<u>Maraven "F-6" Production Water Treatment</u>
Pilot Plant Study

Background

During the period of December, 1995 Blue Diamond Water Treatment Company, of Two Rivers, Wisconsin and ESTR Inc. of Brussels, Wisconsin in conjunction with their local representatives, Servicios Blue Diamond de Venezuela, conducted a seminar in Caracas, Venezuela for Maraven. This seminar was presented to Mr. Jaime Gutierrez and Mr. Enrique Garcia Asesors de Protection Ambiental. This seminar focused on the recently developed and patented wastewater treatment technologies and their potential application in the treatment of production water and domestic waste from the oil platforms. Based on the response from this seminar, it was decided to do an on-site pilot test of the technologies to see if they are suited to treat these waste streams.

Following a closely coordinated exercise, the technologies to be used were selected and shipped to the F-6 location for the pilot. The following report outlines the technologies involved and the results of the pilot plant study.

Pilot Plant Study

The pilot plant consists of an **ESTR, Inc. Advanced Oxidation Process (AOP**) unit and supporting equipment which is designed specifically for the AOP pilot plant and is used to assist the operators in the development of the potential remediation alternatives for the wastewater stream. The purpose for a pilot plant study is to identify and properly size the type of equipment ultimately required for treatment of a specific wastewater stream problem. Based on the results of the treated samples gathered during the study, an analysis is made using proprietary procedures involving flow rates, retention times, contaminant levels, dosage rates and discharge parameters. The results of this analysis provide the required design parameters for the technologies to be employed for treatment of the wastewater.

Technologies Involved

The **ESTR, Inc. AOP** combines four proven wastewater treatment technologies: ozone, ultraviolet (UV) light, dissolved air floatation and highly efficient ultra fine bubble generation. The ozone is excited by the UV light and creates hydroxyl radicals, which break down, or oxidize, the contaminants in the wastewater stream. The proprietary manner in which the ozone is introduced to the contaminants is what enables the **ESTR, Inc. AOP** to achieve its high level of destruction at a low energy consumption level. Additional proprietary design enhancements allows the **ESTR, Inc. AOP** to function unaffected by high levels of suspended solids in the stream.

Since the **ESTR, Inc. AOP** has such a high level of efficiency, there is no need for use of additional chemicals, such as hydrogen peroxide, to augment the process. Replacement or regeneration of expensive filter media is also eliminated. Air and water are the only active agents and electricity is the only operating requirement. Thus, the overall operating costs are substantially reduced, plus the storage and handling hazards of chemicals are no longer of concern.

The **ESTR, Inc. AOP** can treat the following contaminants:

- **Amines**
- **Anilines**
- **Benzene**
- **Chlorinated Solvents**
- **Chlorobenzene**
- **Complex Cyanides**
- **Creosote**
- **Hydrazine**
- **Isopropanol**
- **Methyl Ethyl Ketone**
- **Methylene Chloride**
- **PCB's**
- **Pentachlorophenol**
- **Pesticides**
- **Phenol**
- **RDX**
- **TNT**
- **Toluene**
- **Xylene**
- **Polynitrophenols**
- **MTBE**
- **PCE**
- **Dioxins**
- **Dioxins**
- **Freon 113**
- **TCA**
- **Dichloroethylene**
- **bis (2-Chloroethyl) Ether**
- **Polynucear Aromatics**
- **Trichloroethytlene**
- **Tetrahydrofuran**
- **Dichlorethane**
- **Vinyl Chloride**

AOP Flow Process

The fluid being treated (influent) enters a surge tank and is pumped into the first stage DAF where it is evenly distributed and mixed with highly oxygenated ultra fine bubbles. These bubbles range in size from sub-micron to 5 microns in diameter. The bubbles adhere to the suspended matter and readily float it to the surface where it is skimmed off. This primary stage removes up to 80% of the suspended mater.

The effluent liquid, which is now highly oxygenated, leaves the first stage DAF, and enters the second stage DAF. In the second stage DAF, the liquid is again evenly distributed and mixed with the minute bubbles. The bubbles adhere to the remaining suspended matter and float it to the surface where it is skimmed off.

At this point in the process, up to 99% of all suspended matter has been removed. The bubbles and highly oxygenated atmosphere begin to oxidize the other pollutants in the liquid.

The purification process, already well under way in the DAF stages, is accelerated after the liquid leaves the collecting tank, passing through treatment by ultraviolet light. The UV treatment creates hydroxyl radicals which act as a catalyst on the liquid.

