The Collapsing Operating Envelope
of the
Modern Sulphuric Acid Plant

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Introduction

In aviation each model of aircraft has its own operating envelope that defines its:

Maximum air speed

Maximum ascend rate

Maximum weight load

If a pilot goes outside this envelope, problems can arise. The aircraft may go into a stall or the aircraft may not get off the runway. In the operation of sulphuric acid plants there is also an operating envelope that the plant operator must stay within or problems will result. We will review this operating envelope and how it has changed and some of the reasons why.

The Operating Envelope of years prior

The plant operators from the sixties were confronted with many plant challenges, but a much wider operating envelope. The wider the envelope the greater the variations from an ideal plant operation can be tolerated. If the plant performance drifts from side to side it stays within the wide envelope. Let's examine some of the differences.

No mass conversion emission requirements

Emission limits were defined as maximum volume concentration limits of sulphur dioxide. Many states did not require continuous monitoring of the stack emission. If the stack was almost clear there was no problem. If stack monitoring was required, a little more air corrects the emission problem.

Less community concern with emissions

Community accepted plant emissions.

Less regulation

There was no OSHA. The EPA was just trying to figure out its mission. The environmentalist and conservationist movement was just beginning. Citizen groups, except to support their local industry, did not challenge state agencies.

Fewer lawyers

The need to sue everyone had not yet fully developed. Therefore, a plant upset did not have the same potential consequences as at the present time when we have a surplus of lawyers.

Lower energy prices

Oil prices were under $2/barrel in the sixties and rose to $30/barrel by 1980. Steam energy available from sulphuric acid production was considered available at no cost. Energy recovery was not justified due to the low cost versus capital expenditures. Generation of electric was not practical due to the electric industry's prorated rules. It was not until the passage of PURPA (Public Utility Reform Policy Act) of 1978 before cogeneration of power and thermal energy was practical. Partially due to regulation, but also because electricity costs were not significant due to the underlying low cost of oil.

The new challenges

If you were a sulphuric acid plant operator from 1960 and were thrown into a plant in 2000 what are some the obvious differences?

Rules & regulations

Since 1960 many new government agencies have been established to protect, inform, and make the general population more knowledgeable about plant operation. The Federal government took a more active roll in protecting workers. New Government agencies have put new challenges on the industry such as:

OSHA

EPA

FDER

Stringent emission requirements

Continuous monitoring of sulphur dioxide emissions is required on all stacks in Florida and in all new plants. A clear stack will no longer mean the emissions are in compliance. Stack emissions are based on the mass conversion of sulphur input to sulphuric acid production. Simple air dilution of the stack will not correct emission problems.

Communities concerns and awareness

Communities many miles away from the plant are now concerned of how the plant conducts their business, such as the Manasota 88.

Higher energy costs

Significantly higher energy costs and the reform of the monopoly of electric and gas utilities have caused plants to invest in energy recovery technology. No longer could the energy produced by the sulphuric acid plant be taken for granted. Now, a BTU used by the phosphoric acid operation was a BTU not available for power generation.

Plant and equipment design

Some of the new alloys available demand more accurate process controls to prevent high corrosion rates. These new alloys have extremely low corrosion rates when operating at correct conditions. Plant designers have reduced the corrosion allowance due to the potential performance of the alloys shifting the burden of control to the plant operator.

Heat recovery processes create new concerns for our plant operators, which violates many of the principles that he knows to be true. These concerns are cooler process gas, prevention of acid getting into boilers, and air drying.

Fewer people and more demands

Management of many companies has decided to eliminate people to reduce production costs while requiring more responsibilities from the remaining few. Government and Corporate policies and rules and regulations have burden plant management to the point that they are not managing the plant, but managing the paperwork.

We will explore some of these differences.

