Identifying the Hidden Cost Drivers of Refinery Shutdown Decontamination
Since the early days of the refining industry, shutting down process systems has been required to perform mechanical maintenance and debris removal to maintain operating efficiency and/or to upgrade operating systems. Because these activities require staff to enter process vessels to perform inspection, cleaning and hot work maintenance, the “safing” of these systems is required. Fire prevention has been always been a paramount concern in oil refinery systems. Initially, as work was being performed inside process vessels, fire hazards existed due to potential ignition sources coming in contact with hydrocarbon vapors, liquids, and solids remaining in the vessels. As refining industry knowledge increased concerning the risks of personnel exposure to the carcinogenic nature of certain hydrocarbon vapors such as benzene, and toxic, noxious gases such as hydrogen sulfide and mercaptans, the liability of exposing personnel to these hazardous compounds became apparent. To minimize personnel exposure to these risks, the refining industry recognized the need to clear these process vessels prior to performing turnaround activities.

At first, removing these hydrocarbon compounds from the internal surfaces and voids of refinery process equipment was facilitated by using readily available resources. Flooding the vessels with water to remove and de-inventory hydrocarbon liquids was a common practice. This practice would remove most of the liquid hydrocarbons, but the odors from adhered debris would remain. This practice did achieve de-inventorying, but at the cost of producing a large volume of a water/oil mixture. To increase the effectiveness of this liquid-filling procedure, early attempts were made during water flooding to add alkaline chemistry and a single surfactant to these fluids. This practice produced emulsified water/oil waste that was difficult to treat. This is still practiced today where vessels become nondrainable due to plugged lower drain connections. The size and capacity of refinery process vessels increased with time. However, they were designed for normal operation, which did not include the weight of their entire internal volume being completely filled with liquid. As a result, their support structures could no longer accommodate the increased weight of the vessel internals.

Another option commonly used to minimize hydrocarbon liquid and vapor residuals in refinery process vessels was turning on the tower steam injectors and steaming out the towers to the refinery flare or to atmosphere. As environmental regulations increased and negative public opinion on industry odors became apparent, steaming these residuals to atmosphere generating heavy hydrocarbon odors in the environment became an issue. Fines and penalties for license breaches and bad publicity due to environmental pollution increased over time and resulted in tighter standards and restrictions for these practices within the industry. Steaming to flare and burning off these vapors has been an acceptable practice. However, with time it has been discovered that steaming process vessels to drive volatile materials to flare produces undesirable effects in the residuals that remain in the process vessel. The most notable of these undesirable effects are hydrocarbon solids and films that could not be vaporized with saturated steam, and that became dehydrated and more coke-like in appearance. Even though the debris that remained after steaming was not coke, the hardness of the debris made it more difficult to remove by mechanical means (hydro-blasting). Thick, heavy debris in areas such as tower bottoms and knockout pot sumps remained in the system after prolonged steaming, and they regenerated hydrocarbon vapors when this debris was disturbed by mechanical removal efforts.

Though earlier methods of vessel clearing by liquid-filling and steaming were effective in de-inventorying hydrocarbon liquids from the process equipment, these methods were very time consuming. Five to eight days of flooding and steaming were average required times to prepare vessels for entry and turnaround work. The steaming, using saturated steam to form condensate to wash the vessel internals as vapors were carried to flare, generated large amounts of water/oil waste that had to be processed through in-plant wastewater treatment facilities, removed from the site, or in a worst-case scenario, dumped into the environment.
Responsible oil companies realized that much of the expense and the real cost of lost production was not in the downtime during cleaning or in the cost of the industrial service companies performing this work, but in the ever-increasing costs of hazardous waste disposal for these waste streams.

