Catalyst management

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Synopsis

Sulphuric acid plants now and then see unexpected increases in SO_2 emissions. Our experience is that it is not always easy for the acid plants to pinpoint the exact reason for the SO_2 increase.

Sometimes a catalyst bed is sacrificed even though reliable temperature readings and gas analyses could have verified satisfactory activity. Hence the leaking heat exchanger is never discovered and after the shutdown the SO_2 emissions are still too high.

This paper will look into some basic catalyst management tools: good record keeping is a necessity for collection of representative catalyst samples; reliable operating data is an inevitable starting point for all analysis; and trending of operating data is a must for plant optimization and troubleshooting. In addition, these catalyst management tools will give continuous updated knowledge of the catalyst status in each bed, providing the basis for a more effective replacement strategy.

The most typical reasons for increasing SO_2 emissions will be presented together with easy guidelines for cross-checking operating data, temperature optimization and good record keeping.

Introduction

Sulphuric acid plants occasionally see unexpected increases in SO_2 emissions and the cause of the increase is not always easy for the acid plants to pinpoint.

Sometimes a catalyst bed is replaced when the real problem is a leaking heat exchanger. The leaking heat exchanger is not discovered until after the catalyst replacement when the SO_2 emissions are still too high.

This paper will look into some basic catalyst management tools: good catalyst record keeping is a necessity for collecting representative catalyst samples; reliable operating data is essential for all performance analysis; and trending of operating data is a must for plant optimization and troubleshooting. The use of these basic catalyst management tools will provide the basis for the most effective catalyst replacement strategy.

The most typical reasons for increasing SO_2 emissions will be presented together with easy guidelines for cross-checking operating data, temperature optimization, and good record keeping.

Collection of reliable operating data

Reliable operating data is an inevitable starting point for all analysis. The three most important control parameters for optimum catalyst performance and early detection of potential problems are:

➤ Catalyst temperatures at the inlet and outlet of each catalyst bed
➤ Gas compositions at the inlet and outlet of the converter or preferably the inlet and outlet of each catalyst bed
➤ Pressure drops across each catalyst bed.

It is important that these parameters are measured on a regular basis. We recommend that pressure drops are measured once per week. The data should be graphed either manually, in a spreadsheet, or in a DCS. Any sudden step changes should be investigated to determine the cause.

The reaction of sulphur dioxide with oxygen to form sulphur trioxide is a highly exothermic, reversible reaction, associated with a reduction in gas volume:

$$SO_2 + \tfrac{1}{2}O_2 \leftrightarrow SO_3 + heat$$
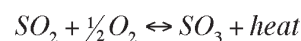
Since the reaction is exothermic, the temperature will rise with approximately 28°C per mole % of SO_2 converted across the catalyst bed, i.e. the total theoretical temperature rise across the converter can easily be calculated from:

$$\Delta T_{total,theoretical} = \%SO_{2,inlet} \times 28°C$$

The actual temperature rise across the converter can be calculated from the temperature rise across each catalyst bed:

$$\Delta T_{total,actual} = \Delta T_{bed\ 1,actual} + \Delta T_{bed\ 2,actual} + ... \Delta T_{bed\ n,actual}$$

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The million dollar question now is: is the total temperature rise across the catalyst passes in agreement with the SO_2 inlet concentration?

$$\Delta T_{total,\ actual} = \Delta T_{theoretical} = \%SO_{2,\ inlet} \times 28°C$$

If a disagreement between total actual temperature rise and the SO_2 inlet concentration is observed, it is important that the reason for this inconsistency is pinpointed and rectified. The following may be considered in the search for possible reasons:

➤ Temperatures should be taken with thermocouples located in the interface between the catalyst and the inert material. Thermocouples located in the gas stream may read 10–20°C too low due to poor heat transfer in the gas phase and heat loss to the surroundings via the thermowell. Thermocouples must be checked and calibrated regularly.