The New Envelope and reasons why

There were many reasons why a new operating envelope was being created. Many experienced plant operators did not understand that the envelope was collapsing. When the plant design was modified to get more out of the process, like more energy recovery, the envelope got a bit smaller. Some understood and found justification to upgrade process controls and had qualified people to review the changes. Most jump in and hoped for the best. The major reasons for the envelope are as follows.

Energy recovery

Energy prices increased 800% during the period of time between1960 to 2000. This drastic shift in energy prices caused the Federal government to review its policies concerning energy and the energy utilities. In 1978, the US Congress enacted the Public Utilities Regulatory Policies Act (PURPA) that established the right of the electric utility customers to serve their own load by the use of cogeneration. The industry faced with inflation from all sectors and most significantly from energy took action. The industry installed power generation equipment and improved the energy recovery of their sulphuric acid plants. Some of the approaches that were used are:

Low temperature approach economizers

Heating boiler feedwater with hot acid

Higher pressure steam

Heat recovery systems

Innovative processes

  Heat recovery with Freon

HRS technology

Each of these approaches recovered more energy tightening the operating envelope. Many of these options have proven to be manageable, others have been burdens, and still others have been cast aside.

The ultimate heat recovery process proposed is the Monarch process offered by Monsanto Enviro-Chem Systems. To-date no one has found energy costs high enough to invest in this technology.

Emissions

The emissions from sulphuric acids plants has been mandated to be reduced by an order of magnitude. The stack emissions are continuously monitored with stringent rules established for minimum mass conversion, which cannot exceed thirty minutes on an average basis. Opacity limits were established. After a few start-up incidents, the Florida Phosphate Council agreed to an understanding that covers plant start-ups.

Neighbor's complaints and government oversight has significantly changed. Plant operations are acutely aware of their emissions and impact on their neighbors. Most plant operators have taken an aggressive proactive position with the community, environmentalist, and government agencies.

Plant design

Traditional sulphuric acid design canons:

Over many years dating back to the early twenties there have been canons that all plant designers believed in. These were as follows:

Never cool the gases below 450°F

Keep SO_3 gases on the tubeside

Never cool SO_3 gases in upflow heat exchangers always downflow

Keep gas as dry as possible

In the pursuit to reduce capital costs and increase energy recovery, these canons were violated or redefined.

New plant design includes new features

To achieve more energy recovery tighter approaches to acid dewpoints were required. This was one of the first canons to be violated or redefined; never cool the gases below 450°F. The typical coldest water temperature fed to an economizer is in the range of 212 to 228°F. This temperature is dangerously close to normal acid dewpoints of the SO_3 rich gas stream being cooled.

The Monsanto Monarch process violates all of the canons because there is no need to dry air and proposes the induction of steam directly into the ductwork. This steam induction can work, but the requirements for water induction into the process subjects the plant to potential catastrophic damage.

Challenges with the new envelope

Real events do happen

Drying towers do not always perform correctly. The performance of a tower can be affected by acid temperature and concentration. These are usually easy to correct. The performance can decrease due to low circulation and uneven distribution of the acid, which can be caused by a failed acid distributor or fouled or damaged packing. Drying tower performance can go undetected for months.

Most plants do not have acid dewpoint analyzers permanently installed to detect changes such as the decreased performance of a drying tower. Most plants do not have a moisture analyzer installed to alert operators of a drying tower problem. Most plants run routine tests to measure dewpoints. Almost all plants have fewer people to monitor tower performance. Routine tests like:

Stick tests

Water dewpoint tests

Acid dewpoint tests

Sometime are put off for weeks, months, or quarters due to other plant priorities. Therefore, the problem goes unnoticed.

Electrostatic mist precipitators do not always perform correctly

In wet gas sulphuric acid plants, which includes all other sources of sulphur dioxide except sulphur burning, usually uses electrostatic mist precipitators. A sulphur dioxide rich gas stream is cleaned and cooled. The gas stream will contain fine particles of acid mist, which must be removed before entering the rest of the plant, that is a drying tower, blower, many gas-to-gas heat exchangers, and a typical converter and absorption towers. In the precipitator the mist particles are subjected to a high voltage electrical field that builds an electrical charge on the particles. The charged particles move towards a grounded surface and are collected.