Conventional chemical cleaning methods using alkalis, acids and emulsions made from solvents and acids were initially cost effective, but had hidden costs. The most significant hidden cost was the disposal of the large volumes of waste generated that usually had to be taken off-site to a licensed waste treatment plant. The initial cost of these conventional methods was low. However, the added cost of disposal of large volumes of hazardous waste would more than double or triple the overall project cost of these conventional chemical cleaning methods. It was also apparent at this time that some of these early conventional chemistries may have contributed to chloride stress-corrosion cracking and exacerbated the problem of polythionic acid stress-corrosion cracking. Most of these corrosion issues were compounded by poorly practiced standards of chemical cleaning, such as inadequate flushing of the cleaning chemistry from the systems being cleaned, or insufficient neutralizing and passivation of the system metal surfaces following cleaning.

In addition, standards governing vessel clearing of hydrocarbons did not exist prior to the 1980s. The only standard was to get the equipment as clean as possible by visible inspection. The goal of conventional chemical cleaning was to get the vessels as close to 100% clean as possible. For the most part, this objective could be accomplished with conventional chemical cleaning methods. However, with the changes in equipment metallurgy to address increasing corrosion issues producing no clear answers, conventional chemical cleaning methods became less favored.
Developments in the 1980s and 1990s

With increasing costs of ownership, operating practices changed as refinery process owners fought for profits on several fronts, including the ever-volatile environment of crude prices, increased upgrade and process equipment costs, and the ever-increasing health, safety, and environmental regulations. In light of these increased operating costs, process yields had to improve to keep refineries profitable. As production costs escalated, refineries had to operate more efficiently, lost production became more costly, and the ability to operate profitably within the cost restraints became a major challenge. Many capital upgrades and improved processes were developed during the last 20 years, but increased operational efficiency became paramount.

Process treatment programs also evolved to somewhat address many process corrosion and fouling issues. The primary purpose of these specialty treatment programs was to keep the operating systems running longer between shutdowns. The chemistry that developed to control fouling and reduce corrosion in the operating systems vastly improved plant performance and reduced costs. The most immediate impact allowed for extended operation during production runs with fewer turnarounds.

The success of these specialty chemical treatment programs had many positive impacts in decreasing refiners' operating costs. In the presentation of this information, we will address only some of the impacts these programs had on the issues of plant turnarounds and decontamination of process equipment required during turnarounds.

One of the subtle impacts from specialty chemical corrosion and antifoulant treatment programs was the type of deposits and contamination that remained on the equipment. A well-designed chemical treatment program that had positive effects on process operation changed the type of deposits that remained and needed to be removed in a turnaround. The debris remaining in process equipment following specialty chemical process treatment programs became more predominantly hydrocarbon debris, rather than a mixed matrix of hydrocarbon and inorganic debris. Corrosion control reduced the amount of inorganic metal salts in the debris.

More effective desalting operations and specialty chemical treatments greatly reduced the occurrence of water hardness and silica deposits in downstream equipment, resulting in an overall reduction in inorganic debris. The baked-in-place organic residual contamination was also reduced as a result of these chemical treatment programs. However, it was still present in varying amounts, depending on the length of time between turnarounds and the success of the specialty chemical treatment programs in place.

One somewhat negative effect that resulted from the efficient process treatment program extension of operating times between turnarounds was that heat exchanger maintenance became more challenging. In areas of reduced flow, heavy debris would accumulate over time. This required more aggressive use of mechanical tools to disassemble shell and tube heat exchangers, causing damage to the bundles when extracted. This also increased the time required to mechanically clean the bundle using high-pressure hydro-blasting. Antifoulant programs helped, but in some cases just moved or transported debris to these low-flow areas for collection, which increased fouling in certain localized areas. One approach used to address this problem was to add to the plant's heat exchange capacity, to enable pulling an exchanger out of service while the plant remained operating and to clean the heat exchanger offline (in place) or with the bundle pulled.