The liquid then enters an injector where it is mixed with ozone and transferred to the contact tower. This ultra-saturated liquid is combined with recalculated liquid in a highly reactive oxidizing environment. The micron-sized bubbles increase the surface area of the dissolved oxygen/ozone, enhancing the oxidation of the contaminants and making efficient use of the ozone. The liquid is re circulated within the contact tower to allow complete oxidation to occur.

After a period of time, dependent upon the liquid being treated, a diverter valve opens and allows an amount of treated liquid to be discharged from the system. The discharged liquid (effluent) meets discharge requirements.

A portion of the treated liquid is re-cycled back into the system to continue the process. This liquid is transferred from the contact tower, via the suction side of a mixer pump, where it is pressurized to 80-90 PSI. The liquid is then injected into a mixing chamber where further mixing of the solution occurs and the non-emulsified gasses are vented off. A portion of this liquid is diverted to another injector where the vented gasses from the mixing/purge chamber are re-injected. This liquid passes through an ultraviolet light and then returns to the contact tower.

The remainder of the liquid is re-injected back into the DAF's, continuing the process. This additional mixing creates a highly oxygenated/ozonated bubble. The liquid, at atmospheric pressure, has a dissolved oxygen content of 180-210% saturation.

Technical References

- The **ESTR, Inc. AOP** is fully patented and protected under United States law.

- The Advanced Oxidation Process is recognized by the United States Environmental Protection Agency (EPA) as an approved remediation technology for a wide range of contaminants. The EPA Risk Reduction Engineering Laboratory has produced a computerized treat ability database regarding the ranges of contaminants and their treat ability by the process. There are over 600 entries concerning the process. (Specific contaminants provided upon request.)

- The **State of California Department of Toxic Substance Control (DTSC) for the treatment of hazardous and toxic organic compounds approves the ESTR, Inc. AOP**. California Code of Regulations (CCR), Title 22.

- The **ESTR, Inc. AOP** is approved by the State of New Jersey for the treatment of all non-hazardous waste material.

- Numerous technical papers exist concerning advanced oxidation process technology and are available upon request.

Advantages of the ESTR, Inc. AOP Technology

- High efficiency
- No chemical requirements
- Low maintenance
- Excellent safety features with no moving parts exposed
- Low operating costs
- Complete mobility (if specified)
- Durability
- Remediation flexibility over wide ranges and levels of contaminants

Advanced Aeration Process (AAP)

The “Advanced Aeration Process” (AAP) employs a recently patented injector design that generates ultra fine air bubbles via the Hydro-Sparging™ Process and is ideally suited for DAF’s and high efficiency aeration applications. The AAP technology entrains atmospheric oxygen into the waste stream in the form of micron-sized bubbles. These bubbles range in size down to 0.5-5.0 microns. This is a significant improvement over conventional aeration technology, which produces bubbles in the 50-1000 micron range. Due to their smaller size, the bubbles created by the AAP technology increase the lift of the contaminants, entrain more usable oxygen and stay in solution longer. Furthermore, the AAP employs no compressors, blowers or associated equipment and is driven by a re circulation pump. The AAP can be employed separately as a post treatment process for the AOP in certain applications.

Fractionation

The Fractionator employs membrane technology that is specifically designed for use with the AOP technology. Membrane separation is used to separate components of an aqueous solution. The separating agent is a semi permeable membrane. This element, cast in a thin film, can pass certain molecules and rejects others, depending upon membrane formation and pore size. The resultant, typical of the membrane separation process, is as follows:

1. Spiral elements are coupled and fitted into containment tubes.
2. Permeate passes through the membrane from both sides of the permeate channel.
3. Concentrated solution leaves through feed spacer.
4. Permeate flows spirally in the permeate channel.
5. Last layer contacts holes in the central tube for exit to collection system.

Hydro-Lesser

The Hydro-Lesser™ process employs a patented coalescer technology, plus the AAP technology in combination to produce efficient removal of oil and water. The coalescer technology is designed to remove a discontinuous oil phase from a continuous water phase. If the degree of droplet dispersion is at or below the design point then the amount of oil removal should be sufficient to meet disposal requirements. By combining the AAP technology to the coalscer technology, produces a higher degree of efficient oil/water separation than previously obtained with only the use of a coalscer.

The unit consists of a polyethylene tank, PVC inlet and outlet, ancillary piping and internal polypropylene packing.

The oil/water influent enters the separator inlet piping where the flow is directed into the center of the inlet head. The majority of the solids settle immediately and the kinetic energy of the influent stream is dissipated.

The head of the vessel reverses the oil/water influent direction. Gross oil separation (including oil slugs) is accomplished rapidly by gravity.

