Chemical cleaning and degassing refinery equipment

The safe removal of volatile hydrocarbons, hydrogen sulphide gas and pyrophoric iron sulphide from refinery equipment before inspection is indispensable. A chemical cleaning programme reduces downtime and the need for mechanical cleaning

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In petroleum refineries, distillation and storage equipment frequently needs to be inspected during turnarounds. Necessary cleaning procedures can require several weeks of downtime if storage tanks, distillation columns, product lines and heat exchangers have to be drained. The presence of volatile hydrocarbons and hydrogen sulphide gas, as well as deposits of pyrophoric iron sulphide and other fouling material, can be particularly problematic, which is why they have to be removed before inspection.

For many years, traditional mechanical cleaning methods such as high-pressure and ultra-high-pressure water jetting, steaming procedures and cold or hot water washing methods have been used to remove volatile hydrocarbon and hydrogen sulphide gases. However, large volumes of water are required and the resulting wash water can be high in TOC. Based on regulatory, safety and environmental requirements, more powerful chemical cleaning and degassing products have been developed to shorten downtime by reducing the need for mechanical cleaning.

The applied technology and cleaning procedure will depend on the equipment to be cleaned. For example, the chemical cleaning of a crude oil tank or sludge oil system using external mobile heat exchangers will take longer than the chemical cleaning of a distillation column or heat exchanger, where high-pressure cleaning equipment can be used. The chemical cleaning itself is defined as the removal of organic and inorganic fouling material from process lines, distillation equipment and metal surfaces by a combination of solvency, fluid velocity and, in most cases, heat. While the fluid velocity comes from spraying, stirring, circulation, steam or air addition and the heat will be supplied through steaming, hot water injection or heating up the metal surfaces, the solvency depends on the chemistry of the cleaning agent and its concentration.

Types of cleaning chemicals

The most common types of chemicals used for the cleaning of equipment are inorganic and organic acids, chelating and complexing agents, alkaline cleaners, surfactants, organic solvents and speciality additives.

For the removal of oxides and scales, common acid cleaning agents such as inhibited sulphuric acid and hydrochloric acid, phosphoric acid, citric acid or other weaker acids are used. By varying the chemical concentration, temperature and agitation, the metal surface can be cleaned slowly or more rapidly. Concentrated solutions and higher temperatures will accelerate the cleaning procedure, but leads to the generation of dangerous and corrosive fumes as well as increased corrosion potential.

Caustic cleaning agents are less efficient and less economical compared with acid cleaning agents, but they can remove organic soils, including oils and grease, better than acids.

Chelating and complexing additives containing EDTA, NTA and sodium diethanolglycine or ethylenediamine play a less important role in refinery cleaning procedures because of their negative environmental impacts.

Surfactants can contain anionic, nonionic or amphoteric compounds and sometimes they are formulated together with organic solvents to improve their cleaning performance.

Cleaning and degassing chemicals

In general, cleaning agents are designed for scale and fouling removal (ie, viscous fouling, pyrophoric iron sulphides) with metal surface cleaning. In addition to these requirements, the cleaning and degassing agents for refinery and petrochemical applications are designed for the reduction of benzene and other volatile hydrocarbons, as well as hydrogen sulphide in the vapour phase.

These chemical programmes are typically injected into an aqueous phase, which requires the draining of the hydrocarbon phase first. The cleaning and degassing programmes are commonly designed for injection into the wash water phase at temperatures between 60°C and 100°C with circulation times of 2–16 hours. Some cleaning programmes create a temporary emulsion for scavenging the hydrogen sulphide and volatile hydrocarbons. The emulsion will later break down on its own in the API separator or in a separate holding tank. The addition of an emulsion breaker after the cleaning procedure is completed can accelerate the separation process. In many cases, the intermittent storage of cleaning solutions for emulsion breaking is limited, because the necessary holding tanks are occupied for other purposes during planned turnarounds, and some refiners refuse to apply chemical cleaning programmes that create emulsions. Kurita is asked to deliver cleaning and degassing programmes that create a temporary emulsion, as well as programmes without any emulsification tendency.

Removal of pyrophoric iron sulphide deposits

Due to the pyrophoric nature of iron sulphide and the potential for spontaneous ignition, refiners are very interested in removing or neutralising iron sulphide deposits. Although some chemical programmes are fairly effective and can eliminate small, localised iron sulphide deposits, they have limitations and are often less effective when the iron sulphide deposits are spread throughout the packing material of the distillation equipment.