The specialty chemical process treatment programs were very successful in:

- Controlling process corrosion in the refinery operating systems
- Extending plant operating times between turnarounds
- Minimizing process fouling, allowing for extended run times between turnarounds
- Changing foulant deposit characteristics of the unwanted debris that remained in process equipment following shutdowns to mostly organic contamination
- Reducing inorganic contamination content in the debris matrix, which is typically pyrophoric iron
Another development that occurred in this time frame was the addition of specialty chemicals to the steam used to steam-out the hydrocarbon vapors from the equipment. Though a similar approach had been used in the past by adding alkaline chemistry to steam, the use of a simple, single surfactant was successful in shortening the time required to clear vessels of hydrocarbon vapors.

Standards and testing instruments were developed to measure the level and composition of contaminants remaining in process vessels during the steam-out process. Lower explosion limits (LEL) test methods, along with accurate testing for benzene levels, enabled better progress monitoring of the steam-out decontamination process. The ability to determine the endpoint of the steam-out decontamination process helped reduce the time to clear vessels of hydrocarbons.

Much knowledge has been acquired regarding how to properly apply and monitor these steam-out processes. The limitations of the application, along with other effects of using simple, single-component decontamination chemistries on other operating costs of the refinery plant, became more apparent. For example, over time it was learned that certain refinery processes should not be decontaminated using a steam-out approach because of the type of process equipment service and related metallurgical constraints.

In general, the use of simple, single-surfactant decontamination products reduced the time required to clear vessels. If systems were first properly de-inventoried of hydrocarbon liquids, such as the common practice of first using a cycle-oil flush to remove hydrocarbon liquid residuals, the time to complete process decontamination during a steam-out was reduced from a week or longer to only a few days.

If unwanted hydrocarbon solids remained after a simple, single-surfactant steam-out for decontamination, longer periods of steaming would be required. We will discuss this topic later in this document to reveal the effect of the increasing use of “opportunity crude” processing in the refinery market and how it is impacting decontamination practices today. However, let us first discuss other issues with the use of simple, single surfactants that result in increased operating costs and indicate a need to improve the specialty chemistry used for performing process vessel decontamination.

As the use of steam-out decontamination using specialty chemical cleaners became more prevalent, one issue that surfaced was that certain refinery process systems should not be cleared using steam because of equipment metallurgies and their protective coatings. Exposure to elevated temperatures beyond the design for the equipment service would cause damage. Though the benefits mentioned earlier, such as a significant reduction in the volume of liquid waste and time, were good drivers for the use of the steam-out approach, certain operating systems have temperature limitations based on the service. One example of such equipment is refinery amine systems that treat acid gases. These systems are inherently alkaline and are not designed for exposure to saturated steam temperatures. Most of these systems require clearing and decontamination using liquid chemistry applied at a maximum of 150°F (65°C). In the absence of the elevated temperatures associated with using specialty chemicals in the steam-out decontamination process, a significant decrease in product performance for single-component, simple-surfactant cleaning products was observed due to their inability to completely remove hydrocarbon debris.

Refinery desalters are another example of refinery process vessels that by design are not suitable for the use of specialty chemical treated steam-out processes to clear the equipment. Past attempts in using simple, single-surfactant cleaners in clearing a desalter were plagued with problems. Some of these problems included recontamination of residual hydrocarbon liquids due to early release of these materials prior to exiting the vessel, and in some instances, the creation of gels and very stable post-cleaning emulsions. As a perceived benefit, many of these single-surfactant formulas were designed to quickly “break out” or allow quick resolution of the post-cleaning hydrocarbon/cleaner emulsion, with the intent of better water and oil separation on completion of the vessel clearing process. However, in practice there have been many observations where the ability to emulsify and release oil changes for certain types of single-surfactant cleaner chemistries, depending on other contaminants that may come into play. As an example, one widely used single-surfactant decontamination product that has been used in steam-out applications for process decontamination is primarily a nonionic, surface-active material. As this product is exposed to acidic contaminant materials such as degraded hydrocarbon carboxylic acid salts that may occur in desalters, or if the pH of the cleaning environment decreases...
to a level that is less than neutral, the nonionic, surface-active character of this material is modified to a more cationic surface-active function and becomes more hydrophobic or “oil-loving.” As this transition from a nonionic function to a cationic function progresses, tenacious emulsions have been observed as well as semigels, which are a problem in desalters and wastewater treatment facilities. These formed emulsions are difficult to remove during desalter cleaning, and these residuals are known to create havoc in the desalter operation if left in the equipment. Additionally, these formed emulsions result in major waste-processing issues as they pass through the plant’s API separation area into wastewater treatment plants.

