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Standard
Recommended Practice

Recommended Practice for the Design, Fabrication, and Inspection of Tanks for the Storage of Petroleum Refining Alkylation Unit Spent Sulfuric Acid at Ambient Temperatures

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Foreword

Sulfuric acid (H_2SO_4) is the largest-volume commodity chemical in use today. It plays some part in the production of nearly all manufactured goods. One large use of concentrated sulfuric acid is as a catalyst for refinery alkylation units. In these units, C_3-C_5 olefins such as propylene or butylene are reacted with isobutane to form gasoline-blending components such as isoheptane and isooctane. These products are used to boost octane for automobile and aviation fuels.

Most refineries have an alkylation unit that uses either hydrofluoric acid (HF) or sulfuric acid as the alkylation catalyst. This standard deals with spent sulfuric acid associated with the sulfuric acid alkylation process only.

Refineries using sulfuric acid alkylation typically require tanks for the storage of fresh (not yet used in the alkylation process) and spent (used in the alkylation process and in need of regeneration) acid. Design, fabrication, and inspection of fresh sulfuric acid tanks are covered in NACE Standard RP0294.[1] This standard covers additions and deviations from RP0294 that apply to spent sulfuric acid storage tanks.

Large vertical sulfuric acid storage tanks are usually built in accordance with API[(1)] Standard 650[2] or API Standard 620,[3] and horizontal cylindrical tanks are built in accordance with the ASME[(2)] Boiler and Pressure Vessel Code, Section VIII, Division 1.[4] While these codes and standards are sufficient for design strength and toughness considerations, they do not address the peculiarities of corrosion by alkylation unit spent sulfuric acid service. In addition, alkylation unit spent acid can contain dissolved hydrocarbons and hydrogen that release into the vapor space of these tanks and potentially produce an explosive environment. Thus, special care must be taken to deal with vapor leakage from the vapor space of these tanks and air intrusion into the vapor space of these tanks.

Carbon steel corrodes moderately when in contact with alkylation unit spent sulfuric acid. If tanks are properly designed and adequately maintained, use of carbon steel is an economical option for the storage of these acids at ambient temperatures. However, accelerated corrosion can occur in various forms, and a catastrophic failure of a spent acid tank in Delaware City, Delaware, U.S.A., has focused attention on the hazards associated with corrosion, vapor space leakage, and hot work on or around alkylation spent sulfuric acid tanks. The Chemical Safety Board[(3)] report[5] can be reviewed for more details regarding this failure.

This standard is to be used in conjunction with NACE Standard RP0294. It is intended for use by owners/operators and fabricators of alkylation unit spent sulfuric acid storage tanks. This standard was prepared by Task Group (TG) 300 on Petroleum Refining Spent Sulfuric Acid Storage Tank Requirements: Standard. TG 300 is administered by Specific Technology Group (STG) 34 on Petroleum Refining and Gas Processing, and sponsored by STG 36 on Process Industry—Materials Performance in Chemicals. It is issued by NACE International under the auspices of STG 34. These committees include representatives of companies involved in the production, transportation, and use of large quantities of spent sulfuric acid.

In NACE standards, the terms *shall*, *must*, *should*, and *may* are used in accordance with the definitions of these terms in the NACE Publications Style Manual, 4th ed., Paragraph 7.4.1.9. *Shall* and *must* are used to state mandatory requirements. The term *should* is used to state something good and is recommended but is not mandatory. The term *may* is used to state something considered optional.

(1) American Petroleum Institute (API), 1220 L St. NW, Washington, DC 20005.
(2) ASME International (ASME), Three Park Avenue, New York, NY 10016-5990.
(3) U.S. Chemical Safety and Hazard Investigation Board (CSB), 2175 K St. NW, Suite 400, Washington, DC 20037-1809.

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Section 1: General

1.1 Spent sulfuric acid, generated by refinery alkylation units (spent acid), may differ from fresh sulfuric acid (fresh acid) in several ways. The most notable differences between alkylation unit fresh acid and spent acid are the acid concentration, water content, possible contaminants from the alkylation process, temperature of the spent acid entering the tank from the alkylation unit, and the presence of dissolved hydrocarbons and hydrogen. These differences must be taken into consideration when developing inspection strategies, setting inspection intervals, conducting an external inspection, and/or internally inspecting a tank that is in spent sulfuric acid service. This standard was developed to address these differences between fresh acid and spent sulfuric acid as they may have an impact on the integrity of spent sulfuric acid storage tanks.

1.2 NACE Standard RP0294 shall be followed for all aspects of spent sulfuric acid storage not covered by this standard.

1.3 This standard presents additions to and deviations from NACE Standard RP0294 that apply to alkylation unit spent sulfuric acid storage.

1.4 HF alkylation unit spent acid is not within the scope of this standard.

Section 2: Corrosion Concerns

2.1 See Paragraph 2.8 of NACE Standard RP0294.

2.2 Upset Conditions

Owners/operators should be aware that alkylation unit upsets or operation outside normal ranges of acid concentration and water content and contaminants and temperature, as described in Paragraphs 2.3, 2.4, and 2.5, can be the primary cause of the corrosion concerns for alkylation unit spent sulfuric acid tanks. The owner/operator should have a method to identify these conditions and notify those involved with spent acid storage tank integrity in a timely manner.

2.3 Acid Concentration and Water Content

Spent acid is typically lower in sulfuric acid concentration (88 wt% to 90 wt%) than fresh acid (95 wt% to 99.5 wt%) and can contain more water and be more corrosive. Water in spent acid should be less than 5 wt% to avoid corrosion. Common corrosion rate references for sulfuric acid corrosion include the sulfuric acid isocorrosion curves and corrosion versus concentration curves for stagnant conditions and ambient temperature (Figure 1). Caution should be taken when utilizing these references to assure that the appropriate acid concentration is used, because water content can have a large impact on the effective acid concentration.

2.3.1 The effective acid concentration should be calculated in accordance with Equation (1). For example, a spent acid containing 89 wt% sulfuric acid, 4 wt% water, and 7 wt% organics, the effective acid concentration would be:

$$\text{effective acid concentration (wt\%)} = \frac{\left(100 - \left[\text{wt\% water} + \text{wt\% organics}\right]\right)}{\left(100 - \text{wt\% organics}\right)} \qquad (1)$$

or

$$95.7\% = \frac{\left(100 - \left[4 + 7\right]\right)}{\left(100 - 7\right)}$$