

REGENERATION OF SPENT ACID FROM CHEMICAL PROCESSES

BACKGROUND

Monsanto Enviro-Chem is big in the business of Spent Acid Regeneration (SAR). Our experience and expertise spans more than forty years with the number of SAR plants designed and built by Monsanto Enviro-Chem exceeding our number of years in the business.

SAR facilities by Monsanto Enviro-Chem range from shop fabricated skid mounted 20 TPD capacity units to full field constructed 1000 TPD plants.

The demand for SAR plants is on the rise. Several factors are attributed to this. First and foremost, the requirements for dealing with spent acids in an environmentally safe manner and the shift toward a refinery alkylation process to avoid the possible hazards from hydrogen fluoride. Second, "tolling" or transporting spent acid long distances to independent regeneration plants for recycling is hazardous and may be cost prohibitive. Third, Monsanto Enviro-Chem design technologies and process equipment quality allow these plants to operate virtually uninterrupted for two years or more.

THE PROCESS

The process consists basically of four steps. First, the process requires formation of sulfur dioxide. This is accomplished by spray burning spent sulfuric acid or other sulfur containing compounds in a direct fired combustion chamber under controlled conditions. This decomposition process produces an SO₂ gas stream which is ready for the second step: Gas purification. The SO₂ gas stream passes through a waste heat boiler and then on through gas cooling and cleaning equipment. Once gas purification is achieved, step three requires gas drying and compression. SO₂ is passed

through an acid drying tower for the removal of water then through the compressor where its pressure is increased to 7-8 psig. Step four is the absorption of converted SO_3 in oleum and/or sulfuric acid. This is accomplished by converting the SO_2 gas to SO_3 in a multi-pass converter (to comply with environmental emission standards) and then having it absorbed in an interpass absorption tower where effectively all remaining SO_3 is absorbed in 98.5% sulfuric acid.

FEEDSTOCKS

Suitable feedstocks for regeneration include:

1. Alkylation Spent Acid: This is the most common feedstock for SAR plants. With typical 90% acid, 2-5% water, and the balance hydrocarbons, these feeds can be handled with a minimum of problems. Most refineries for whom we have built SAR plants, including Conoco, Unocal, Chevron, and Hess, provide alkylation spent acid as a feedstock.
2. Nitration Spent Acid: Generally about 70% acid, 30% water, with only traces of other components. Combustion air needs to be preheated in order to allow the production of 98.5% acid from this lower concentration acid. Several installations have been made for the U.S. Army ammunition plants.
3. Methyl Methacrylate Spent Acid, along with caprolactum and acrylonitrile, are similar in that they are typically low concentration, containing mostly ammonium sulfate or bisulfate. We have built multiple SAR plants for MMA producers.

Other feedstocks such as H₂S gas, sulfur, sludge acid, and sour water stripper gas are generally by-products of refinery alkylation spent acid and normally are burned with other feeds. There is value in burning these stocks as they lessen the amount of direct fuel needed to fire the combustion chamber, and they provide a sulfur source. Coke oven gas is a feedstock consisting primarily of dirty H₂S and is sourced from steel mill production. Mills such as Bethlehem Steel have purchased our SAR plants for their regeneration requirements.

MONSANTO ENVIRO-CHEM PRODUCTS

Many Monsanto Enviro-Chem proprietary products are used in our SAR design. For example, in the SO₂ gas cooling and cleaning stage, the DynaWave[®] engineered scrubbing system is used to quench the gas and remove particulate. This technology, licensed by Monsanto Enviro-Chem, provides:

- (1) Lower capital and maintenance costs compared to humidifying towers and lead-lined electrostatic mist precipitators;
- (2) high cleaning efficiency comparable to a venturi but with half the energy requirement;
- (3) non-clogging characteristics by utilizing large diameter nozzles.

Monsanto Brink[®] High Efficiency mist eliminators used in the drying tower maximize protection to equipment downstream of the drying tower.

