Question 2: What metallurgy works well and does not work well for use in alkylation units? In what applications does the alternate metallurgy perform better/worse?

LANCE TALLMAN (CITGO Petroleum)

HF

The standard metallurgy for use throughout HF alkylation units is carbon steel. Showing a high degree of corrosion resistance in both low and very high acid concentrations, carbon steel is also useful for its relatively low cost compared to more exotic materials. In most applications throughout the unit, carbon steel will display a general corrosion loss rather than the more difficult to detect pitting or localized corrosion. However, it must be noted that when used in a stream that will contain HF acid, there are several restrictions that are placed on the steel composition (particularly Cr, Ni, and Cu) in order to try and reduce the unique circumstances that can set up localized areas of accelerated HF corrosion. Despite the possibility of accelerated corrosion, carbon steel has a long history of suitable use throughout Alkylation Units throughout the country and performs well in most streams present in an Alkylation Unit.

There are some streams that, through use and time, have been found to require an alternate metallurgy to the standard approach of carbon steel. These areas typically involve a higher temperature than are encountered in most of the unit (most refiners using carbon steel for HF containing streams at operating temperatures below 150 – 200°F). At temperatures higher than this, or in areas that previous experience with carbon steel has provided unsuitable corrosion resistance, consideration is made for employing the use of a high nickel alloy. The common choices for use vary between Monel 400 and various Hastelloy's (C-276, B grades, etc.), with Monel getting the preponderance of use. These high nickel materials provide suitable corrosion resistance at the higher temperature operation than are possible with carbon steel. Monel 400 brings about its own set of challenges with the possibilities of cracking due to high residual stresses, particularly in services that contain oxygen or mercury contamination. A stress relieving heat treatment is usually performed at initial fabrication to reduce the possibility of this catastrophic failure mechanism.

Most notable of the common materials used in refining that should not be employed in HF Alkylation units are stainless steels. While they can sufficiently resist corrosion in anhydrous environments containing HF acid, they perform worse than carbon steel under aqueous conditions. All grades of stainless steel can undergo rapid corrosion losses (sometimes on the order of 100 mpy) at certain conditions and should therefore be avoided. Other materials to avoid are those that contain silicon, as this will react with HF acid and form a highly corrosive fluorosilicic acid.

Sulfuric Acid

Carbon steel is used for most of the equipment and piping in sulfuric acid alkylation units including the reaction zone (contactors & acid settlers). However, CS doesn't work well in the presence of sulfuric acid with high temperatures and/or high velocities. The fresh and spent acid piping is typically constructed of 300 series SS, and/or Alloy 20; however, some units have successfully operated with CS piping in this service. Additionally, in the effluent treating section & depropanizer feed treatment system, the static mixers and upstream/downstream piping are typically upgraded to Alloy 20 and/or Hastelloy C. Although the contactors (shell & tube bundle) are constructed of CS, due to the highly turbulent service, the internals such as the reactor impeller & distributors are upgraded to Hastelloy C which will significantly extend the life of this equipment.

Monel is not recommended for material of construction in sulfuric acid alkylation units as it is not compatible with equipment and piping containing large amounts of sulfuric acid.

KURT DETRICK (UOP)

API RP 751 has a good description of the experience with different materials in the HF Alky unit in Section 3 and Annex D.

Carbon steel is the most common material used in HF Alky units in areas of relatively low temperature and low water content in the acid. The surface of fresh steel reacts with HF to form iron fluoride, but under the proper conditions (primarily low water concentration in the acid), this layer of iron fluoride protects the underlying steel from further attack.

Monel is used in areas of the HF Alky unit where temperatures are higher, or water content of the acid is higher (such as in the Acid Regenerator or Rerun tower). Hastelloy (primarily C276) has also been used successfully in these areas of elevated temperature and/or water concentration.

316 Stainless steel vessels are used for transporting fresh anhydrous HF to the Alky unit, but stainless steel should only be used for high purity fresh acid. In commercial experience, stainless steels (both Austenitic and Martensitic) are aggressively attacked by the plant acid in an HF Alky unit and these stainless steels should never be used in the HF Alky unit itself.

ROMAIN LEMOINE (McDermott Lummus Global)

In less than 7 years, McDermott's Lummus Technology has successfully commercialized and licensed an advanced version of sulfuric acid alkylation technology, called CDAlky®, to clients worldwide. CDAlky technology focuses on effectively eliminating the root cause of drawbacks inherent to conventional alkylation units. A leading area of concern is excessive corrosion and the need for higher-grade metallurgy.

