- By-products/disposal

Carbon Dioxide Overview

- Carbon Dioxide (CO₂) is used in industries to neutralize high pH water
- Carbon Dioxide (CO₂) is a by-product of many industrial processes, and it is readily available for purchase
- Dissolved CO₂ reacts with water with the following reaction scheme:
 - $\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_2\text{CO}_3$
 - $\text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^-$
 - $\text{HCO}_3^- \rightarrow \text{H}^+ + \text{CO}_3^{2-}$



Dissolved oxygen, when used in water treatment...

- decreases pathogenic activity
- creates an aerobic state – promoting natural decomposition of organic matter by microbes
- eliminates anaerobic microbial activity (cause of harmful products like H_2S and CH_4)
- increases water quality

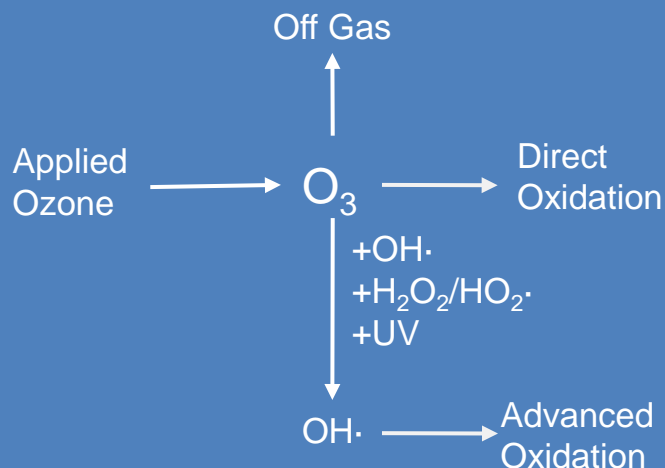


Oxygen can be diluted in air or concentrated through a PSA, VSA or cryogenic system

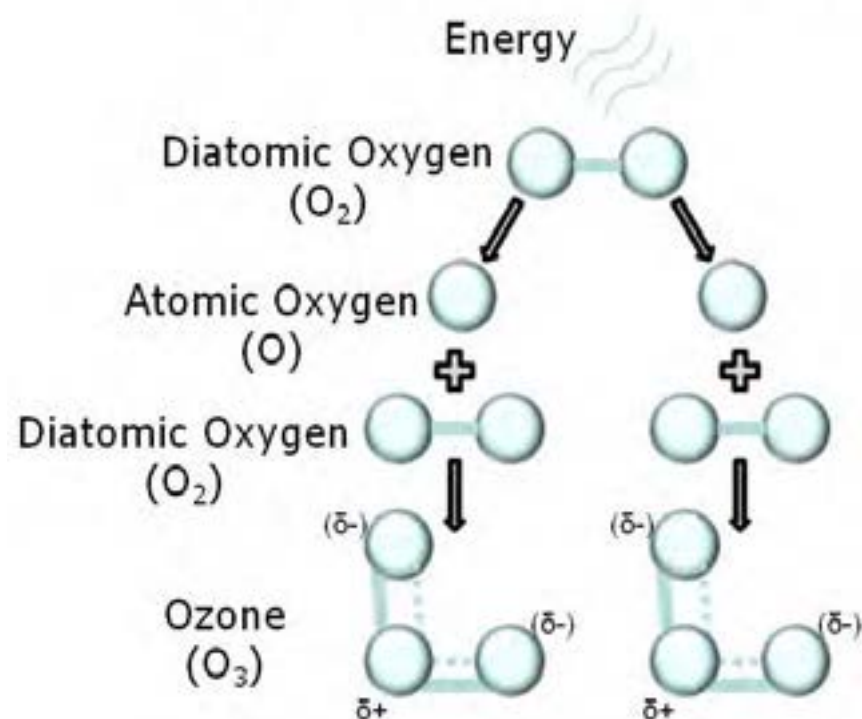
Ozone Overview

- O_3 generated on-site
- Direct oxidation of contaminants
 - oxidation of organic compounds
 - oxidative precipitation of metals
- Advanced oxidation (O_3 /UV)
- Full oxidation of most organic compounds
- Toxicity removal

Oxidation Pathways



Production of Ozone



Oilfield Treatment Overview

Diffused ozone can be used in oilfield water treatment to reduce:

- toxicity
- oils and greases; and
- heavy metals (by precipitation)



Hydrocarbon oxidation in Produced Water



Iron oxidation in Flowback water

Problem: Sulfides in Oilfield

Sulfides found in Oilfield waste (H_2S , HS^- , S^{2-}) are:

- Dangerous and hazardous
- Flammable
- Toxic
- Corrosive
- Odorous



Solution: Sulfide Elimination

Gas treatment system can eliminate and prevent sulfides formation by:

- (1) Destroying sulfate reducing bacteria through Oxidation with O_3 (effective alternative to Biocides)
- (2) Promoting an aerobic environment, increasing ORP (oxidation-reduction potential)
- (3) Oxidizing sulfides before they are released by vent scrubbing and oilfield wastewater treatment

Hydrocarbons + O₃

Dissolving O₃ in oilfield wastewater oxidizes any residual hydrocarbons

Decreasing Toxicity
Reducing Filter Fouling
Removing Colour



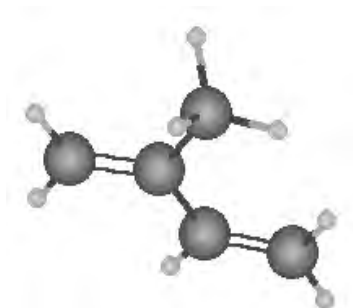
Hydrocarbon Contaminated Oilfield Wastewater

Complete oxidation can be achieved with the gas treatment system— by products are **carbon dioxide, water, and oxygen**

Hydrocarbons + O₃

Ozone also readily reacts with un-saturated hydrocarbons found in oilfield waste such as:

Alkenes



2-methyl-1,3-butadiene

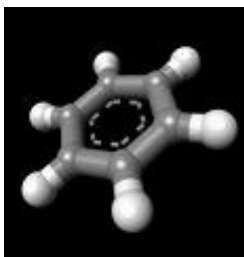
Alkynes



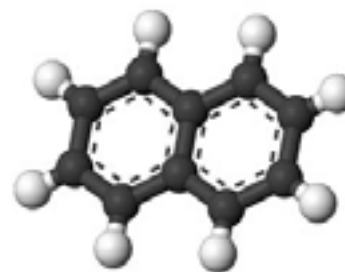
1-Butyne

and Aromatic compounds

Benzene

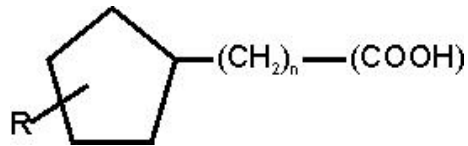


Naphthalene



Oilsands Process Water

Naphthenic acids are naturally-occurring, aliphatic or alicyclic carboxylic acids found in petroleum



Water used to extract bitumen from the Athabasca oil sands becomes toxic to various organisms due to the presence of naphthenic acids released from the bitumen



Oilsands Process Water Study



Gas treatment systems have been shown to be effective in eliminating Naphthenic acids from oilsands process water through the use of O_3

Independent studies have proven that ozone alone is effective in a 95% reduction in Naphthenic acids

VEK is currently researching other gas treatment systems for use in treatment of oilsands process water using new advanced oxidation methods

- R&D program to start April 2015 / Nait/ COSIA - Primozone
 - Determine the efficiency of the Primozone Ozone for the treatment of OSPW and other oilfield waters
 - Now being transitioned to commercial implementation

Heavy Metal Removal



Heavy Metals are often present in Oilfield waste

Iron (Fe)

Manganese (Mn)

Lead (Pb)

Arsenic (As)

Metal Precipitates



Ozone Treatment is very effective at precipitating out certain heavy metals

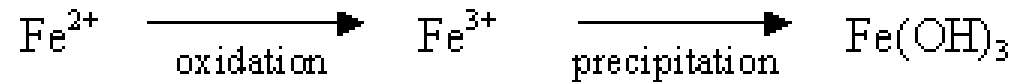
Especially metals that are already dissolved:

Iron

Manganese

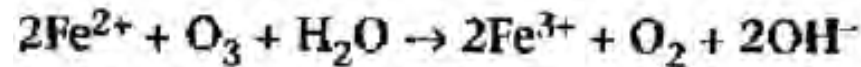
Forming insoluble precipitates that can be easily filtered out

