

EnvTech, Inc.

Process Equipment Decontamination & Environmental Solutions

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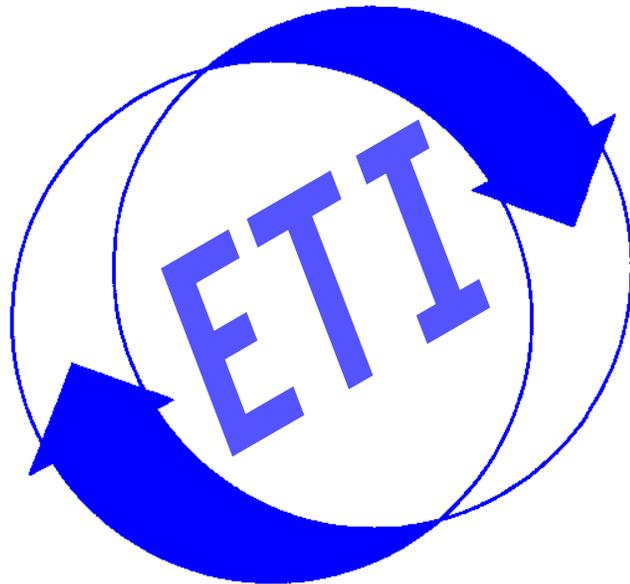


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Overview

EnvTech, Inc. (ETI) has been offering expertise and products for refinery and chemical plant maintenance, operations, and environmental needs since 1991.

EnvTech's main focus is providing procedures for (and supervision of) chemical cleanings in order to prepare entire process units for turnaround maintenance (or for long-term lay-up or closure).

In today's constantly expanding oil and gas industries every minute of production time is necessary to fulfill production requirements. Lost production time means lost revenue. With this in mind, EnvTech has developed a chemical cleaning process that can be completed in less than 48 hours, and leaves the entire unit gas-free and ready for hot work. The proprietary buffered cleaning solution EnvTech uses is non-corrosive and can be drained directly to the plant sewer (with no ill effect on the wastewater treatment plant).

As a consulting firm (not a contractor) EnvTech will provide the best procedure to clean a particular process unit, and work with the plant's staff (or a qualified contractor) to complete the project successfully.

EnvTech has developed procedures for and supervised chemical cleanings of process units of many types, including:

- ◆ Atmospheric Crude Distillation
- ◆ Gas Oil Fractionator
- ◆ Distillate Fractionator
- ◆ Vacuum Crude Distillation
- ◆ Visbreaker
- ◆ Visbreaker Vacuum Flasher
- ◆ Delayed Coker
- ◆ Flexicoker
- ◆ FCC
- ◆ Cat Poly
- ◆ HF and Sulfuric Alkylation
- ◆ Naphtha Hydrotreater
- ◆ Hydrocracker
- ◆ Platformer

References are available for each of these projects.

The EnvTech Process

In general each process unit is cleaned by recirculation of ETI Cleaning & Gas Freeing Solution™ using the unit's pumps. All vessels and exchangers are liquid filled except for large columns such as main fractionators or isostrippers, which are cascaded. The solution is heated to a temperature range of 180°F to 200°F using process unit reboilers, furnaces, and/or direct steam injection. The goal is to provide adequate flow through the entire system while minimizing the amount of temporary connections and blinding required prior to the start of the cleaning.

ETI Cleaning & Gas Freeing Solution™

EnvTech's proprietary ETI Cleaning & Gas Freeing Solution™ utilizes a strong buffer system in combination with appropriate chelants and surfactant in order to: neutralize polythionic acids on contact, dissolve all scales found in nearly any refinery process unit, and emulsify any hydrocarbon residue contained in a system. The mixture also renders pyrophoric substances inactive and has proven excellent for polymer removal. Additionally, Benzene and other regulated air contaminants have been absent from the vapor spaces of vessels opened after these cleanings.

ETI Cleaning & Gas Freeing Solution™ is effective, non-toxic, non-flammable, non-hazardous, and non-corrosive. It does **not** make **stable** emulsions. Any emulsified hydrocarbons can be recovered in the refinery's API separator and in most locations the solution can be drained directly to the plant sewer with no ill effect on the wastewater treatment plant. Thus, ETI Cleaning & Gas Freeing Solution™ not only saves valuable time, but also virtually eliminates waste disposal costs.