If higher amounts of iron sulphide deposits are expected (ie, in packing areas), the cleaning and degassing chemicals may reach their limits, as they are designed mainly for volatile hydrocarbons and hydrogen sulphide removal. For this reason, a formulation for providing fast and efficient removal of iron sulphide deposits has been developed. This formulation does not

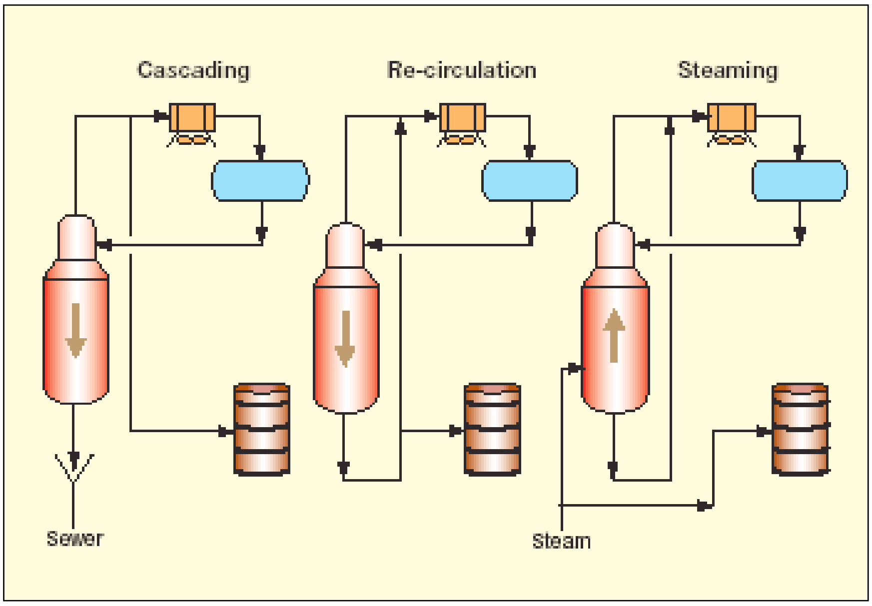

***Figure 1** Fouled heat exchanger*

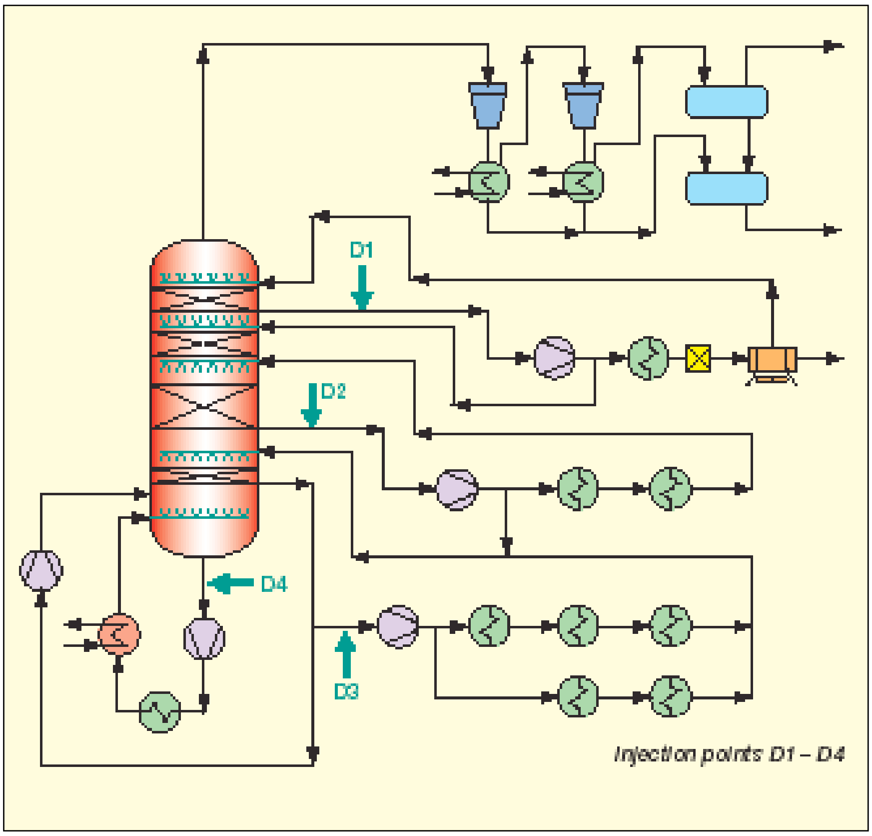

***Figure 2** Cleaning methods*

generate hydrogen sulphide or produce solid reaction products, which is why it is ideally suited to iron sulphide dissolution applications. As a further advantage, it can be injected into both hydrocarbon and aqueous product streams and combined with Kurita's proprietary hydrogen sulphide and benzene scavengers to provide a highly effective all-round chemical-treatment programme (Figure 1).