Iron Removal

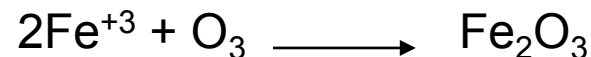


Soluble Iron is present in its divalent state Fe^{+2} (ferrous)

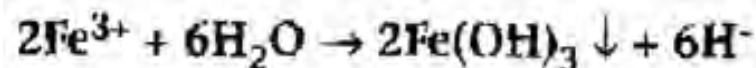
Ozone reacts with Fe^{+2} to reach iron's higher oxidation state Fe^{+3} (ferric)



Ozone reacts with ferric iron to produce insoluble ferric oxide



Hydrolysis also occurs producing gelatinous, insoluble ferric hydroxide



Which can then be filtered out

Pond Reclamation

- Aeration
 - Increase biological activity
 - React with some highly reactive hydrocarbons.
- Ozonation
 - Lower COD
 - Decrease toxicity
 - Remove sulphides

Dewatering and Water Sweetening

- Inline Oxygenation
 - for release of water to dissolved oxygen (“DO”) regulated basins
 - reduction of biological oxygen demand (“BOD”) in the water
- Sulphide Removal
 - oxygen or ozone treatment to remove sulphides from water...“sweetens” the water
- Toxin Removal
 - oxidative removal of toxic compounds
 - eliminates water storage criteria



Diffusion tower installed in dewatering at an oil sands mine

Oil Sands Process Water R & D



Oil Sands Process Water R & D



Oil Sands Tailings Pond Water R & D



Oil Sands Dewatering System Requirements

- Installed in-line on existing wells
- No pump or additional power required, existing flow of water sufficient for unit to operate
- No consumables, units use ambient air drawn in via venturi
- No operator required
- No moving parts makes equipment virtually maintenance free
- Diffusion towers sized to match flow rate



What is Frac Flow Back Water and why treat it?

Water that is returned back to the surface after hydraulic fracturing has occurred. The volume is usually 25-40% of the total volume used when Fracturing, but can be as high as 70%

The water contains oil, hydrocarbons, proppant sand, guar gum or polyacrylamide, bacteria, chemical cross-linkers, enzymes, and induced or naturally occurring mineral compounds

Removal of these contaminants allows the water that is normally disposed of as a hazardous waste to be recycled and used as an alternative to fresh water make-up for the next hydraulic frac.

NO ENVIRONMENTAL LIABILITY – COMPLETE REUSE OF WATER!

Frac and Produce Water R & D



Frac Water Treatment



What is a Hydro-Pod™?

- A unique combination of technologies in a proprietary sequence to treat frac flowback water and production water
- An effective and efficient system on the market today.



Frac Water Treatment



How does the Hydro-Pod™ work and why is it effective?

The first step is to oxidize the flow back water that contains the oil, hydrocarbons, guar gum or polyacrylamide, bacteria, chemical cross-linkers, enzymes, and induced or naturally occurring mineral compounds with the ozone – O₃

Why ozone?