Heavy Oil Units

For equipment containing atmospheric resid or heavier hydrocarbon our newest highly biodegradable solvent additive, **EcoSolvent**, is recirculated with ETI Cleaning & Gas Freeing solution. The 100% biodegradable **EcoSolvent** vastly improves the removal of asphaltenes, coke deposits, and heavy hydrocarbons with no ill effect to the environment.

HF Alkylation Unit One Step Cleaning & Neutralization

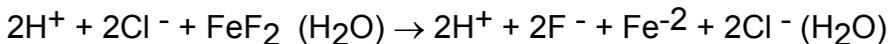
EnvTech's particular specialty is the HF Alkylation Unit one step cleaning and neutralization process. With this revolutionary process the Alkylation unit is cleaned for entry by circulating ETI Cleaning & Gas Freeing Solution™. The cleaning solution neutralizes acidity immediately in addition to dissolving any Iron Fluoride Scale and removing Polymer found throughout the Alky equipment. This type of cleaning is completely non-corrosive to the process unit and can be completed in less than 48 hours. In some locations the used cleaning solution can be drained directly to the plant sewer.

Overview of Past Methods

The best way to demonstrate the advantages of EnvTech's one step cleaning and neutralization process is by comparing it with alternative HF Alkylation unit chemical cleaning techniques.

Inhibited HCL

When inhibited hydrochloric acid is used to remove iron fluoride scale, the equilibrium in the solution could be described as:



The actual amount of HF ($\text{H}^+ + \text{F}^-$) available in the circulating cleaning solution depends on the amount of iron fluoride scale dissolved, and on the quantity of HF remaining in the system after it is evacuated for the cleaning.

The problems with this mixture as a cleaning solution for HF Alkylation units concern both corrosion rates and cleaning performance:

- Corrosion inhibitors are inhibitors not preventers. Inhibitors slow down the corrosion rate of hydrochloric acid on carbon steel, but high temperatures or high liquid velocities compromise this performance. Any cleaning solution must be heated to at least 180°F for effective polymer removal, but even hydrochloric acid alone (without the fluoride in the solution) is effectively inhibited to only 140°F.
- The HF is not inhibited nearly as effectively as the HCl. In utility boiler cleanings, where HCL + HF mixtures are often used to remove silica scale, EPRI (Electric Power Research Institute) guidelines dictate that no more than 0.25% HF should be present in cleaning solutions due to excessive corrosion rates encountered where more HF is present.

- The addition of Boric acid or other organic acids to these HCL mixtures makes them more corrosive and less susceptible to inhibition.
- When HCl solutions are re-used on multiple circulations in an HF alkylation unit (or in any equipment) the solution becomes corrosive due to the total concentration of dissolved iron. This becomes a severe problem at about 1% total iron (ferric iron, which would rarely be seen in an alkylation unit cleaning, and can be reduced to ferrous iron by simple means, is a problem at much lower concentrations). Accelerated corrosion resulting from high iron concentrations is due to a mechanism that is unaffected by conventional inhibitors.

In addition to high corrosion rates and polymer removal problems, the fact that acid cleanings require both rinsing and neutralization creates two distinct disadvantages to this method. The first is added downtime. EnvTech's method saves valuable time by including the neutralization in the same step as the cleaning. The second disadvantage is the increased volume of waste liquids created by the rinsing and neutralization. This extra volume is very significant when a large system like an HF Alkylation unit is cleaned.

Furthermore, there is always the risk of leaving something full of acid in a large, complex system like an entire HF Alkylation unit. The failure of even a small piece of piping is a big problem when the unit is started up.

Finally, acid cleanings leave carbon steel surfaces in a very "active" condition. In other words, the surfaces are very susceptible to additional corrosion.

Ammonium Citrate

One alternative is ammonium citrate. The ammonium citrate is typically applied in the low pH / high pH mode (as in the "Citrisolve" process).

A significant down side to this method is that ammonium citrate is not a very strong buffer system. When the system is inventoried, the pH of the circulating solution will often drop to 2.0 (or lower), requiring the addition of ammonia to restore the system to neutral pH. This in turn means that some small areas could be left at an acid pH. Ammonia is also (usually) a very significant problem in refinery effluent.

The EnvTech Difference

EnvTech Inc.'s proprietary "Clean & Gas-Free" process utilizes a strong 8.8-pH buffer with appropriate chelants, eliminating even more of the disadvantages of the acid cleaning, and avoiding the use of ammonia in the cleaning solution.