As briefly mentioned earlier, in equipment designed for low-flow velocity or increased residence time in various refinery processes, for example a refinery desalter, another problem that occurs with the use of simple, single-component cleaners is their inability to keep hydrocarbon liquids emulsified in the cleaning solution in the absence of mechanical agitation or increased flow velocity. Comparative oil-holding performance show that in areas of low-flow velocity or the absence of mechanical agitation (complex vessel internals as well as large dead-volume vessels, for example: desalters, knock-out tanks, tower bottoms), these single simple-surfactant products lift oil from equipment internal surfaces but do not hold it in the cleaning solution without significant sheer or flow. As mentioned, these simple, single-component decontamination products are designed to break out when they are not moving.

Decontamination performance has been observed in the past for these simple, single-component decontamination products where high-velocity saturated steam was the medium for delivery, consequently maintaining sufficient sheer to facilitate continual mixing of the unwanted oil into the condensate. However, in many past cases where saturated steam velocity was not maintained, either by application engineering error, process equipment design (complex internals), or inadequate utilities, the absence of mechanical agitation or decreased flow velocity was not sufficient to keep unwanted oil emulsified in these simple, single-component cleaning solutions. Instead, the hydrocarbon contamination relocated to areas of low flow and redeposition occurred, resulting in recontamination of the equipment. The time required to clear a vessel was extended (or worse, required a repeated attempt to adequately clear the equipment for entry).

A shift occurred in addressing equipment decontamination and unwanted debris removal in refinery process vessels when more focus was placed on the changing matrix of what affixed the unwanted debris to the internal equipment surfaces as a result of specialty chemical process treatments for corrosion and fouling. As the debris or contamination matrix increased in organic composition and decreased in inorganic material, the formulation approach of specialty chemical decontamination products shifted toward compromising the integrity of the binding material (or binders) that affixed the unwanted debris to internal surfaces rather than attempting to dissolve all of the unwanted debris. Over time, trends in the composition of these organic binders indicated they predominantly comprised asphaltenes and paraffin. These asphaltenic and paraffinic binders were discovered to be the “glue” that held much of the inorganic corrosion materials, metal salts as well as organic coke/carbon particulates and catalyst fines in the unwanted debris covering the equipment internal surfaces.

As more knowledge of these binders surfaced, increased focus was placed on formulating multifunctional specialty chemical decontamination products that would compromise the integrity of these asphaltenic and paraffinic binders, liberating the remaining debris from the equipment internal surface and facilitating its removal from the process equipment. In short, if the binders could be loosened and dispersed, then the remaining debris would be released and removed from the system by flow, by filtration, or eventually by mechanical means (vacuumed out). The small amount of residual inorganic debris and insoluble organic debris remaining was easily removed by mechanical means, because it had been released and made flowable.

In more recent times, as certain heavier crude slate oils (higher viscosity, increased asphaltenes and high-molecular-weight paraffin content and increased contaminants such as minerals) are processed, the composition of fouling deposits in refinery process equipment is changing toward more paraffin and wax content, coupled with an increase in inorganic iron sulfides.

As the profit-driven motive to process heavier crudes increases, the resulting composition of process equipment contamination that compromises the efficiency of process operations continues to change. This shift by refiners toward processing heavier opportunity crudes has resulted in a significant decrease in
the performance initially observed for simple, single-surfactant decontamination products. As they process more complex mixtures of crude under more severe processing conditions, refiners are realizing that the poor performance of the simple, single-surfactant decontamination products required more scientifically engineered decontamination chemistries designed to target specific contaminant composition to successfully remove unwanted process contaminants.

