**2015 Chief of Naval Operations Environmental Competition Award**
**Award Category: Sustainability, Industrial Installation**

**Narrative**

*Combating Hydrogen Sulfide and Accelerated Corrosion in Fuel Tanks and Piping*

## Introduction

The NAVSUP Fleet Logistics Center (FLC) San Diego mission is to provide combat capability through unmatched logistics support to 86 home-ported ships, submarines, and transient vessels, and 11 over-the-horizon regional naval bases and air stations in California and Nevada. The command is comprised of over 221 Navy personnel and 729 civilian employees and provides a host of logistics services and support, including fleet supply assistance, food service and subsistence support, contracting support, cargo loading and offloading services, postal services, material handling equipment maintenance/repair services, material management services, flight line cargo and personnel transportation, and personal property shipping services for DON, DOD, and Coast Guard units operating in the Pacific Southwest.

NAVSUP FLC San Diego is also a designated Defense Logistics Agency (DLA) Energy Defense Fuel Support Point (DFSP). Operational control of the DFSP is performed by the FLC San Diego Fuel Department, charged with storing, managing, and providing fuel and petroleum products, as well as assurance that the fuel meets pre-determined quality standards for use by the Fleet, Homeland Security, and National Oceanographic and Atmospheric units. Additionally, it is responsible for providing logistics support to eight naval air bases located in the command's area of responsibility (AOR). The FLC San Diego Regional Fuels Team, with support from the Naval Facilities Engineering Command, provides technical oversight for environmental regulatory compliance, facilities maintenance and construction, and technical oversight to all the regional bulk fuel and air stations located in California and its AOR.

## Sustainability Industrial Installation Team

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DFSP Point Loma Aerial Photo

## Background

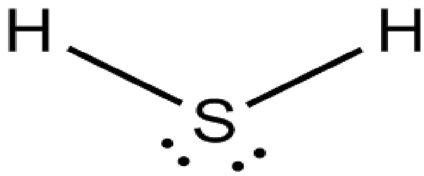
When water and petroleum fuel exist together, yeast, fungus, and bacteria may be present at the interface of the two fluids at the water/steel interface level. These organisms live in water and feed on petroleum fuels. Only a small amount of water is required to support large colonies of organisms, which can develop into Hydrogen Sulfide (H2S) or Microbiological Induced Corrosion (MIC) and can accelerate metal loss corrosion and lead to serious health and safety problems.

## Health Effects of Hydrogen Sulfide

In September 2013, the FLC San Diego Fuels Team discovered a serious H2S problem in the contaminated petroleum product (CPP) tank that shut down the Fuel Oil Reclamation (FOR) plant. The plant was newly constructed in 2011 and operated successfully without problems prior to developing the H2S contamination problem.

H2S is classified as a chemical asphyxiate and acts much like carbon monoxide and cyanide gas by obstructing cellular respiration and essential oxygen intake. At certain exposure limits, the end result is biochemical suffocation. Physical reactions to hydrogen sulfide range from eye irritation and metabolic damage, to brain damage or even loss of life if not treated immediately. Figure 1 represents a H2S corrosion cell.

Figure 1: H2S Corrosion Cell




Hydrogen sulfide is a chemical compound with H2S formula. It is a colorless gas with a rotten egg odor characteristic. Heavier than air, it is a poisonous, corrosive, flammable, and explosive gas. It is considered a poison that can affect several different systems of the body. Prolonged exposures can lead to migraine headaches, pulmonary edema and loss of motor coordination. Most notable impact is to an individual's nervous system.

Over the course of the next several months, FLC San Diego discovered that the H2S problem was the result of anaerobic microbiological bacteria found in the water fraction permitting sulfur oxidizing microorganisms to feed on the sulfur content within the fuel fraction. Further investigation revealed the H2S problem was due to oily water contents removed from a series of underground storage tanks that were replaced by a military construction project that modernized the facility.

On 16 October 2013, waste water samples were taken from the CPP tank. Laboratory analysis determined that the water in the tank contained a significant source of hydrogen sulfide as depicted in Figure 2. The dissolved sulfides were greater than the San Diego Municipal Code limit of 1 mg/L. Both oxygen and pH levels were very low and total sulfides were extremely high providing ideal conditions to allow anaerobic and microbiological bacteria to thrive.