Because of the strong buffer, everything that comes into contact with the cleaning solution is neutralized immediately, avoiding potential high corrosion rates while pH is being adjusted and eliminating the chance of leaving any area at an acid pH. This mixture has proven excellent for polymer removal and can be heated too much as 225°F without adverse effects. In most locations, the cleaning solution can be drained directly to the plant sewer when the cleaning has been completed.

References are listed on accompanying pages. An asterisk denotes HF Alky Unit references. For further information, please contact us at (775) 856-2200, fax (775) 856-3303, or e-mail: info@envtech.com.

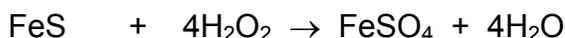
ETI Oxidizer #1™

In addition to its flagship product, EnvTech now offers a novel oxidation technology which includes all of the advantages of Hydrogen Peroxide with none of the hazards. We have recently applied it in conjunction with ETI Cleaning & Gas Freeing Solution to clean and deodorize several Mercaptan storage vessels, quickly and effectively remove iron sulfide scale from refinery process equipment, and destroy benzene in refinery waste water.

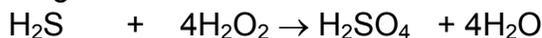
While ETI Cleaning & Gas Freeing Solution has proven excellent for the cleaning & decontamination of many types of refinery process equipment, it does not destroy sulfide but rather puts it into solution. As a result, the removal of iron sulfide scale is relatively slow with ETI Cleaning & Gas Freeing Solution alone. However, the introduction of an oxidant (such as Hydrogen Peroxide) would speed up the dissolution of iron sulfide by oxidizing the sulfide in the solution to sulfate. Unfortunately, as the following reactions will demonstrate, the safety of introducing Hydrogen Peroxide into hydrocarbon-containing process equipment is questionable at best.

Reactions of Hydrogen Peroxide with ferrous sulfide and hydrogen sulfide follow:

ferrous sulfide

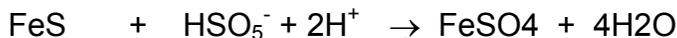


hydrogen sulfide



While the hydrogen peroxide accomplishes the desired result, it can decompose, releasing free oxygen and creating explosive conditions. The hydrogen peroxide can also accumulate and suddenly react when the proper conditions are reached. For these reasons, the addition of hydrogen peroxide must be carefully controlled and temperature and ORP carefully monitored. In many cases, these measures do not satisfy the safety concerns of oil refinery clients.

ETI Oxidizer #1 is a binary salt which supplies the Monopersulfate ion (HSO_5^-) as the oxidizing agent in solution. The similar oxidations are:



The above equation illustrates how ETI Oxidizer #1 accomplishes the desired results. The advantage of ETI Oxidizer #1 is that the decomposition of the Monopersulfate ion will release sulfate ions rather than free Oxygen. Furthermore the oxidizing reaction of ETI Oxidizer #1 has a much lower heat of formation than that of hydrogen peroxide. Thus, ETI Oxidizer #1 can **safely** and effectively remove sulfides from refinery process equipment.

ETI-916™ Universal Acid Inhibitor™

EnvTech's exclusive acid reaction inhibitor protects metals (including carbon steel and aluminum) from corrosion during cleanings with nitric acid. This allows for the quick removal of the most difficult deposits (including Calcium Sulfate) at ambient temperatures. This proprietary inhibitor also protects metals of construction from ferric ion corrosion in any mineral acid solution.

This product was recently used with nitric acid at a Northern California Refinery for the chemical cleaning of cooling water exchangers representing a variety of metallurgies, including carbon and stainless steels. As this was a pilot study by the refinery, the heads on five exchangers were pulled and the exchangers were examined before and after the cleaning. In addition, an in line corrosion monitor was used to monitor how well the inhibitor protected carbon steel from the nitric acid. A brief summary of the results follows.

- The first pair of exchangers cleaned were the least fouled. Approximately 99% of the deposits were successfully removed.
- The third exchanger was 80% plugged. The flow through this particular exchanger had been reduced to less than 20 gallons per minute. When the cleaning was complete 95% of the deposits had been removed and only 15 tubes were left with reduced flow.
- The fourth and fifth exchangers were 10% plugged and heavily fouled with a hard deposit containing significant levels of silica. The initial flow rate was minimal. However, the cleaning removed 98% of the deposits and renewed the exchangers to near maximum efficiency.
- Furthermore, at no point during the cleaning was a corrosion rate reading exceeding 1.87 mpy observed.