We are starting to see what we call “hidden costs” of using certain chemical decontamination processes.

Though not a comprehensive list, the following are typical hidden costs:

- Higher process treatment costs after decontamination to return operation to peak performance
- More waste disposal issues in the API separation plant and wastewater plant
- Time required to clean various processes extended and second recleaning effort required
- Desalter performance recovery and upsets occurring more frequently
- Processing time of the waste stream generated was greatly extended, increasing waste storage costs or resulting in the use of off-site

The primary cost drivers in the list are lost time and increased cost for post-cleaning waste processing. Time lost or increased time to move into the inspection and maintenance turnaround phase of the project ultimately means lost production time. Increased waste costs due to extended decontamination times resulting in larger volumes of disposed hazardous waste are the most tangible and probably the highest costs that can be directly impacted.

In past applications of simple, single-surfactant decontamination products, the elevated level of organic content remaining in the simple-surfactant post-cleaning waste stream resulted in high chemical oxygen demand (COD) and biological oxygen demand (BOD) that made on-site treatment of this waste difficult for an extended time period. In many such cases, the need for off-site disposal, more extensive treatment, and/or storage with extremely slow processing in the on-site processing facilities to prevent biological kills or other waste process system upsets was required.

Oil Refining Decontamination Today

With the economic push to process “opportunity crude,” higher-gravity crudes with increased levels of asphaltenes, paraffin, wax, and sulfur (just to mention a few of the contaminants known to contribute to fouling) are being blended into the crude diets of many refineries. Specialty chemical process treatment development is responding to these challenging feed mixtures with better corrosion control over increased iron sulfides and enhanced antifoulant programs to mitigate fouling. However, when the plant turnaround occurs to restore process integrity and efficiency, debris composition appears to be changing and the amount of contamination that occurs is increasing from processing these heavier, more profitable crudes.

Inorganic contamination in the form of iron sulfide has become more common. However, due to the nature of the materials present in the refining process that contribute to the formation of iron sulfide, these types of deposits tend to occur (or become concentrated) in the tops of towers, in packed sections of towers, and in the overhead sections of refinery processes. In many cases, because these iron sulfide deposits are relatively localized in these specific areas of the refinery processing equipment, they may be chemically treated separately in the decontamination process to chemically change these deposits and fully mitigate potential hazards.
As the processing of opportunity crude increased, heat exchanger fouling deposit composition changed with a noticeable increase in the amount of heavy organic material and a corresponding increase in the frequency of cleaning crude preheat exchanger trains. In addition, because they are the next piece of refinery processing equipment following the preheat exchangers, an increase in furnace fouling has also been observed.

Although somewhat affected by the length of time between major turnarounds, fouling deposit composition in downstream equipment is also exhibiting a marked increase in the amount of organic materials present in the unwanted debris. As the composition of fouling deposits continues to change and shift with varying opportunity crude composition, the removal of these deposits presents some new opportunities and challenges for treating the waste streams associated with various decontamination chemistries and application methodologies.

In the early 2000s Baker Hughes, as the foremost refinery process treatment technology leader and supplier of specialty chemical process treatments, surveyed the refining industry for issues in turnaround decontamination. Baker Hughes representatives within various refineries observed many issues in turnaround practices that have been previously discussed. In addition, these on-site Baker Hughes technicians were able to observe repeated operating problems during the recovery of refinery operating systems that were related to the decontamination products and practices being used. Consequently, Baker Hughes embarked on developing decontamination chemistry to specifically address the various issues refinery clients expressed in surveys regarding past decontamination projects.