It is the most powerful and safest oxidizer that exists

It can be made on-site

It has a very short half life and is gone in 20 minutes

Non toxic to humans or animals

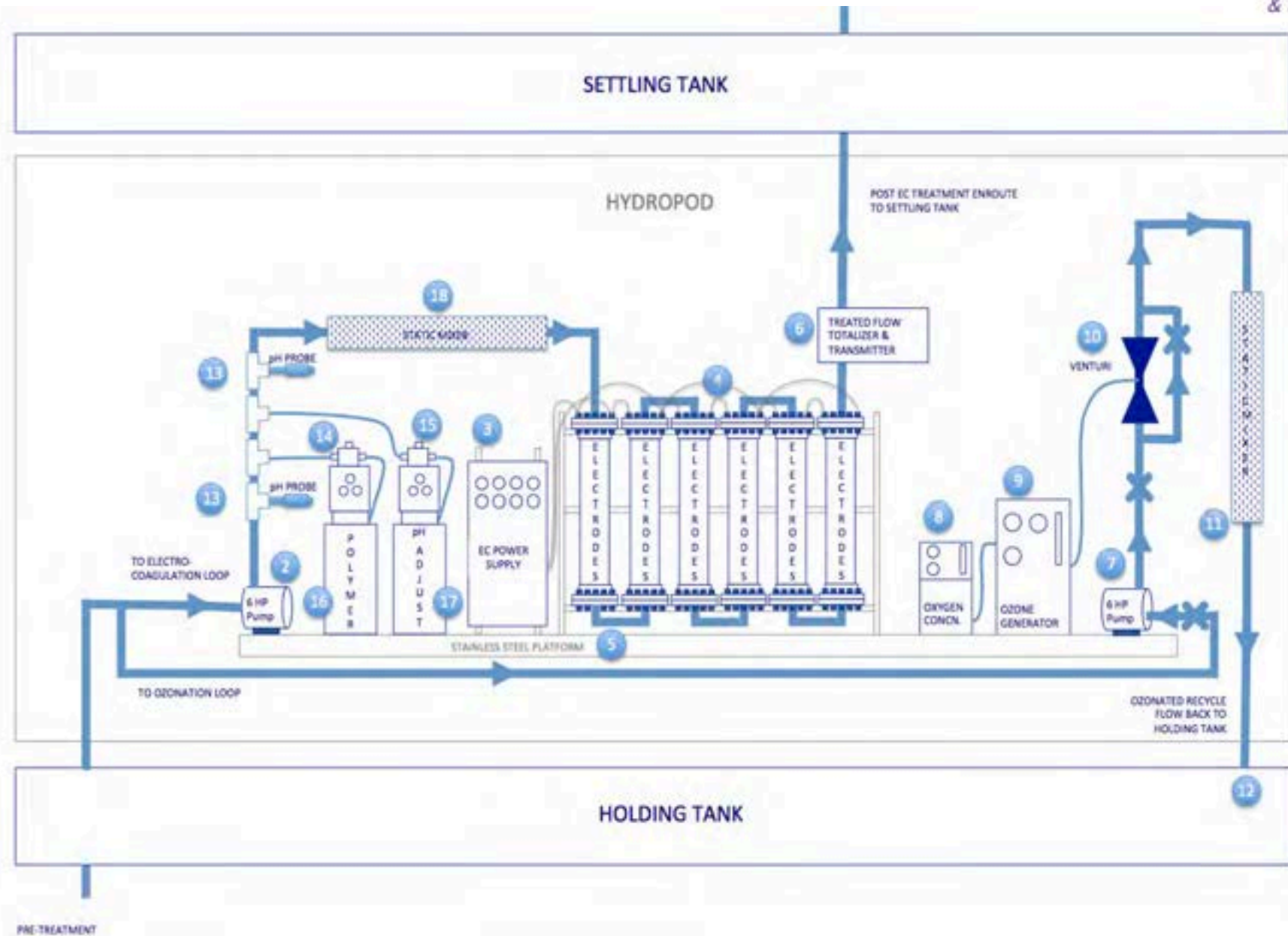
Very cost effective

Many years of effective use in a wide variety of industries



NO ENVIRONMENTAL LIABILITY – COMPLETE REUSE OF WATER

Frac Water Pre Packaged units



Frac Water Pre Packaged units



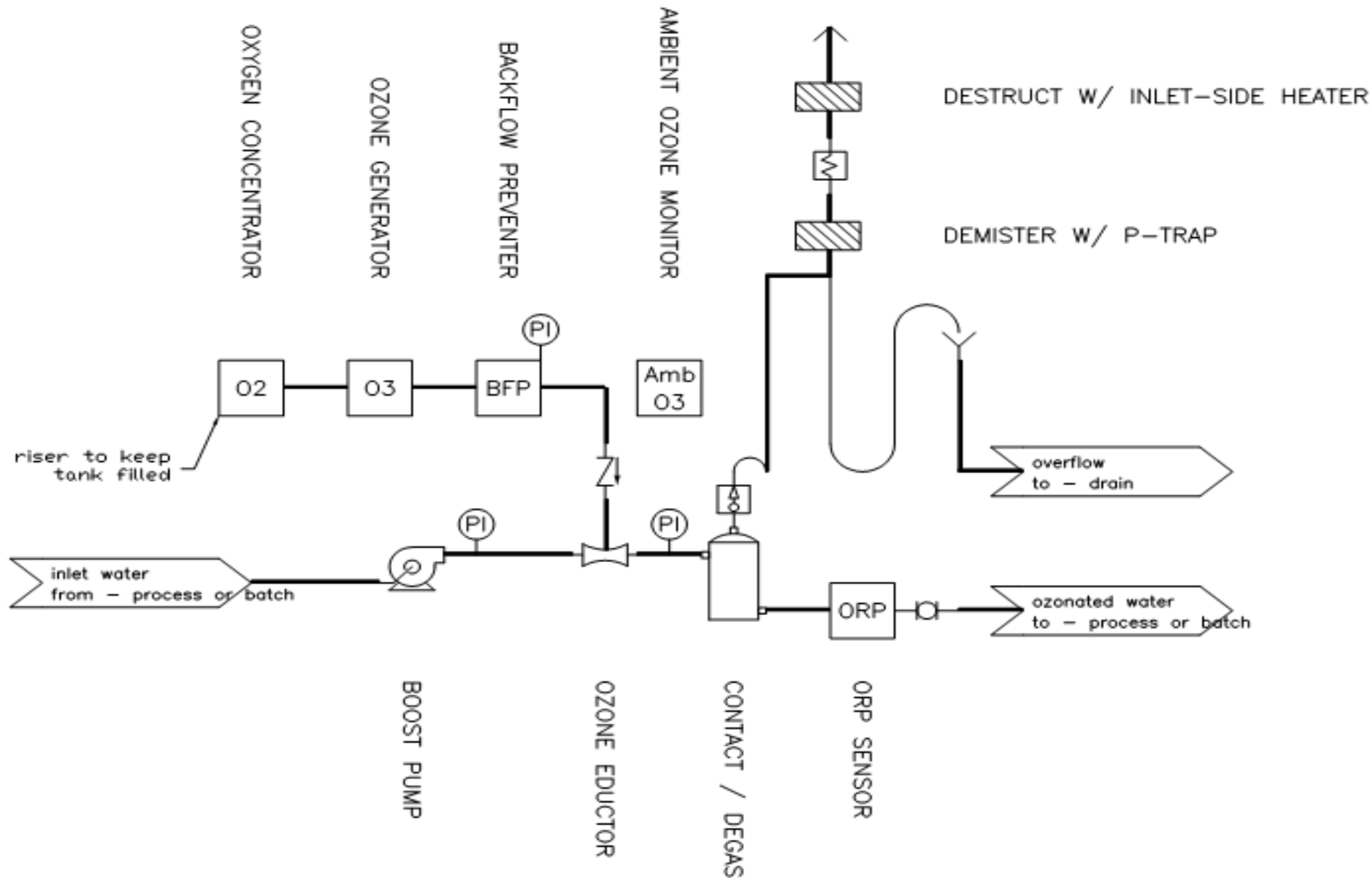
Canadian Alberta Frac Project-
Flow Rates 4000 Barrels per day
Objective- Reduce H₂S levels
H₂S-starting point 350 ppm
H₂S- Finishing points > 1 PPM
TSS reduction of 78% including reduction of iron and heavy metals

Ozone System Overview

1. Air/Gas Preparation
2. Ozone Equipment Manufacturers
3. Ozone Monitors
4. Ozone Contacting
 - Backflow Prevention
 - Control
 - Relief Valve
 - Chemistry (Salt/Fresh)

Frac Water Pre Packaged units

Ozone System Overview



REDEFINING OZONE TECHNOLOGY™



Primozone®
Clean water. The natural way.™

Primozone Overview

- Founded in 2000, Sweden
- Wholly owned by industrial owner Westfal-Larsen Technology, Norway
 - invested \$20 million USD in R&D
- First installation in 2006 – now in over 20 countries world-wide
- Preferred supplier by AECOM & Yorkshire Water for Acomb Landing WTW project
- Experienced ozone provider – designs complete ozone solutions

Primozone Overview

- Built-in redundancy
 - No need to oversize
- Smallest footprint
 - Easy retrofitting
 - Saves installation cost
- Quiet and EMC-approved
 - Can be placed anywhere
- Sophisticated control system
 - Exact dosing based on need
- Module for distribution & individual dosing
 - For different treatment lines
 - No need to oversize



Primozone Overview

- Highest ozone concentration – 20 wt% (300g/Nm³)
 - Saves cost for oxygen and energy
 - Efficient dissolution
 - For demanding applications
- Highest gas pressure – 30 psi g (2.2 bar g)
 - Efficient dissolution
 - For demanding applications
 - Possible to distribute ozone long distances
- Modular and scalable design
 - Design to fit the actual need
 - Easy upgrade over time