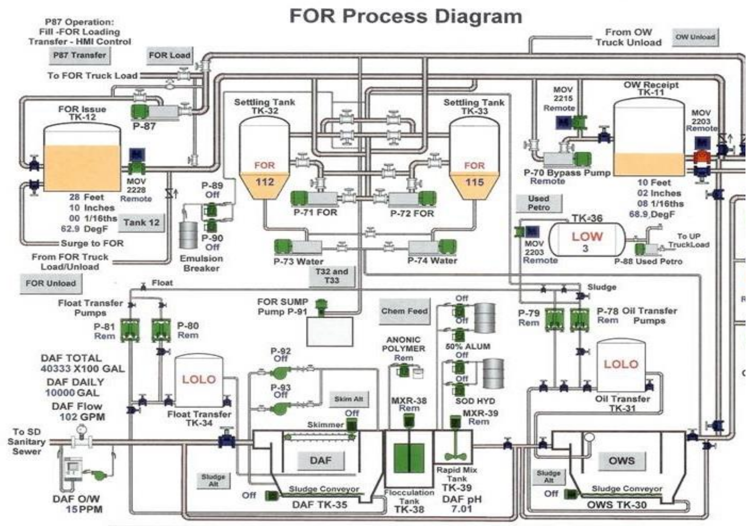
Figure 2: 16 October 2013 Waste Water Sample Analysis & Results:

| GRAB SAMPLE | RESULTS | GRAB SAMPLE | RESULTS |
|---|---|---|---|
| Total Sulfide | 76.5 mg/l | Dissolved Sulfide | 56.1 mg/L |
| Biochemical Oxygen Demand | 3,920 mg/L | Chemical Oxygen Demand | 10,500 mg/L |
| Nitrate as N | <0.05 mg/L | $O_2$ Consumption Rate | 457 (mg/g)/h |
| pH | 6.69 SU | Total Organic Carbon | 670 mg/L |
| Total Suspended Solids | 930 mg/L | Sulfate as SO4 | 94.8 mg/L |
| Volatile Suspended Solids | 590 mg/L | Temperature | 26° C |

Armed with the laboratory analysis, FLC San Diego consulted the U.S. Environmental Protection Agency's (EPA) design manual for "Odor and Corrosion Control in Sanitary Sewerage Systems and Treatment Plants" and noted that hydrogen sulfide odors present themselves in the presence of total sulfide in wastewater with low pH levels. The design manual also indicated that sulfides are typically produced under anaerobic conditions through the reduction of sulfates that are present in wastewaters. The test results substantiated that the oily water from the closure of the decommissioned underground storage tanks that was processed through the new FOR plant was the chief culprit for the H2S contamination. The EPA design manual also suggested that raising the wastewater pH from 6.69 to greater than 8.5 could help reduce the concentration of hydrogen sulfide by approximately 90%. By converting the hydrogen sulfide into an ionic sulfide it would significantly decrease the pungent odor. The process, however, did not reduce the dissolved sulfides within required discharge limitations, so the team went back to the drawing board to determine a new course of action.

The next step was to conduct a comprehensive review of the FOR plant design features and system limitations. The 2011 Fuel Oil Recovery system was designed to receive, store, and separate oily water, while simultaneously recovering the petroleum fraction as fuel oil reclaim and allow for the discharge of the treated processed water into the City of San Diego Metropolitan sanitary sewer system within discharge limitations. The City of San Diego permit imposed restrictions on total petroleum hydrocarbons (TPH), oil and grease, acidic and alkaline limitations measured by symbol pH, flash point, and dissolved sulfides. For NPDES compliance monitoring, the pH is measured accurately and reproducible to within 0.1 Standard Units (S.U.).

Figure 3: FLC Fuel Oil Reclamation Plant Process




The meter has a range from 0 to 14 S.U. and is equipped with a temperature compensation adjustment with limitations shown in Figure 4.

| Figure 4: San Diego Sanitary Sewer Discharge Permit Limitation | | |
|---|---|---|
| TPH, Oil & Grease | mg/L | 500 |
| pH | SU | 5 to 12.5 |
| Flash Point | Degrees F | >140 |
| Dissolved Sulfides | mg/L | 1 |

Figure 5 shows the typical water quality parameters and unit limitations of the contaminated petroleum products for which the FOR system was designed to handle. The facility does not conduct any operations subject to federal categorical pretreatment standards. However, since the amount of industrial processed wastewater discharged may exceed 25,000 gallons per day and free product is present in the oily water fraction being processed, FLC San Diego is classified by the City of San Diego as a Category 2 Significant Industrial User. Figure 5 highlights a number of regulated pollutants and their permit limits.