1. First and foremost, in formulating these new decontamination products, the drive to deliver environmentally responsible products required they did not contain any of the following:
   - Alkylphenol ethoxylates (APEs)
   - USA EPA VOCs
   - Slow degrading chelant salts
   - Free amines
   - Metal phosphates or organo-phosphates

2. These newly developed decontamination chemistries and application methods scientifically target unwanted debris by characterizing the composition, screening appropriate products for removal, and matching the best product for decontamination performance while minimizing waste volumes.

3. These scientifically engineered decontamination products and application methodologies take into consideration several factors, including operational treatment and recognized areas of decontamination impacted by the process treatment, while minimizing impact on plant recovery in returning to production after the turnaround.

4. The decontamination chemistries developed took into account the cost impact that the generated waste stream would have on being treatable using on-site facilities and minimizing the costs of post-cleaning waste treatment.

5. The application methods that developed included making significant changes in the decontamination approach to improve the level of cleanliness achieved, minimize post-cleaning waste volumes, improve the predictability of the decontamination, and lower the overall cost and impact of the decontamination process for the refinery owner.
The Decontamination Improvements
Waste-Stream Phase Separates:

Process improvement #1:
Improved surfactant-based chemistry
Baker Hughes developed a unique surfactant blend that improved the steaming processes. The blended product exhibits superior performance in removing oils/greases from process vessel internal surfaces and has sufficient alkalinity to stabilize the hydrocarbons being emulsified to maintain the emulsion. This multiple-surfactant mix is low chloride in content. In the absence of flow and mechanical agitation, the post-cleaning waste stream phase-separates out the oil/water when allowed to stand in storage within 24 hours. An extremely low BOD and COD content can be realized within hours following the optional addition of calcium chloride to the stored waste.

Process Improvement #2:
Additives for light cycle oil flushing to improve its cleaning ability
Baker Hughes has taken some of the technology originally developed for process antifoulants and built on these technologies to develop solvency-enhancing additives for light cycle oil. Tests of hydrocarbon solids debris have demonstrated an overall solubility in neat diesel fuel of only 10 to 25%. In light cycle oil, because of its increased aromatic content, solubility of this same hydrocarbon solids debris was improved to 50 to 60%. In other words, during elevated temperature recirculated light cycle oil flushes, at best, 60% of the hydrocarbon solid debris will be brought into solution for removal. By adding one of the solvency-enhancing additives developed by Baker Hughes, the solubility of the hydrocarbon solids debris was increased to more than 90%, turning it into a pumpable liquid. With proper assessment of debris composition and properly designed cleaning chemistry applications, the addition of Baker Hughes’ solvency-enhancing additives opens up many areas for improved process decontamination results:
- a. Furnaces operating under 700°F (370°C) can be chemically decontaminated of non-coked deposits. This is less damaging and much quicker than hydro-blasting or stud pigging furnace tubes.
- b. Crude preheat bundles or the entire heat exchange train can be cleaned in place. This requires less mechanical preparation that is less costly and quicker than mechanical cleaning methods.
- c. By adding solvency-enhancing chemistry to light cycle oil de-inventorying of towers and pumparounds, more solids are removed, shortening the steam decontamination time and minimizing mechanical cleaning needs for heat exchangers, tower trays, and tower bottoms.