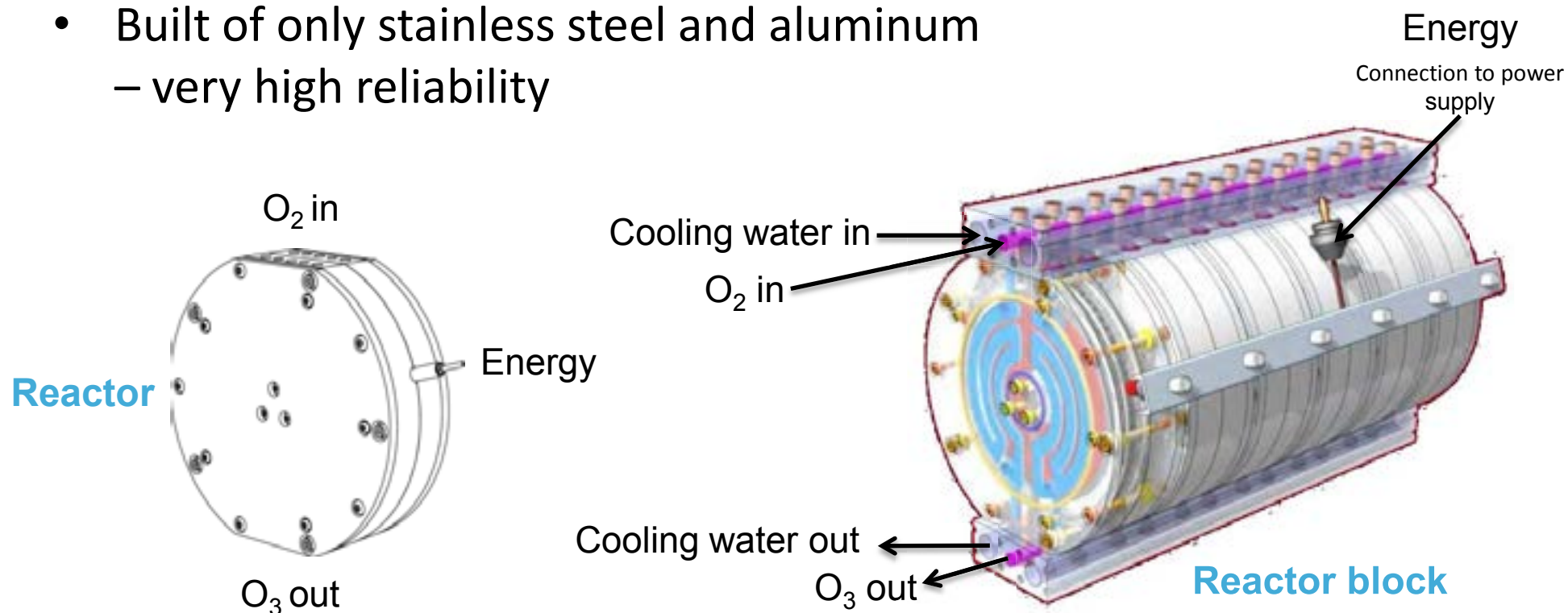
Primozone Overview

- Lowest energy/oxygen consumption
 - Up to 50% savings
- Maintenance free
 - No moving parts
 - No tubes to replace
- Lowest life cycle cost (CAPEX+OPEX)
 - Designed to fit the actual need
 - Savings in peripheral equipment
 - Up to 50% savings in Energy/Oxygen
 - No maintenance
- Easy to use
 - No specialists needed



Frac Water Pre Packaged units

- Cold plasma ozone reactors mounted in blocks
- Built of only stainless steel and aluminum
 - very high reliability



Frac Water Pre Packaged units

Ozone Effectiveness



Frac Water Pre Packaged units

Primozone Overview



Frac Water Pre Packaged units



Step 2- Electro Coagulation Overview

- All of the contaminates are agglomerated into large particles by the alternating currents passing through a series of proprietary metal plates.
- Removes suspended solids to sub-micrometre levels
- Breaks emulsions such as oil and grease and can oxidize and aid in the removal of heavy metals



Frac Water Pre Packaged units



Step 2- Electro Coagulation Overview

- The EC columns are run in series and each unit has a capacity of 650 cubic meters a day (150 gallons per minute)
- Hydro-Pods™ may be run in parallel to obtain the desired daily treatment rate.
- Each unit comes with an option of a 30kw generator. All systems are simple 230v.



