
Question 27: It has become increasingly common to chemically neutralize / passivate refinery towers and vessels prior to entry. What are the recommended practices for implementing these tasks? In your experience, what conditions trigger the need for chemical treatment?

Alec Klinghoffer (Coffeyville Resources)

Although this list is not “all-inclusive”, here are some general recommended practices when chemical cleaning and/or neutralizing towers and vessels. First, there needs to be a single point of contact for the chemical cleaning vendor. This person is responsible for the planning, preparation and execution of the chemical cleaning process. Prior to cleaning, P&ID’s need to be marked up to identify all injection points, steam and chemical flows and even line ups for the chemical cleaning. In addition, all points should be marked with robust tags so that there is continuity between shifts if the cleaning is going to last longer than 12 hours. The chemistry of the system should be discussed in depth with the vendor to ensure the chemical is compatible with the process stream for cleaning. From personal experience, it is very important to fabricate all piping necessary for the job weeks in advance to save any last-minute confusion. One item that might get overlooked is to make sure any and all environmental issues are addressed before the actual cleaning takes place. Any additional environmental waste permitting should be done in advance but typically, the current chemicals used for cleaning are “environmentally” friendly. It is still a good idea to check with environmental before any cleaning is done and discharge to the wastewater system.

Conditions that trigger the need to chemically clean a tower include the service of the vessel. For example, vessels/towers in HF service (HF alkylation) need neutralized before any work is done on that vessel. A vessel where there might be suspected highly pyrophoric material might be an excellent candidate for chemical cleaning. One condition that would trigger the need for chemical cleaning is time. Towers and vessels typically clean up with long periods of steaming but in the current market, time can be saved when equipment is chemically cleaned. Again, there are a lot of instances where chemical cleaning can save multiple shifts in a shutdown scenario. Finally, vessels and towers may need to be chemically treated before a startup to ensure the service is clean to improve reliability and long operational duration. This is especially true for cooling towers and boilers.

Greg Harbison (Marathon Petroleum)

All of our refineries utilize cross functional Area Teams to manage the daily operation and maintenance of the facility. A sub-set of our Area Teams (Operations, Maintenance, Safety, Inspection, and Technical Service) reviews shutdown and maintenance work scopes and discusses which towers and exchangers will be opened and the type of work that will be performed (Hot Work, Cold Work, Entry, etc.). Based on this review, the equipment metallurgy and type of deposits expected are determined from engineering judgment and past experience. The Technical Service process engineer will then consult with the refinery laboratory chemists, outside chemical treatment vendors, and our Corporate Process Technologists to determine the appropriate treatment plan. A treatment guideline/procedure is

subsequently issued.

There are numerous conditions that can trigger the need for chemical treatment to safely remove a potentially hazardous deposit, condition equipment for safe entry, or help ensure future safe and reliable operation.

Reliability

1. The neutralization of chlorides in austenitic stainless-steel services prior to exposing to air (oxygen) helps prevent future failures due to stress cracking and corrosion. For clean services, washing with a soda ash solution and then passivating with a solution of sodium nitrite is often a successful treatment. In fouling services like naphtha Hydrotreater feed/effluent exchangers, we will either acidize and neutralize or potassium permanganate (KMnO₄) clean and neutralize the exchangers prior to exposing to air (oxygen). One cautionary note when using potassium permanganate is that it is a mild oxidizer, and free oil in the system should be absolutely avoided.

2. We take special precautions with titanium bundles. We will have an argon tube trailer on the job site to use in the event we have a titanium metal fire. One of our refineries experienced a fire several years ago on a set of titanium bundles. Nitrogen and steam/water should not be used to put out a hot titanium metal fire (nitrogen can react exothermically with the hot titanium, and water can react with the hot metal and form hydrogen gas). Thus, only Class D extinguishers and extinguishing agents can be used. Each refinery should have a plan in place (and review prior to each shutdown) to prevent a titanium fire, and how to extinguish a titanium fire.

Safety

1. Sulfidic caustic solutions are treated by utilizing a potassium permanganate solution to prevent the liberation of toxic hydrogen sulfide (H₂S). The permanganate treatment converts the hydrogen sulfide (H₂S) to sulfate (SO₄) and converts the iron sulfide to iron oxide.

2. Refinery sour water tanks are typically circulated back through the SWS tower to decrease the hydrogen sulfide (H₂S) and ammonia concentration. The remaining solution is permanganate treated to convert the hydrogen sulfide (H₂S) to sulfate (SO₄) and convert the iron sulfide to iron oxide.

3. Pyrophoric material is neutralized, handled inertly, or kept wetted while the possibility of exposure to air (oxygen) exists. Iron Sulfide deposits can be present in any sour service equipment, and the hazards of combustion and toxic gas (sulfur dioxide - SO₂) should be considered while developing any maintenance plan. Particular care should be taken when iron sulfide may be present in a packed vessel. Our practice is to ensure the packing remains wetted until it is either removed or the equipment is returned to service.

4. Steam, degassing chemicals, and mechanical ventilation are normally used for benzene and LEL reduction. Both steam purging and steam purging with degassing chemicals are utilized to breakup deposits and LEL free process equipment prior to maintenance work. Where demister pads or coalescing pads are present, removal is sometimes required to remove the contaminants.

5. HF Alkylation Units can be cleaned in a number of ways: 1) vapor phase (ammonia) or liquid phase

neutralization, 2) acidizing and neutralization (we have experience with Hydrochloric Acid (HCl) and Citric Acid), and 3) utilizing a chelating agent.

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