Process Improvement #3:
A micro-emulsion product using renewable resource biodegradable citrus-based solvency
This product was developed to improve the efficiency of steam-out and liquid decontamination applications, particularly where heavy, tar-like, asphaltic, baked-in-place debris occurs. This product provides several benefits to the user in the decontamination processes practiced:
- a. This product has a high level of a terpene solvent in the micro-emulsion. The added solvency significantly decreases the time required for decontamination and improves the removal of heavy-hydrocarbon contamination over using just surfactant chemistry.
- b. The formulated product has a higher volatility as a water-based product than as a surfactant-based chemistry. Tests have shown that in application with steam, 80% of the formulated product will volatilize in the saturated steam and be transported to the flare.
- c. The product will effectively extract hydrocarbon from sludge that occurs in tower bottoms, desalters, tank bottoms, and separators, leaving the remaining mixture of insoluble organic debris (carbon particulates, etc.) and insoluble inorganic corrosion products virtually hydrocarbon free.
- d. The remaining waste-stream chemistry allows for bulk-phase separation of the oil/water emulsion with 24-hour storage. However, with the addition of calcium chloride, the residual micro-emulsion chemistry is designed to partition with the organics going to slop oil. This delivers an extremely clear water supernatant waste stream that can be quickly processed through the wastewater plant. The residual micro-emulsion chemistry in the slop oil will not cause any downstream emulsions or poisoning of process systems.
- e. The micro-emulsion product was specifically developed to facilitate a quick, efficient break of the post-cleaning waste emulsion when treated with calcium chloride to produce very low levels of residual oil and grease in the aqueous phase. Depending on specific local requirements, subsequent treatment may not be required to allow discharge to municipal water treatment plants if on-site water treatment does not exist.
Process Improvement #4.
Treatments for pyrophoric iron from the iron sulfide contamination

Some of the above-mentioned processes as well as older decontamination processes will partially remove iron sulfide contamination present in refinery process equipment by flushing out loosened iron sulfide particulates in aqueous post-cleaning waste streams. However, because there are higher sulfur levels in most of the heavy crudes being processed, higher levels of iron sulfide contamination are occurring and in some cases forming an inorganic scale underneath debris of mixed organic/inorganic composition. Again, these contaminants tend to occur in the tops of towers, in the overhead areas of refinery process, equipment and in structured and random packing, an area of particular concern for refiners. Being localized and concentrated in these areas, the entire process train usually does not have to be treated to effectively mitigate the hazards of pyrophoric iron sulfide.

Baker Hughes has found that after the heavier hydrocarbon contamination has been removed by treated light cycle oil flushing and/or the chemically treated steam-out processes, the potential hazards of remaining localized pyrophoric iron contamination (typically in the form of an inorganic scale directly contacting the equipment’s internal metal surface) can be chemically mitigated using a weak oxidizer solution. These localized areas in the top of the towers and overheads can also be steamed using this weak oxidizing solution. These localized areas in the top of the towers and overheads can also be steamed using this weak oxidizing solution. Mitigating the hazards of pyrophoric iron sulfide is an area where Baker Hughes has continued to invest research and development resources to identify potential alternative chemistries to currently accepted industry-standard oxidizers. Though these industry-standard oxidizers are highly efficient in mitigating pyrophoric iron sulfide, alternatives are being sought, due to increasing governmental regulations and oversight on some of these existing industry-standard oxidizer products.

At this time, Baker Hughes advocates the use of a weak permanganate solution for its performance reliability, field application safety, and monitoring—and it is the only process that delivers an absolute proof of complete treatment of the pyrophoric iron and iron sulfide contamination. In field application, the weak solution of permanganate oxidizer is applied at a low concentration to facilitate steady consumption of available oxidizer until a slight residual is established. By establishing a low concentration of residual oxidizer, complete mitigation of pyrophoric iron is confirmed. Following confirmation of pyrophoric iron mitigation and prior to wastewater discharge, the oxidizer residual is spent using a marginal amount of reducing agent. To facilitate the desired chemical reaction between the oxidizer treatment and the iron sulfide contamination, it is important that this weak oxidizer treatment application be completed following hydrocarbon organic contamination removal to avoid undesirable spending of the oxidizer on hydrocarbon contamination.

Other pyrophoric iron-mitigation treatments exist; however, to date a reliable definitive means of confirming the progress of the reaction and determining the completion of treatment using these chemistries has yet to be developed.

To ensure successful refinery process equipment decontamination, adherence to recommended, proven application techniques and use of a decontamination chemistry specifically designed for effectiveness based on the composition of the unwanted debris to be removed is paramount. To achieve decontamination performance excellence, good engineering principles and project management processes must be coupled with proper application of debris-specific removal technologies to realize maximum benefits in rapid vessel decontamination and minimized waste volumes.