The oil/water mixture passes into the coalescing medium where oil droplet removal is accomplished by the following two mechanisms:

1. Oil droplets rise and impinge upon the horizontal surfaces of the coalescing Medium.
2. Oil droplets travel a tortuous path with impingement upon perpendicular surfaces of The medium.

The top portion of the tank serves as a holding reservoir. Accumulated oil resides in the top 40% of the separator tank. The accumulated oil is dewatered and stored until removed through the oil discharge valve.

Cleanest water is drawn off from the bottom of the separator as water flows up the outlet piping down comer. Water flows out through the effluent water outlet piping.

Wastewater for Treatment

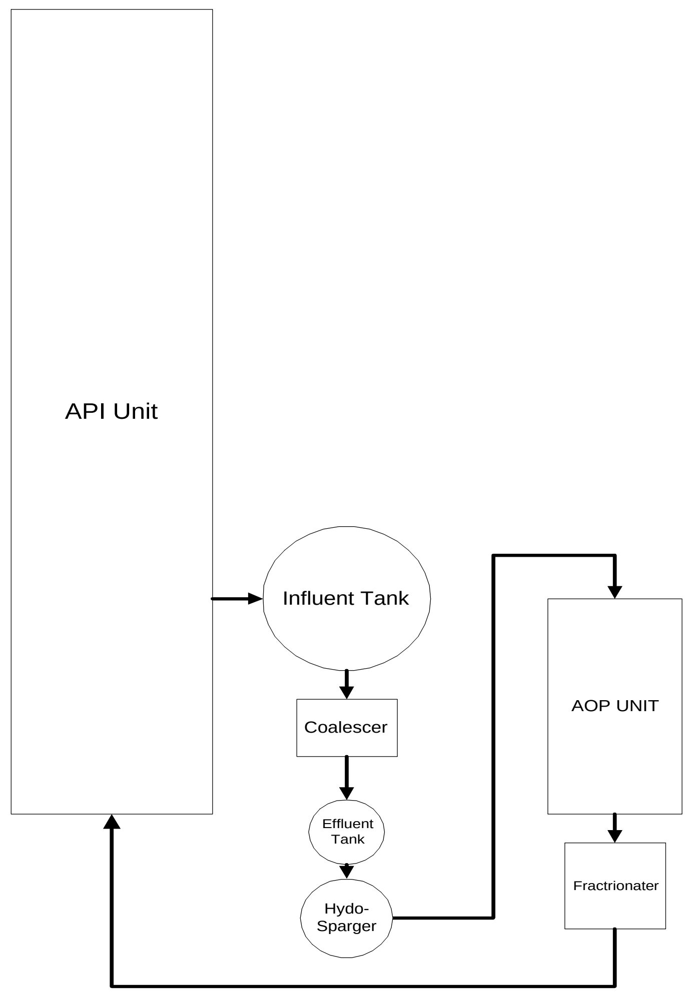
Prior to the arrival of the technologies at the F-6 site, Blue Diamond was provided with analyses of the wastewater at the site.

Initial wastewater samples were drawn from each phase of the existing treatment system to quantify what each part of the system was actually accomplishing. Blue Diamond was given a complete walk through and explanation of the entire system so as to be able to understand the flow and workings of the existing component. Test results of the actual componentry are provided later in this report.

Site Layout

The equipment was uncrated, inspected and positioned adjacent to the outlet tank of the API separator. The AOP, AAP, Hydro-Sparging™ Process, Coalescer and associated equipment were assembled and tested. The laboratory equipment was transferred to an office on the site. Two containment vessels were positioned for retention of the influents and effluent of the various processes involved. Connections to and from equipment and the tank age were completed using PVC piping. A submersible pump and hose provided the influent supply from the API unit. Maraven people for protection from the elements erected an overhead cover. The equipment was connected to an electrical panel positioned at the site by Maraven service personnel.