The benefits of this type of cleaning include:

- Increased availability of equipment as the inhibited nitric acid is effective in a short contact time. Thus drastically reducing the out of service time associated with mechanical cleaning.
- Significant cost savings (approximately ¼ the cost of normal mechanical options)
- Extended equipment service life due to the effectiveness of the inhibitor and the fact that the scale removal decreases or eliminates the "pitting" associated with under-deposit corrosion.

Upon completion of this pilot study our client discovered that by employing this type of cleaning on a regular basis to routinely remove waterside deposits rather than waiting until a severe loss of efficiency is observed it is possible to enhance refinery productivity.

Stabilization & Contaminant Fixation Products

EN-1 bonds soil into a hard (rock-like) material, which will pass TCLP for hydrocarbons and metals. This has been used to treat the area inside a refinery tank firewall after a large spill of vacuum resid.

Urrichem is a cementation promoter, which has been used successfully to treat mercury, arsenic, chromium and vanadium contaminated soils and sludges so that the resulting solids pass TCLP for non-hazardous disposal. Urrichem has been used for many diverse purposes: from treatment of filter press cake to pass TCLP for non-hazardous disposal to repair of a leaking clay pond bottom without emptying the pond.

Other Unique Products

ETI can provide procedures, supervision and products for the use of accelerated, enzyme-enhanced biodegradation technologies to treat various refinery sludges, as well as a wide range of hydrocarbon and pesticide-contaminated soils and water. This often can offer major reductions in treatment, time, and cost (versus other methods).

EnvTech's **zeolite material**, a synthetic absorbent that is selective for Benzene, Toluene, Ethylbenzene and Xylene (BTEX compounds) will hold benzene equivalent to 14% of its weight, and can be used in flow-through systems similar to those used for activated carbon. Thermal regeneration is possible for up to four cycles, and (unlike activated carbon) the regenerated material has the same capacity as virgin material. This material makes possible the treatment of large volumes of liquid to low BTEX concentrations without removing less regulated hydrocarbons to the same low concentrations.

This same synthetic absorbent is also effective (and selective) in removing BTEX compounds from air (or other gases) in the same type of apparatus in which activated carbon is used for this function.

Other synthetic zeolites are available for removal of benzene from hydrocarbon mixtures, for removal of PCB from hydrocarbon mixtures and for removal of various elements (such as: selenium, cadmium, chromium, mercury, lead, nickel and zinc) from water.

Consulting, Supervision & Oversight

ETI also offers consulting and project oversight services in cleaning of tanks (and other types of liquid receptacles), and in treating of the waste generated for easier (and more economical) disposal (or recycling). A program to optimize tank cleaning practices, as well as waste treatment and disposal practices includes:

1. A review of past practices for cost-effectiveness and environmental hazards.
2. Evaluation of the environmental safety of the prior tank cleanings.
3. Collecting data about tanks to be cleaned in the near future.
4. Selecting the optimum methods for cleaning of each tank to be cleaned in the near future, (and for treatment and disposal of the wastes generated).
5. Assistance with contractor selection and project oversight.

ETI personnel can provide expertise and unique technologies to resolve emulsions in product or waste tanks, with emphasis on removing solids from the tank (in the oil or water phase) rather than depositing them on the tank bottom.

Your First Choice

ETI offers many other services, including process unit startup and shutdown assistance, process troubleshooting, assistance with emulsion problems, on-stream (or semi on-stream) chemical cleaning procedures and unique, non-corrosive water side cleaning procedures. References are listed on accompanying pages.

Of course, all inquiries and evaluations are performed in strict confidence, and all information obtained and results produced are presented to the customer's representative. ***Please contact us for your free evaluation and estimate.***

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Refinery Case Histories
(starting next page)



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Refinery Case History Decontamination of HF Alkylation Units

EnvTech Inc. has developed a state-of-the-art cleaning process for HF Alkylation Units. Most chemical cleaning contractors rely on a three phase procedure using an acid for polymer and scale removal. Some utilize an ammoniated chelation process that has a low pH step as the initial phase. The best way to demonstrate the advantages of EnvTech's single phase cleaning and neutralization process is by comparing it with these alternative techniques.