Baker Hughes has successfully developed debris-specific decontamination technologies to effectively decontaminate process equipment, avoid producing waste streams that are difficult to manage, and prevent chemical residues that may contribute to upset process streams on return to production.

Proper application of these debris-specific decontamination chemistries depends on completing a thorough process flow review, identifying areas where higher levels of contamination may exist, and designing the decontamination application to ensure all areas of contamination are fully contacted and addressed. Risk-assessment review and planning are important to address health and safety issues, along with monitoring of project progress to endpoint confirmation and final waste stream implications.

Implementation of these concepts and practices has proved to lower the direct and hidden costs that may occur during turnaround decontamination activities.
A Best-Practices Review for Effective and Safe Plant Decontamination

- Review process treatment chemistries used, sites of known fouling and corrosion, and, if possible, determine chemical and physical characteristics of unwanted debris to be removed.
- Complete a thorough risk assessment of processes and areas of application.
- Use effective chemistry that will successfully:
  - Remove the residual hydrocarbon solids, liquid and vapor.
  - Extract hydrocarbon constituents from sludge and other porous material sources of hydrocarbon vapor and liquids.
  - Affirm oxidation to neutralize effects of iron sulfides to avoid any higher safety occurrences with remaining pyrophoric and hydrogen sulfide.
  - Ensure 80% of the chemistry goes to the flare with the steam vapor being used to carry the chemistry through the process. This reduces the volume and concentration of waste to be processed.
  - Separate by conventional treatment methods to achieve very clear supernatantates with clear separation of hydrocarbons and water.

- Detailed project planning to accomplish the following:
  - Meet and exceed the refinery expectations.
  - Fully address all the refinery needs.
  - Provide an integrated decontamination plan that will be incorporated in the refinery turnaround schedule, minimizing its time on the critical path.
  - Develop detailed engineering procedures, drawings, and safe working practices.
- Complete a thorough process flow assessment of the process system flows to ensure all heavily fouled areas are addressed in the application procedures.
- Establish decontamination progress-monitoring criteria in to determine a definitive endpoint that would indicate decontamination process completion.
- Evaluate the outcome of the decontamination process for effective debris removal and determine if modifications of future process treatment programs and future decontamination projects may be required.
- Evaluate the wastewater facility during planning to ensure that the plant can handle the waste or if additional treatment is required to avoid upsets, license overages, and fines.

In this paper we have identified the key issues that can significantly escalate in the hidden costs within a refinery decontamination program when ineffective decontamination chemistries and application methods are used:

- An increase in lost production time as a result of ineffective decontamination, requiring a longer time to achieve decontamination, and usually requiring rework of the decontamination process or additional mechanical cleaning during the turnaround activity.
- Leaving noxious gases and pyrophoric iron within vessels, leading to safety and risk issues with endangerment of staff entering vessels for inspection, cleaning and repairs, as well as potential fire damage to the plant assets.
- Difficult-to-treat emulsified waste streams lead to increased waste-processing costs; such as having to use off-site disposal, or prolonged temporary storage and treatment due to slower processing rates to stay within the operating limits of the plant’s wastewater treatment systems, or environmental license breaches and subsequent fines and punitive damages.
- The creation of bad odors and toxic atmospheric discharges delivering negative public perception and bad press because of perceived environmental damages.
- Leaving debris in the process equipment after the decontamination turnaround activity, causing premature loss of heat transfer and loss of flow on return to production.
- Leaving residual decontamination chemical in the systems or entering the hydrocarbon recovery systems through slop oil and API separation, leading to catalyst poisoning, desalter upsets, and interference of process treatment programs.

We would like to thank the Global Refinery Summit organization for the opportunity to share the observations and developments that Baker Hughes has undertaken to improve the process of hydrocarbon process equipment decontamination.