AOP Pilot Plant Layout



Test Agenda

An initial charge of 130 gallons of fresh water was transferred to the AOP. The AOP was operated for 2 hours to ensure functioning of all components and to “charge” the system. The wastewater from the outlet side of the API unit was drawn into the influent tank and allowed to cool overnight. This was done because the pilot unit, being plastic, has a maximum operating temperature of 120° F. The following morning, the influent supply from the influent tank was provided by a compressor driven diaghram pump, though the coalescer and stored in the effluent tank. A 15-gallon sample was taken from the effluent tank and pumped, with a submersible electric pump, into the Fractionator tank. The Fractionator was run to show the removal of solids capability. Following this test, wastewater from the effluent tank was transferred to the AAP unit. We were asked by Maraven personnel to run the wastewater through the entire system to see how clean we could get the final discharge water. Visual results of the Fractionator test showed a discoloration to the discharged water. This led to a test in the laboratory with the addition of aluminum sulfate into a sample of the discharged water. The water sample cleared almost immediately. Preliminary calculations were made to determine the amount of aluminum sulfate to be used in the testing of the stream. These calculations showed that it would take 80 grams of aluminum sulfate to be added to the 350 gallons of liquid in the AAP unit. A hose was installed on the air inlet of the injector on the unit, and the aluminum sulfate was sucked and mixed into the system via the open end of the hose. There was an instantaneous reaction with the liquid and aluminum sulfate. The wastewater from the AAP unit was periodically drawn into the AOP system and allowed to process. The AOP operates in static or batch mode, which involves mixing influent with previously, treated water. Periodically, samples were drawn off of each step or phase of the treatment process and analyzed. Based upon the results of the analysis, adjustments were made on the equipment to derive the operational ranges and to develop the ultimate equipment and process design parameters. The objective was to obtain a balance between pollutant loading and oxidative capacity of the system, as adjusted and regulated during the pilot, which remains saturated with ozone. The sampling and testing continued for an eight-day period to allow sufficient data to be collected for final analysis by ESTR, Inc.

Analysis and Testing

Servicios Blue Diamond de Venezuela C.A. provided the analysis and testing of influent and affluent samples and an independent laboratory provided by Maraven. Blue Diamond and ESTR, INC provided test equipment. The Office provided by Maraven provided the work area for the testing and analysis. Standard Hach test equipment and procedures were used throughout the test period for the on-site testing.

Results

The following charts depict results of the technologies on the contaminant levels and the currently installed system ability to meet discharge requirements. It clearly demonstrates the ability of the technologies to meet and exceed the requirements for re-injection of the water. These results were analyzed by ESTR, Inc. to determine the appropriate type of technologies required for the treatment of the production water at the F-6 site.

	Temp°C	PH	TSS	Total Hydrocarbons	Phenol
Influent	72	7.4	6,480 mg/l	2,600 mg/l	--
API Effluent	68	7.4	6,180 mg/l	1,500 mg/l	9.0 mg/l
Wamco	56	8.0	233 mg/l	230 mg/l	--
Pit	60	8.2	77 mg/l	8.3 mg/l	--

-- Means no test taken

A test was done to show what the Hydro-Lesser and the Fractionator could do. The wastewater was taken out of the API discharge and put through the Hydro-Lesser, than run through the Fractionator; the following shows the results of that test.

	Temp°C	PH	TSS *	Total Hydrocarbons	Phenol
Hydro-Lesser	47	7.9	4,650 mg/l	920 mg/l	--
Fractionator	47	8.8	90 mg/l	ND	--
Hydro-Lesser Solids	47	10.1	4,960 mg/l	--	--
Fractionator Solids	47	12.1	9,300 mg/l	1,350 mg/l	--

-- Means not tested for
* Suspect inaccurate readings on the high end due to turbidity in the liquid

We were than asked to run the entire AOP system to see what that would do. From the results it can be noted that the only advantage of using the entire AOP system would be to remove the soluble contaminants, such as BETEX and phenol. The re-injection requirements can easily be met with the use of the Hydro-Lesser dissolved air floatation and the Fractionator. The following table shows the results from the remainder of the pilot.

	Temp°C	PH	TSS	Total Hydrocarbons	Phenol
Hydro-Lesser Eff.	47	8.6	3410	190	--
	47	9.1	3560	330	--
	47	8.3	4445	400	--
	47	8.3	3440	270	--
DAF Effluent	47	8.2	890	50	N/D
	47	7.7	230	40	N/D
	47	7.8	270	40	N/D
	47	--	460	30	--
AOP Effluent	47	8.2	700	50	N/D
AOP Effluent	47	8.2	700	50	--
	47	7.8	290	30	N/D
	47	--	415	20	--
Fractionator Eff.	47	7.8	55	N/D	--
	47	7.8	55	N/D	--
	47	7.8	10	N/D	N/D
	47	--	N/D	N/D	--
	47	--	N/D	N/D	N/D

Recommendations

The F-6 site wastewater currently collected into the large storage tank can be effectively and economically treated. The treatment process allows for simplification of the overall wastewater treatment process ultimately saving both capital equipment and operating costs. The production water, with a maximum flow of 50,000 barrels per day, is easily treatable by ESTR, Inc. Hydro-Lesser process, Dissolved Air Floatation and a Fractionator technology to meet the requirement for re-injection into the oil field. The system would be configured to try to retrofit the currently installed API system and to have as much equipment as possible to be built in country.

We are currently developing a proposal to out line the concepts and requirements for presentation to Maraven to take this to the next step of installing a system at F-6 or equivalent.