Tank cleaning

In crude oil and heavy oil storage, sludge always accumulates at the bottom of the tank. When such storage tanks are emptied to be cleaned, conventional cleaning methods may require some days or even weeks. For this reason, new chemical cleaning programmes have been developed to reduce the time required to remove the sludge from the tank.

There are a number of different standard cleaning procedures introduced to the oil refining industry, and each cleaning technique can be characterised according to a cleaning procedure. Some cleaning procedures will require the use of a suitable chemical in combination with high-pressure or ultra-high water jetting, while other techniques will require the use of a chemical in combination with mobile heat exchangers, hot water, gas oil or diesel diluents, or other mechanical technologies. In all cases, it is important to specify requirements and verify limitations in advance (ie, availability of water, heat, diluents such as gas oil or diesel).

The most efficient chemical cleaning method is usually the circulation method, where the pumped cleaning solution is fed back to the tank to reduce chemical costs. In this case, the tank should be pumped down as low as possible to check the actual sludge level. The sludge level will determine the amount of chemical, water and, in some cases, diluent (ie, diesel). As a rule of thumb, a warm chemical dilution with fluid velocity will provide better results than a cold dilution with poor agitation.

The success of the selected chemical cleaning programme can be determined by using a good tank survey and laboratory testing. Large storage tanks are often not homogenous, which is why samples should be taken from as many points as possible. The definition of a clean tank is that the floor is clean of hydrocarbons and dirt, and the tank is free of gas.

In certain special cases where catalyst slurry has been stored in the tank, the chosen chemical cleaning technique may not be applicable. The cleaning and degassing products in tank cleaning also have their limitations if higher amounts of pyrophoric iron deposits are present. In such cases, specific chemicals for pyrophoric iron sulphide removal such as Kurita CD-5101 will skip this hurdle.

Chemical cleaning of distillation equipment

While tank-cleaning procedures may require dosing pumps for the chemicals, mobile heat exchangers, high-pressure or ultra-high water jetting, steam, hot water, gas oil or diesel diluents, the application of a chemical for a tower-cleaning and degassing procedure is more simple. During the turnaround procedure, the refinery heat exchangers and pumps can be used to provide the heat and fluid velocity. The way in which the chemical is applied to the system depends on the process conditions.

It is sometimes not possible to provide a system where the chemical can be pumped back. More chemical and wash water is therefore required. In this case, the chemical has to be applied to the wash water at the top section of the distillation column or reflux line (cascading method). Steam can be added to supply more turbulence on the trays or packing. The chemical will cascade down together with the wash water to the sewer.

Again, the most efficient method is the circulation method, where the chemical can be pumped back, which will reduce chemical costs. The products first have to be drained off. Depending on the chemistry of the cleaning chemical, hydrocarbons or water are applied to flush and fill the system. Ideally, the system should be filled one-fifth to one-third of its volume before the cleaning and degassing chemical can be injected at the defined temperature range as soon as possible. It is important to monitor the cleaning process. The flow of the cleaning solution, temperature conditions, chemical activity and colour change of the samples during the cleaning are all good indicators for evaluating the progress of the cleaning. After circulating the cleaning solution for some hours (cleaning time depends on the type of chemistry and process conditions), it should be drained off and the system flushed again.

Figure 3 *Injection points D1-D4 at a vacuum distillation unit*

For aqueous applications, in some cases the chemical has to be dosed continuously in the steam phase (steaming method), which requires condensation in the distillation column. Small air-driven pumps can be used, which provide a constant flow of the chemical (Figure 2).

While the circulation method is already the most economical method, it has another big advantage, provided the chemical can be injected at different areas of the system to shorten the mixing of the chemical and the washing liquid. Small suitable and powerful air-driven pumps can be used to inject the chemical at locations where it is more difficult to install an electrical dosing pump (Figure 3).

Depending on whether only the chemical cleaning of the distillation equipment is required or volatile hydrocarbons or hydrogen sulphide also have to be eliminated, the total time for one cleaning cycle will generally be 2–16 hours. A cleaning cycle is defined by draining the distillation products, flushing with a suitable washing solvent, filling with the washing solvent, injection of the chemical, circulating for some hours and draining within two to three hours. From the point of cleaning efficiency, it is always better to apply a 1% dilution twice than a 2% dilution once. However, due to time limitations during turnarounds, this cannot always be realised. After opening of the manholes and piping, no pyrophoric iron deposits, volatile hydrocarbons and hydrogen sulphide should be detectable.