When electrostatic precipitators are not performing correctly it is usually easy to detect, but the cure may not be. In many plants the precipitators are handling more gas than they were originally designed to process. The collection efficiency of the precipitator is almost directly proportional to retention time. Greater gas flows cause lower collection efficiency of acid mist. The replacement of precipitators is a very capital intensive undertaking and is usually avoided until it is absolutely necessary.

Inefficient precipitators allow acid mist to enter the plant. This mist increases the acid dewpoint throughout the plant and is normally detected on the coldest surfaces first encountered such as the first cold gas-to-gas heat exchanger.

Steaming equipment do fail and will leak

A modern sulphuric acid plant typically is made by a series of waste heat boilers (normally firetube type), superheaters, and economizers. With proper designs and good care and operation these plant components will operate trouble free year after year. Design flaws and poor operation will lead to failures and, even with the best of designs and care, leaks will occur.

Once a leak occurs acid is formed and will condense on the first cool surface contacted. The water intrusion into the process causes the acid dewpoint to raise. Therefore, areas of the plant that do not normally condense acid can at the higher dewpoint. Condensing acid will cause corrosion.

Fewer people to monitor plant performance

In attempt to be more competitive and reduce production costs many plants have eliminated supervisors leaving hourly union workers in charge. Many plants have seen it necessary to eliminate process engineers and technicians to make their plant competitive. As people are dismissed the work load is transferred to the remaining few. Tasks that were performed cannot be and are dropped or such a low priority is put on them they never get done.

Many plants have no one to review the plant data. Plant operators religiously log plant data and the data is religiously filed away without even a cursor review. Most good superintendents from years ago had time to review logsheets. Plants with computer control data logging have tons of data that is only reviewed when something finally breaks. Typically, the data shows that there was an unnoticed trend developing which would have foretold of a pending failure.

Control systems in many plants are antiquated and do not provide the information necessary for efficient plant operation with fewer people. Some plant operators have got rid of the people, but have not spent the money to upgrade the control systems. These plants are just waiting for enough justification. Will it take a major incident before they find the justification for investing in the future?

Problems have occurred with non-realistic designs

Upflow heat exchangers have been installed in many plants

In recent years a number of upflow cold gas-to-gas heat exchangers have been installed. In most cases costly problems have occurred. These heat exchangers were installed due to convenience and lower capital costs.

A review of normal acid dewpoints and normal tubewall temperature shows no condensation will occur. No condensation, therefore, no corrosion and no problems. What these heat exchanger designers lost site of is the acid dewpoint in a plant is not always normal.

Upflow heat exchangers cannot tolerate real events

Situations and incidents really do occur in any plant that can cause an increase in the acid dewpoint. If there is a surface cooler then the acid dewpoint then acid condensation will occur. Condensing sulphuric acid will corrode most material. Carbon steel tubes used in the cold heat exchanger do not have a chance to survive.

Once condensation begins in the upflow tube the gas flow keeps the acid refluxing in the tube. Acid and the corrosion products cannot be blown from the tube and they accumulate. The corrosion products will foul the tube reducing the heat transfer of the heat exchanger. The corrosion products can actually fill the tube totally blocking the tube. Corrosion continues causing the eventual failure of the tube.

When real events occurs they cause:

Corrosion from condensing acid
Fouling
Higher pressure drop
Loss of thermal performance
Tube failure

Examples of upflow heat exchanger failures

If a heat exchanger fails due to an upstream upset, is the heat exchanger design defective or is it the poor operation of the plant? This was briefly discussed at a sulphuric symposium and the designer of the heat exchanger said it did not fail. The design created a significant economic impact for the upflow heat exchanger owner:

Significant increases in production costs

Increase fuel usage

Increased electrical usage caused by process changes and much higher than design pressure drop

100"s of thousands of dollars of clean-up costs

Failure of several tubes

Real life example no. 1

A spent acid regeneration plant made major modifications to their converter and heat exchanger system. Part of this modification was the installation of a new cold heat exchanger which cools process gas leaving the converter (rich in SO_3) on the tubeside in an upflow arrangement while heating cold SO_2 gas from the main gas blower on the shellside. To reduce capital cost and to ease the transition from the existing to the new system an upflow (on a SO_3 rich gas) heat exchanger was used.