| Figure 5: Oily Water Quality Parameters for Acceptance Parameter Units Limitation | | |
|---|---|---|
| Oil & Grease | mg/L | 10,000 to 50,000 |
| Emulsified Oil & Grease | mg/L | 0 to 2,200 |
| API Gravity of Oil at 60 deg C | Degrees API | 25 to 40 |
| Oil Viscosity at 50 Deg C | SU | 30 to 90 |
| Temperature | Degree F | 40 to 100 |
| Suspended Solids | mg/L | 60 to 620 |
| Chloride | mg/L | 17,000 |
| pH1 | mg/L | 5 to 12 |
| Flash Point1 | Deg | >140 |
| Dissolved Sulfides1 | mg/L | <44 |
| Cyanide1 | mg/L | <1.9 |
| Cadmium1 | mg/L | <1 |

The FLC San Diego Fuels Team also consulted with the FOR plant design agent who put the team in touch with a chemical supplier. When contacted, the supplier provided a Chemical Engineer to assist our team in finding a solution. The previous testing performed by the FLC San Diego Team was reviewed by the Chemical Engineer who also confirmed that the water fraction contained sulfur reducing bacteria feeding on the oil fractions sulfur content. Working with the Chemical Engineer and the design agent, the FLC San Diego Team looked at various potential H2S control strategies based on quantifiable costs, advantages and disadvantages. The list was eventually reduced to six options. Figure 6 lists the six H2S control options that were considered.

Figure 6: $H_2S$ Control Strategy Options

| **$H_2S$ Control Strategy** | **Qualitative Costs** | | **Advantages** | **Disadvantages** |
|---|---|---|---|---|
| | **Construction** | **O&M** | | |
| Option 1:<br><br>Chemical Complexation | Low | Medium | • Binds sulfide into soluble complex. Does not produce a sludge requiring off-site disposal.<br>• Chemicals are neutral pH and non-corrosive.<br>• Removes $H_2S$ potential with non-hazardous chemicals.<br>• Can use existing chemical feed systems. | • Proprietary chemicals. However, chemical cost to treat 160,000 gallons may be less than $1200. |
| Option 2:<br><br>Chemical Precipitation | Low | Low | • Removes dissolved sulfide.<br>• Requires little additional equipment if existing chemical feed systems can be used. | • Ferric-based chemical may require additional caustic soda usage to maintain desirable pH.<br>• May generate sludge that would require off-site disposal.<br>• Chemicals are low pH and corrosive to handle. |
| Option 3:<br><br>Adjust pH to shift hydrogen sulfide to Sulfide $S^{2-}$ | Low | Low | • Requires only caustic soda feed.<br>• Can utilize existing feed system. | • Does not reduce dissolved sulfide concentration. Release of wastewater would violate San Diego Municipal Code.<br>• **$H_2S$** may develop downstream as pH lowers. |
| Option 4:<br><br>Chemical Oxidation | Low | Medium | • Completely removes sulfide using sodium chlorite, potassium permanganate or hydrogen peroxide. | • Significant safety hazard associated with handling strong oxidizer onsite.<br>• Keeping unused chemical onsite is not preferable.<br>• Existing chemical feed systems cannot be utilized. |
| Option 5:<br><br>Green Sand Filter | High | Medium | • Precipitates sulfide onto media.<br>• Removes **$H_2S$** potential. | • High equipment cost. Requires construction of new filter area and hydraulic design.<br>• Future wastewater from CB&I Tank does not require treatment.<br>• May only be utilized to dispose of 160,000 gallon batch load.<br>• Requires hazardous chemicals. |
| Option 6:<br>Aeration (oxidation) | High | Medium | • Removes sulfide without using hazardous chemicals. | • High equipment costs associated with air diffuser system and pumps.<br>• High energy use. |

In the end, Option 1 allowed FLC San Diego to use a closed loop pretreatment plan before discharging the water into the city sanitation system. Because of permit requirements, the team wanted to be sure Option 1 reduced the dissolved sulfides to less than 1 mg/L. The plan called for sending the H2S contaminated water from the CPP tank to the Oil Water Separator, introducing a mixture of chemicals at the Dissolved Air Flotation system, and returning the treated liquid back to the CPP tank. This allowed the team to take periodic samples to verify the contaminated water was being adequately treated. The chemicals used to treat the H2S consisted of a dissolved sulfide coagulate scavenger, a conditioning agent, an odor control agent, sodium hydroxide to adjust the pH range, and an anionic polymer.

**Chemical Pretreatment System**

The FOR plant is equipped with a human machine interface (HMI) controlled pretreatment Dissolved Air Flotation (DAF) tank that was used to remove the H2S odor and clarify the water to meet permit discharge requirements. The chemicals were added through the existing DAF flash mix tank with the existing metering pumps and mechanical mixer. A series of existing feed pumps were utilized to inject chemicals to the polymer blending unit that consisted of a 150 gallon Rapid Mix Tank. A 3,750 gallon Flocculation Tank was then used to introduce the coagulate, odor control and caustic soda chemicals required to adjust the pH levels to meet the discharge limitations. The DAF tank is shown in Figure 7.