Cleaning of fuel gas systems

A refinery generally operates many fuel gas combustion devices. They are connected to a centralised fuel gas distribution system, which collects the gas streams from different parts of the refinery to direct the gases to the refinery heaters or furnaces. The composition and quality of the fuel gas vary with the crude oils, but the main components are methane, ethane and ethylene in combination with excess hydrogen. A hydrocarbon condensate carryover to the fuel gas burners is common, and the hydrocarbon condensate can go all the way in the firebox by creating an unsafe and hazardous situation. Amine carryover with the fuel gas is also common and, besides the condensation of water or heavier hydrocarbons in the fuel gas

Figure 4 Packing area of a distillation column after chemical cleaning

distribution system, the potential formation of ammonium salt deposits is considered to be a critical factor for the continuous and efficient operation of the fuel gas system.

The mechanical cleaning of blocked burner nozzles requires three to four man-hours and an average burner cleaning cycle is three to four months. Having 30–50 heaters with many burner nozzles installed, mechanical cleaning may cost some hundred thousand euros per year. Although ammonium salts are water-soluble, steam-cleaning procedures often show a limited success. An alternative to mechanical cleaning and steam cleaning is the ACF technology developed by Kurita, where the ACF product is injected into the fuel gas system to remove ammonium salt deposits. Within a few minutes, the fouling material can be removed, and burner flames will look good and the burner tips will live longer.

Sampling and monitoring

For tank cleaning, the success of the cleaning technology can be determined by a good survey and laboratory testing before and during cleaning. It is important to obtain information on the composition of the bottom sludge, which can contain oil, water, volatile solids, ash and sediments. The concentration of water and sediment content of crude oils is significant, because it can cause corrosion of the distillation equipment. A determination of water and sediments is required to measure accurately net volumes of actual oil in sales. Based on the cleaning technology, recovered oil can be directed to the refining process again, increasing refinery profit.

The best results are obtained when representative samples are taken. Storage tanks are not homogenous, which is why samples should be taken from as many sampling points as possible. If samples have to be taken from tanks, most refineries use different types of sample thieves. A cage with a sample bottle, or a graduated glass cylinder in a sampling container with a trap door that closes on the bottom of the graduated cylinder are two examples of sampling devices. If there are no sampling points installed, the water draw can be used for sampling. After opening the valve, any sludge-type material can be collected. This way of sampling may not be representative, but it is better than having no sample at all.

The chemical cleaning of distillation equipment will require 2–16 hours. Before and during the procedure, samples can be taken to observe the progress of the cleaning. The concentration of "actives", the temperature of the washing solution, colour, pH, iron concentration, chlorides, ammonia and sulphides are typical parameters for refinery cleaning procedures. During cleaning, the samples appear to look more and more dirty, and the increase in analysed iron, chlorides, sulphides and ammonia indicates the mobilisation of the fouled material. When the increase in concentration of these parameters slows down, it is an indication that the end of the cleaning is imminent or more or new cleaning chemical is required.

The heat-transfer coefficient and the pressure drop of heat exchangers, the sampling of fouled materials, ultrasonic measuring equipment and former turnaround reports on observed fouling are all good tools for estimating the amount of chemicals needed for cleaning. Tanks and vessels with poor agitation, or distillation units with packing, are more difficult to clean. If these areas eventually appear very clean (Figure 4), it is a good indication that the correct cleaning programme and technology were selected.

Conclusions

Refinery equipment that is commonly cleaned chemically includes boilers, tanks, heat exchangers, fin-fan coolers, hydraulic lines, reactors, condensers piping systems, refinery towers and cooling systems. During a refinery turnaround, much of the work involves cleaning, and the turnaround is carefully planned months in advance. Regulatory, safety and environmental requirements are increasing the demands on turnaround operations in refineries and other petrochemical plants.

Whenever a piece of equipment has to be cleaned, there are key parameters to be considered for a proper cleaning method selection:
— The surface to be cleaned
— Waste removal
— Application method
— Present results
— Available contact time
— Chemical content restrictions
— Process conditions
— Final conditions of work.

The type of cleaning chemical has to be chosen carefully. Concentrated solutions of inhibited acid cleaners can generate dangerous and corrosive fumes at higher temperatures, and can cause stress corrosion cracking at high nickel alloys. Alkaline cleaners can remove only limited types of scale, and higher temperatures are required.

Suitable chemicals including proprietary products to remove pyrophoric iron sulphide deposits have been developed for degassing and decontamination, and can be solvent- or water-based products. Refineries generally prefer water-based cleaners and solvent cleaners that do not form emulsions. These products will provide faster and safer results on cleaning the metal surface, reducing benzene and other volatile hydrocarbons, hydrogen sulphide and ammonia levels. This will help reduce the turnaround time, air emissions, waste, labour costs and pollution-control costs.

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