Inhibited HCL, Sulfuric Acid and Ammoniated Citrate

The problems associated with these processes include:

- **Excessive Corrosion** - Corrosion inhibitors are inhibitors not preventers. Inhibitors slow down the corrosion rate of hydrochloric acid on carbon steel, but high temperatures, high liquid velocities, high iron levels and particularly HF concentrations above 0.25% compromise the inhibition performance. EPRI (Electric Power Research Institute) developed guidelines for the boiler industry regarding the use of HF for silica removal. They determined that the maximum level of HF present in the cleaning solution should be 0.25%. The HF is not inhibited nearly as effectively as the HCl. Temperature becomes a factor since polymer removal does not effectively occur at temperatures below 180° F while inhibition benefits begin to diminish above 140° F.
- **Unnecessary Exposure of Personnel & Equipment** - Exposure to the problems associated with hot acid solutions, particularly those containing levels of HF is unnecessary because EnvTech has developed a widely tested and proven non-acidic method.
- **Excessive Time Loss** - Acid cleanings require that both phases (acid phase and neutralization phase) be rinsed thoroughly. This results in more than doubling the amount of downtime necessary to effectively clean & neutralize a system.
- **Excessive Waste Water Generation** - Acid cleanings generate more than twice the volume of waste water and the acid phase needs to be neutralized once it has been drained from the system.
- **Increased Risk To Personnel and Equipment** - Even after the system has been cleaned the complex nature of piping systems containing numerous "dead legs" invariably traps acid solution containing some level of un-neutralized HF in the system.
- **The use of ammonia creates unnecessary personnel risks as well as significant challenges for the refinery's waste water system.**

Refinery Case History Continued

Decontamination of HF Alkylation Units

The EnvTech Difference

The Benefits of ETI Cleaning & Gas Freeing Solution

- EnvTech's proprietary "Clean & Gas-Free" process utilizes a strong 8.8 pH buffer. As a result, neutralization is effected immediately upon contact during the initial phase of the cleaning. In addition, "dead legs" filled with acid are avoided since the solution that fills them is buffered. **Unnecessary corrosion is eliminated because the water that is introduced to the system is buffered. Personnel are not exposed to the risks associated with circulation of hot acid solutions containing levels of HF.**
- EnvTech's proprietary chelant is utilized to create a "single phase" removal of Iron Fluoride deposits in combination with the neutralization chemistry. This mixture has proven excellent for polymer removal and can be heated to as much as 225° F without adverse effects.
- The EnvTech chemistry can, in most locations, be drained directly to the refinery's waste water system. Where fluoride levels present a concern, EnvTech has developed a procedure for reducing the concentration to below 5 ppm.
- This single phase method reduces the duration of the cleaning and neutralization of an entire Alkylation unit to **under 48 hours** and in some cases to 24 hours. This single benefit often encourages many turnaround management teams to utilize the EnvTech Difference.
- EnvTech has demonstrated the effectiveness and reliability of this process throughout the world. Due to the number of HF projects performed, the skill level and experience of ETI personnel is unmatched.
- EnvTech engineers work closely with the refinery's HF Alky team to develop a detailed procedure that ensures all aspects of the system are neutralized in order to avoid leaving any pockets of HF for mechanical teams to discover. In addition, EnvTech is able to offer many cost cutting suggestions. Good planning and detailed discussions involving the EnvTech engineering team early on, create an excellent synergy and worthwhile results.

References available upon request



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Refinery Case History

Removal of Hydrocarbon & Sulfide Deposits from Process Equipment

EnvTech Inc. was awarded a chemical cleaning contract for a Northern California, refinery wide shutdown. The shutdown involved the hydrogen, hydrocracker, sulfur gas, FCC, utilities and pipestills units. In the past, standard cleaning methods for the removal of hydrocarbon and sulfide contamination from process equipment involved the use of a two phase cleaning procedure (alkaline detergent phase followed by an acid phase, which required an additional step for neutralization). However, EnvTech developed an innovative, single phase decontamination process that was applied throughout the turnaround on more than 40 systems.

EnvTech eliminated the use of corrosive products and simplified the cleaning to one phase using two EnvTech products designed for refinery degassing and sulfide removal. The turnaround involved a wide variety of process equipment, including towers, drums, exchangers, piping systems and even a storage vessel that contained a 100% mercaptan, odorant product.

The new procedures allowed refinery personnel and contractors to safely enter these vessels in record time to perform the necessary inspections and repairs.