Figure 7

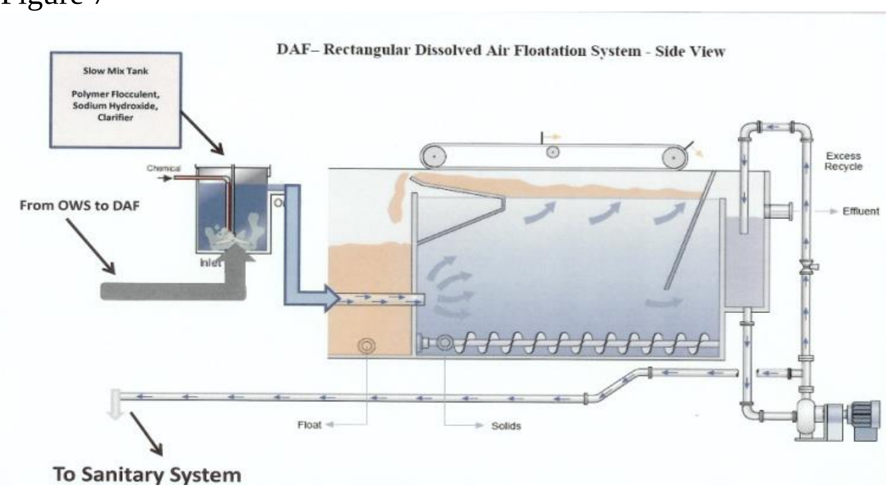



Figure 7 depicts the DAF tank that, in conjunction with the prescribed chemicals, eliminated the H2S odors and helped lower the concentrated cationic or anionic polymer to a suitable level. The DAF unit was able to skim suspended solids sending them to the waste tank, and lower the dissolved sulfides. This allowed the water fraction to be discharged to the sanitary system. The remaining oil effluent was sent to a settling tank for further oil reclaim processing.

**Odor Control Feed System**

The FOR odor control feed system was used to remove the dissolved sulfides. It was operated locally at the DAF Tank control panel by the FOR plant operator. A remote indicator signal generated by the programmable logic controller (PLC) permits feed pumps to control the flow rate of chemical dosage and assisted in the removal of dissolved sulfides. The odor control chemical required a pH level of 9.5 to 11 SUs for effective removal of the hydrogen sulfide and Mercaptans. Approximately **4 pounds of the odor control agent was** used to remove each pound of dissolved sulfide, therefore 100 mg/L of dissolved sulfide at a system flow rate of 120 GPM required a feed rate of **286 mg/L per minute**.

**Water Clarification Agent Feed System**

When the pH levels reached 9.5 and before the caustic soda was added, the system was ready to begin the clarification process. Higher pH levels increased the rate and effectiveness of the chemical reaction resulting in a lower required dosage of odor control agent. The odor control agent was effective in controlling the dissolved sulfide in a water pH range from 9.5 to 11. Since the water pH is normally less than a pH of 7.5, the addition of sodium hydroxide raised the pH to between 9.5 and 11.

**Polymer Feed System**
The FOR process included an anionic polymer feed system that was used to assist in the removal of emulsified oil and suspended solids. The polymer feed system is a pre-packaged and preassembled skid system that includes piping, valves, rotometers, metering pumps, mixing vessel and spill containment pallet. The polymer flocculent is typically used with a coagulant to improve effectiveness of treatment. If the flocculent cannot be removed effectively, then the oil and total suspended solids (TSS) removal efficiency is reduced. The polymer was used to bridge the small pin flocculation particles and make larger, stronger flocculation particles that were more easily removed by the air bubbles.

**Accelerated Internal Corrosion**
Between November 2014 and January 2015, the Fuels Team used the aforementioned processes to discharge 750,000 gallons of treated H2S water into the municipal sanitary system with an average daily dissolved sulfide discharge level of 0.013 parts per million of dissolved sulfides. All of this was done under the watchful eyes of the City of San Diego and Naval Base Point Loma's Environmental Department.