Monsanto catalyst is used in the heart of the plant - the converter. Low pressure drop LP ring catalyst and the newer low temperature cesium catalyst are used in the upper and/or lower passes, depending on specific design. This combination of catalyst ensures conversion efficiencies of SO₂ to SO₃ at a rate of 99.7+% throughout the life of the plant.

Monsanto Brink[®] ES mist eliminators are used to protect downstream equipment as well as ensure the stack gas will be virtually mist free and in full

compliance to EPA standards. The ES series will maintain collection efficiencies even at 50% plant capacities.

The towers and acid distributors, pump tanks, acid coolers, and piping are recommended to be fabricated in Sandvik SX stainless steelTM which is distributed exclusively in North America by Monsanto Enviro-Chem. SX alloy is extremely corrosion resistant to 98% acid showing corrosion of less than 1 mil./year in most applications. With reduced field costs and time, fully fabricated tanks and piping systems having few or no flanges, little or no corrosion, and reduced maintenance costs, SX is by far today's material of choice for sulfuric acid plants.

MONSANTO ENVIRO-CHEM DESIGN AND TECHNOLOGY

Monsanto Enviro-Chem plant technology is based upon three principles: Low cost, energy conservation, and quality. Overall plant cost is kept low by using the highest possible gas strength which will give the required conversion desired by a client. As a mist eliminator supplier and using pilot plant work developed in the 1970's, we have developed high efficiency towers which allow operation at higher velocities without excessive mist generation. As acid cooler manufacturers, we have been able to combine acid cooling systems with the needs of conversion to make the acid cooling systems simple, easy to operate, and low cost.

In gas cleaning, we have licensed and developed the gas scrubbing systems that can more accurately define efficiencies so that, in the case of spent acid plants, we no longer use electrostatic precipitators in the plant design. This results in a major cost reduction as well as a reduction in plant maintenance.

Higher gas strengths also reduce energy consumed on the plant. For weak spent acids, we preheat combustion air to temperatures as high as 750°C. This also increases gas strength by as much as 1.0%, which has a significant effect on energy consumption not only in the main plant, but also in the fuel consumption for preheating and decomposition in the SAR plant. Other energy effects are seen throughout the whole plant in terms of optimized gas heat exchanger designs, low level absorption towers, DynaWave® scrubbers, and low overall pressure drop.

SUMMARY

Monsanto Enviro-Chem is a Total Quality company. We will give the client what he needs. However, economics often play a factor. For example, in certain countries it is necessary to continue to use cast iron piping from a local cost point-of-view compared to the higher quality SX available on new Monsanto Enviro-Chem plant designs. Quality features which sometimes also happen to be cost reduction or energy improvement features include: The DynaWave® scrubbing system, stainless steel converter, high efficiency towers, Monsanto HE and ES mist eliminators, SX acid distributors and piping, and process control system for spent acid plant.

The combination of cost reduction, energy recovery or improvement, and quality is brought about through continuous research and development. A dedicated group of design engineers, design not just the plants but also Monsanto products - acid coolers, mist eliminators, catalyst, DynaWave® scrubbers, acid distributors, etc. The underlying basic philosophy of our plant designs, however, is to have a plant which meets current safety standards, and which has sufficient built-in process safety factors to minimize maintenance and maximize operating time.

This is why Monsanto Enviro-Chem has designed and built SAR plants for Conoco, Chevron, the U.S. Army, Tosco, Du Pont, Texaco, Amoco, Shell, Ecopetrol, Idemitsu, Nippon Oil, and American Cyanamid.

Not only is on-site regeneration economically justifiable, it offers complete integration and control within the plant site. It eliminates hazardous and costly transportation of spent and fresh sulfuric acid. It functions on decomposition fuels available at the site.

And with Monsanto Enviro-Chem technology, customers receive these tangible benefits:

- Lower capital and operating costs
- Safer, more reliable plants
- Reduced maintenance and downtime
- Improved quality of construction
- Guaranteed to meet the most stringent environmental regulations.