Several of the Benefits Included:

- A buffered 8.8 pH solution was used rather than corrosive products such as caustic or hydrochloric acid, thus avoiding unnecessary risks to personnel and equipment.
- The sulfides were oxidized during the degassing phase by the combined use of a newly developed ETI product providing the oxidation equivalent of hydrogen peroxide without the associated hazards.
- **The extreme hazards that result from the liberation of H₂S, when an acid is utilized, were totally eliminated.**
- The spent cleaning solution was environmentally friendly and the refinery's waste water system was able to handle it at a reasonable drain rate. In addition, due to the single phase method, less than half the quantity of previously used cleaning solution was generated.
- The cost of the turnaround diminished thanks to reduced cleaning time, reduced waste water generation, and reduced or eliminated need for follow-up cleaning by mechanical means.
- The **non-corrosive** cleaning method increased the life of the process equipment.

References available upon request



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Refinery Case History Cooling Water Exchangers

EnvTech Inc. was asked to develop a new method for cleaning cooling water exchangers for a Northern California refinery. Because of the degree of fouling encountered, the refinery had typically relied on mechanical cleaning methods such as hydroblasting. Often this involved extensive mechanical efforts to remove the heads, pull the exchangers and transport them to the bundle pad for cleaning. This resulted in significant costs for manpower, equipment and, most importantly, down time.

EnvTech received scale samples and several analysis reports to assist with the investigation for alternative methods. The analysis reports indicated a wide range of deposit constituents that varied from unit to unit and even from exchanger to exchanger within the same unit. EnvTech evaluated these sample deposits thoroughly in the laboratory to determine the best method for removal.

EnvTech and refinery personnel established the following criteria for the evaluation:

- The chemicals must be effective in a relatively short contact time since down time was a critical factor in meeting the refinery's goal.
- The chemistry must be effective on a wide variety of scale compositions since the analysis indicated variations throughout the refinery.
- The chemistry must be virtually non-corrosive since the equipment might require frequent cleaning applications.
- The chemicals must be safe for all of the different metallurgy that might be encountered.
- The method selected must minimize the amount of mechanical efforts required to support the cleaning process.
- The chemicals must be environmentally friendly since the cleaning solutions would be handled within the refinery's waste water system.

EnvTech developed both chemistry and procedures to meet the criteria and the refinery set up pilot studies on 5 exchangers to test the capability of the new method.

The refinery removed the heads on all 5 exchangers before the cleaning and took close up pictures to document the "before" conditions. After the cleaning process was applied, the heads were again removed and the exchangers were thoroughly inspected.

Refinery Case History Continued

Cooling Water Exchangers

The EnvTech Difference

The results were dramatic:

- The first pair of exchangers selected (225 tubes each) were the least fouled, but still contained substantial deposits throughout. Approximately 99% of these deposits were removed with no evidence of corrosion from the cleaning process.
- The third exchanger selected (580 tubes) was 80% plugged at the tube sheet for approximately 6 inches. The actual flow rate at the start of the cleaning was less than 20 gallons per minute at 100 PSI. The cleaning process removed greater than 95% of the deposits and left only 15 tubes with reduced flow rates.
- The fourth and fifth exchangers (690 tubes each) were 15% plugged at the tube sheet for approximately 12 inches. Both exchangers were heavily fouled with a very hard deposit that contained significant levels of silica (greater than 40 %). Chemical cleaning removed 98% of the deposits and renewed the exchangers to near maximum efficiency.

The refinery concluded that EnvTech's chemical cleaning method delivered the desired results at a significantly reduced cost (approximately 25% that of the previously used mechanical methods).

The refinery is currently developing a routine cleaning program for all cooling water exchangers in an effort to perform the cleaning **before** a severe loss of efficiency is observed. This, in turn, would enable the chemical cleaning to provide optimal results. EnvTech further recommends that the entire cooling water system of each unit be cleaned during turnaround outages, thus removing all of the deposits from piping, valves and other components. These deposits typically break loose during unit operation and are trapped in the exchangers.

This innovative cleaning method employs a unique, EnvTech **Nitric Acid Inhibitor** which provides excellent scale removal properties at ambient temperature and is virtually non-corrosive.

Some of the benefits are listed below:

- Equipment availability is increased by minimizing the out-of-service time associated with mechanical cleaning.
- Cleaning cost is reduced dramatically.
- Equipment service life is prolonged because the "pitting" associated with under-deposit corrosion is decreased or eliminated.
- The water- side deposits are removed on a routine basis rather than waiting until severe loss of efficiency is observed. **This provides significant improvements in throughput, which directly impacts the refinery's productivity and profitability.**

References available upon request