Frac Water Pre Packaged units

Step 2- Electro Coagulation Overview



Frac Water Pre Packaged units



Step 3- pH adjustment and Polymer Addition Overview

- pH is adjusted to slightly above neutral to make sure that all metallic compounds are precipitated.
- The addition of a polymer may be necessary to assist in more rapid settling in the event that flow rates are high.
- The water should be passed through a simple cartridge filter to assist in solids removal
- If salinity is an issue, the water which is now free of solids, is passed through a portable reverse osmosis unit.
- The unit is completely PC controlled and monitored.



Frac Water Pre Packaged units

The Unit is PC - controlled and has cell or satellite uplink capability



Frac Water Pre Packaged units

North American Installs



Evaluation results

Pit Water

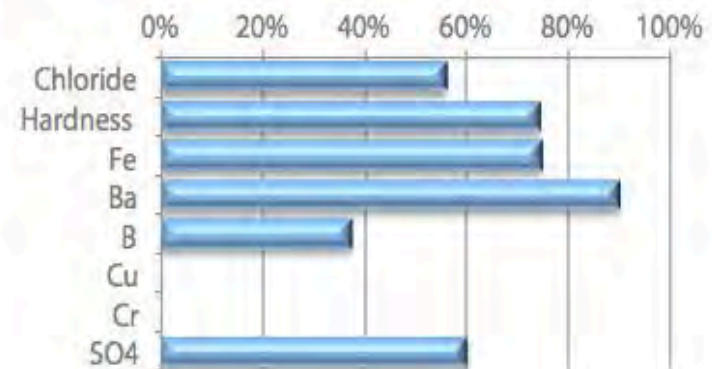


Photo shows before and after results that verified efficiency of treatment technique selected.

Pre-Post Treatment Analyte Values

	Units	Pre-Treatment	Post-Treatment	% reduction
pH		6.58	8	
Chloride	mg/l	35,200	15,500	56%
Hardness	as CaCo3 mg/l	175	45	74%
Fe	mg/l	50.5	12.8	75%
Ba	mg/l	1.00	0.10	90%
B	mg/l	295	185	37%
Cu	mg/l	N.D.	N.D.	
Cr	mg/l	-	-	
SO4	mg/l	10	4	60%
TPH		N.D.	N.D.	
Solids removed	lb/bbl		2.03	

% removal of Analytes



Frac Water Pre Packaged units

North American Installs



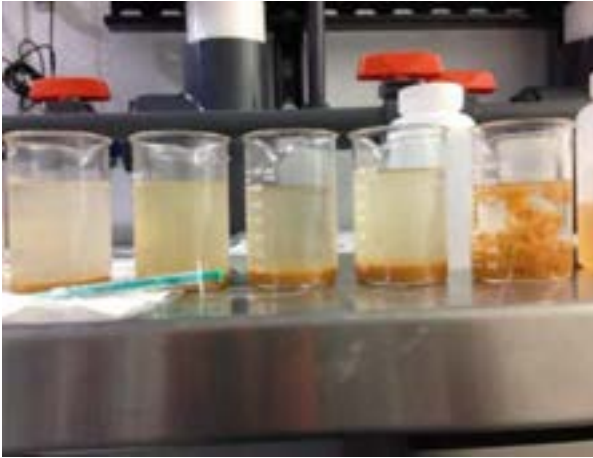
Frac Water Pre Packaged units

North American Installs



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Frac Water Pre Packaged units

North American Installs



Primozone in-house R&D and Assembly



Primozone Ozone System



Primozone Ozone System



Primozone Ozone System



Primozone Ozone System



Containerized Ozone System

Complete system

- Ozone generator
- Air compressor
- Oxygen generator
- System controller
- Chiller

Temporary or permanent installation

Outdoor applications



Fabrication



Fabrication



Fabrication



Fabrication



Fabrication



Arris works with Potable, Wastewater, Stormwater, and Recycled Water. We design, build, operate and maintain all types of water treatment systems. Our solutions are both environmentally and economically sustainable.

We actively work with our clients to ensure they obtain the treatment system that suits their needs in regards to treated water quality, capital budget, installation footprint, and operational requirements.

For more information visit www.arris.com.au