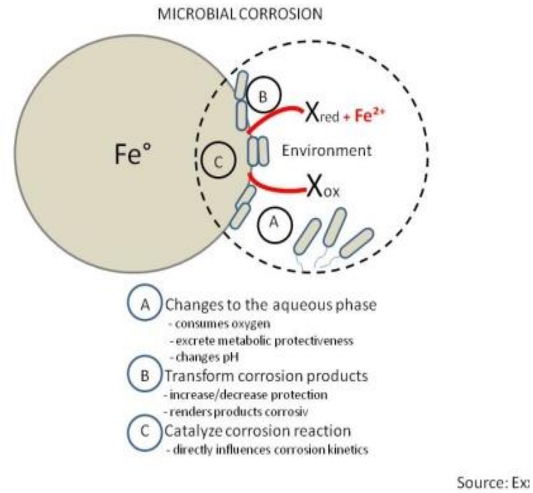
After processing the treated H2S for one month, an 8" pipe used to transfer the oily water failed. The section of pipe, Figure 8, was sent to a forensic laboratory for diagnostic analysis. The examination and testing of the failed pipe concluded the failure was likely caused by internal pitting from microbiological induced corrosion and oxygenated water. The presence of water and sediment accumulating at the low points of the pipe corroded the unprotected carbon steel. The sediment accumulation led to growth of sulfur reducing bacteria (SRB) and accelerated corrosion caused by microbiological induced corrosion (MIC). All three criteria necessary for MIC were present in the pipe, i.e., elevated sulfur, elevated SRB, and tunneling within the corrosion pits. The failed pipe had been in service for less than three years.

Figure 8: Section of Failed Pipe


The laboratory determined that sediment accumulation was caused by a stagnant oily water mixture in the pipe which is a frequent recurring problem caused by intermittent pumping operations. When allowed to stagnate, the oil and water separated and the particulate settled out of the solution onto the bottom of the pipe causing pipe failure at a pipe low point. DNA testing using energy dispersive spectroscopy concluded that anaerobic SRB and oxygenated water contributed to the accelerated corrosion and ultimate failure of the pipe.

**Lessons Learned**
Steel pipe without an interior coating is susceptible to corrosion, and corrosion rates can be very high resulting in premature pipe failure. Figure 9 depicts how microbiological SRB corrosion occurs on carbon steel piping. An American Petroleum Institute (API) 570 inspection of the total 2,800 feet of piping was conducted in October 2015. A significant number of additional corrosion issues were discovered. Meanwhile, the pipe has been taken out of service pending a full replacement of the pipe with internal coated piping.

Figure 9:  Causes of Microbiological Corrosion




Three items are necessary to positively identify microbiological induced corrosion due to sulfur reducing bacteria:

- Elevated levels of sulfur
- Elevated levels of sulfate reducing bacteria
- Physical identification of tunnels within the pits morphology.

All three criteria necessary for MIC were present: elevated sulfur, elevated SRB, and further tunneling with corrosion pitting.

There is some concern that the 1M gallon CPP tank may have also suffered microbiological induced corrosion damage.  The tank's coating has likely prevented similar damage to that sustained to the pipe, but there remains concern that damage from bacteria may have occurred to voids or defects in the tanks coating.  A project to clean and inspect the tank interior has been funded.  The CPP tank inspection is scheduled to begin in January 2016.  Although the CPP tank is out of service pending inspection and repairs, the FLC San Diego Fuels team has been able to remain fully operational.

The Fuel Oil Recovery system is a critical cost savings resource.  Approximately 1.5M gallons of fuel is reclaimed annually, generating over $1M in revenue at FLC San Diego.  The primary source of the oily water comes from Navy vessels entering shipyards for maintenance.  Without the Fuel Oil Recovery system, oily water would be treated as a costly Resource Conservation and Recovery Act (RCRA) hazardous waste.  With the closest transportation and disposal facility located in the Los Angeles Basin, the Navy achieves over $14M annually in cost avoidance by successfully operating the Fuel Oil Recovery system.

**Summary**

Over the past year, the FLC San Diego Fuels Team developed a much better appreciation and understanding of hydrogen sulfide and accelerated corrosion processes.  The team learned valuable lessons from this event and has documented both the challenges and successes associated with hydrogen sulfide and microbiological corrosion.  The team continues to diligently pursue opportunities to enhance infrastructure and implement standard operating procedures to prevent future occurrences.  Likewise the team is committed to assist others in understanding the health, safety, and environmental risks associated with the accumulation of standing water in fuel tanks and piping.  The FLC San Diego Fuels Team displayed unfailing resolve to protect the environment and meet the mission.  Analyzing the H2S problem for over one year, the team developed an effective course of action to successfully resolve an extremely complex environmental problem.  Their experience provides a great opportunity to share with other facilities the potential preventative and corrective actions at their disposal to combat future H2S and microbiological induced corrosion occurrences throughout the Navy.