After three years of service a review determined that the heat exchanger was not thermally performing due to fouling. The pressure drop was 400% greater than design due to this fouling. Upon inspection 25% of the tube were plugged with sulphate. The tubes were plugged solid. Probing the tube to a depth of three feet could not find the end of the pluggage.

Attempting to remove the sulphate by dry means, such as drilling, failed. Hydroblasting was finally used to clean the heat exchanger. Once cleaned the extent of the permanent tube damage could be determined. Several tubes had fail due to corrosion and were plugged.

The cause of the fouling was a higher than anticipated acid dewpoint. This condition was created by improperly performing electrostatic precipitators and a drying tower mist eliminator performance problems. This incident was extremely costly for the plant owner.

Real life example no. 2

A sulphur burning plant designer decided to use an upflow heat exchanger that cooled SO_3 rich gas leaving the converter before the first absorption tower and reheat the cold returning gas from the interpass absorption tower on the shellside. A quick review of the design will demonstrate that no condensation will occur if everything is performing upstream correctly. Well, they don't always do.

The primary steam baffle in the waste heat boiler steam drum failed causing the steam purity to deteriorate. As the baffle failed over many months the purity of the steam worsened. Boiler water salts began fouling the steam superheater and blower turbine. These deposits on the superheater tube led to stress corrosion cracking and tube failure. Superheater leaks developed worsening and finally involved seven tube passes. The presence of this steam (water) increased the acid dewpoint in the plant.

Acid was formed and condensed on the first cold surface it found. The upper section of the cold interpass heat exchanger. Acid was trapped inside the tube due to the upward gas flow. The trapped acid corroded the tubes from inside. This corrosion thinned the tube and with normal stresses from the normal expansion and contraction of the heat exchanger the tubes failed over a period of months.

The tube failure caused SO_3 gas to by-pass the interpass absorption tower. Once the tube failed the overall efficiency of the plant decreased. The by-passing reduces the sulphur conversion efficiency which:

Increased SO_2 emission
Increased air usage of the plant
Increased energy consumption
Decreased plant production

Plant personnel were unaware of the tube leaks. They knew that the pressure drop across the tubeside of the heat exchanger had increased and scheduled to have the tubes cleaned during the next turnaround. As VIP was cleaning the tubes they found that numerous tubes had broken.

Careful and thorough review of the plant data showed the loss of conversion efficiency. The most obvious sign was that more acid was being produced in the final absorption tower due to the failing tubes. The heat load on the final tower had significantly increased. The overall utilization of Oxygen had decreased. They had to run with ever decreasing sulphur dioxide gas concentration to maintain emission compliance.

In this plant, controls were adequate, but no one was looking at the data.

After plugging the damaged tube, this heat exchanger was prematurely replaced with a traditional downflow heat exchanger. A very expensive lesson.

Conclusion

There is an ever ending desire to reduce capital costs, emissions, increase energy recovery, and reduce labor costs. These goals are all noble but miss the point if they do not take into account of real plant facts of life. Processes that cause very tight approaches to acid dewpoints have not given enough thought to unexpected incidents. The one-time cost savings of an upflow heat exchanger can be wiped out by just one incident. The $100,000 to $200,000 capital savings were wiped out very quickly with these two incidents.

A careful analysis must be made to weigh the potential benefits versus the risks. Unfortunately, the benefits get the most attention and little attention is given to the risks. As these projects are approved without a full understanding, the operating envelope will continue to collapse.