Lummus' CDAlky Technology not only operates at lower temperature than conventional sulfuric acid alkylation processes, but it also eliminates the need for a reactor effluent post-treatment section. The key to these technical breakthroughs resides in CDAlky reactor proprietary internals: AlkyPak™ &

Distributor Plates. By eliminating caustic and water introduction in the alkylation section, and by maintaining a low temperature operation, CDAlky technology can eliminate the need for higher-grade metallurgy. Recent turnaround inspections conducted on multiple CDAlky units have confirmed these technical steps out benefits:

- Low Temperature operation reduces significantly the corrosion rates.
- Neither reactor effluent wash nor post-treatment steps are required to remove sulfuric acid or sulfates from the alkylate.
- No fouling material is observed in any fractionation reboilers.
- Stainless steels and carbon steels are suitable material of construction.

GREG TROUTMAN (DuPont)

Although careful consideration is required when selecting appropriate metallurgy for any sulfuric acid alkylation unit, a sound process design relegates the recommended use of exotic material to only a few areas. Carbon steel is by far the most common material found throughout the unit as it is both economical and capable of handling the range of temperatures and velocities observed in normal conditions as well as most alkylation unit excursions. The typical hierarchy of metals found in a sulfuric acid alkylation unit is as follows:

Carbon Steel < 316L Stainless Steel < Alloy 20 (in certain situations) < Alloy C276

With respect to sulfuric acid, carbon steel can be used if the velocity/turbulence through the piping or equipment is not high enough to disturb the protective passive layer of iron sulfate that forms on carbon steel when contacted with sulfuric acid. Many refiners have utilized carbon steel with a corrosion allowance of either 1/8” or 1/4” for normally flowing and normally not flowing lines, respectively. In piping where, high velocity/turbulence cannot be avoided such as through valves, Alloy 20 or PTFE-lined valving should be used to avoid excessive corrosion/erosion. When velocities high enough to avoid hydrogen grooving and low enough to avoid eroding the passive layer are not obtainable with sulfuric acid piping, 316L stainless steel is a good substitute.

Areas where neutralization takes place will require at least Alloy 20, especially since most of the neutralization takes place in a static mixer where there is high turbulence. It should be noted that while Alloy 20 is an excellent material in many applications, situations such as high temperature and certain contaminants or environments can cause it to become active and fail quickly.

For the reactor itself, carbon steel is the preferred choice for the bulk components (shell, heads, tube bundle, etc.). Carbon steel is economical where the process conditions (velocity, turbulence and temperature) are typically mild. Since the carbon steel within the reactor forms a protective passive layer, a long life is typical. The reactor impeller, wear ring, feed nozzles and other high velocity/turbulent

areas can be constructed of Alloy C276 to dramatically improve the life span.

DuPont never recommends the use of Alloy 20 within a sulfuric acid alkylation reactor due to process conditions that can cause the metal to become active and fail. In addition, areas where neutralization takes place with elevated temperatures such as the mixing of sulfuric acid and hot alkaline water are better suited for Alloy C276 rather than Alloy 20.

A few additional considerations:

For areas with high amounts of propane such as the depropanizer overhead, depressurization could result in temperatures cold enough to require low temperature carbon steel.

Carbon steel is suitable for caustic (typically in the 10-12% range) but post weld heat treating should be used in areas where the temperatures are expected to be higher than 180 °F.

Both stainless steel and Alloy 20 should not be used when significant amounts of halide ions such as Cl- are present as these may cause pitting corrosion.

Water is not corrosive by itself, but it can cause major corrosion issues if there is an area with a high probability of contacting trace SO2 or sulfuric acid.

As for metallurgies that are not compatible in sulfuric acid alkylation units, Monel is not compatible with equipment and piping containing large amounts of sulfuric acid. However, Monel has been shown to be effective in hydrocarbon streams with weak acid. This is a benefit when considering HF to sulfuric acid alkylation conversion as Monel is prevalent in HF alkylation units.

Non-metallics such as PTFE, polypropylene, and glass have excellent corrosion resistance and can be considered for various portions of the plant. However, fire resistance and physical strength must be also considered.

Corrosion is a complicated phenomenon and is not always predictable or even explainable by current metallurgical knowledge. DuPont continues to experiment and gain knowhow on the performance of specific materials in sulfuric acid alkylation units. For the latest information, DuPont and/or a metallurgist should be involved in corrosion evaluations and upgrade decisions.

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2018