➤ In order to verify temperature homogeneity in the reactor cross-section it is recommended that multiple thermocouples be installed (e.g. three thermocouples 120° apart) at the inlet and outlet of each bed. Temperature differences at the inlet to the catalyst layer tend to be amplified through the catalyst bed. A locally lower inlet temperature leads to a lower rate of reaction in that section of the catalyst yielding a smaller conversion and consequently a smaller temperature increase. Thus, temperature variations at the entrance to a catalyst layer may result in a temperature and concentration spread at the exit, meaning an inferior utilization of the catalyst mass

➤ Temperature variations may originate from improper mixing of hot and cold process gas before entering the catalyst mass. This may be proved by making holes in the duct and measuring temperature variations by means of travelling thermocouples.

➤ Imperfect gas mixing becomes even more serious if two gases are not only of different temperatures but also of different composition. This will be the case when interbed cooling is performed by injection of cold feed gas or quench air. In these cases cross-sectional temperature as well as concentration variations may occur.

➤ SO_2 measurements should be made on locations that provide gas samples that are representative for the entire gas flow. It is our experience that sample points on the converter wall may produce nonrepresentative gas samples as tiny streams of lower converted gas may channel along the wall, interfering with the samples collected here. More reliable results can be obtained when sampling from points on the inlet ducts and especially the outlet ducts after the gas has been allowed to mix. For this reason, it is preferable that sample points are accessible on the ducts before and after each catalyst bed.

Analysis of operating data

When reliable operating data are secured, more detailed analyses of the converter operation can begin.

All data must be recorded and plotted to better illustrate possible developments in the performance and to provide the best basis for optimization and troubleshooting. Any development in temperature rise, SO_2 emission or pressure drop must be followed closely and can in most cases reveal the root cause for changes in the performance.

Typical reasons for increasing SO₂ emission

Example 1: non-optimum inlet temperatures

Temperature optimization at the inlet of each catalyst bed is crucial for maintaining the lowest possible SO_2 emission. Each set of operating conditions (i.e. inlet flow and SO_2 strength) will require different pass inlet temperatures in order to optimize the operation. Temperatures should therefore be optimized whenever the operating conditions have changed significantly.

Due to the temperature dependence of the equilibrium conversion, the lower the inlet temperature to a catalyst bed is, the higher the equilibrium conversion will be. On the other hand, the lower the catalyst temperature is the lower the rate of reaction will be. For each catalyst bed there will therefore exist an inlet temperature at which the conversion, and correspondingly the temperature rise across the bed: $T_{out} - T_{in}$, is maximum.

Operation at an inlet temperature of T_{in} will correspond to an optimum outlet temperature of T_{out}, which is close to equilibrium, as shown in Figure 1. Decreasing the inlet temperature by ΔT would lead to more favourable equilibrium conditions, but the reaction rate is not sufficiently high to reach equilibrium and hence, the conversion will be reduced. On the other hand, increasing the temperature by ΔT would lead to a higher reaction rate but the equilibrium conversion reached will be lower than at optimum.

Optimization of the converter inlet temperature is therefore a trial-and-error search for the inlet temperature at which $T_{out}-T_{in}$ and thereby conversion will be maximized.

The necessity of increasing the inlet temperatures as activity declines due to catalyst deactivation is illustrated in Figure 2, which shows the conversion as function of inlet temperature and catalyst activity. It is seen that to each activity level corresponds an optimum inlet temperature. The ----- line shows how the conversion is decreasing if the inlet
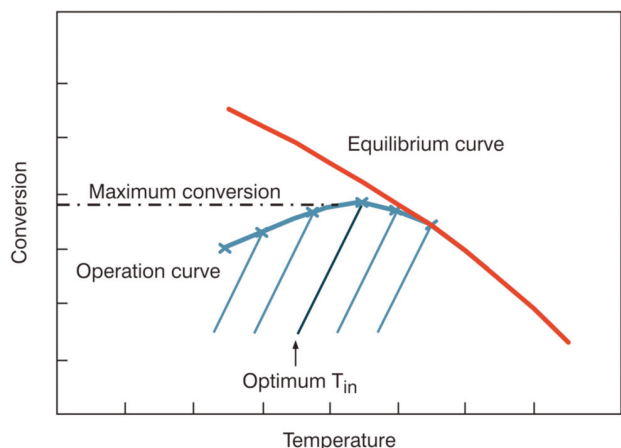

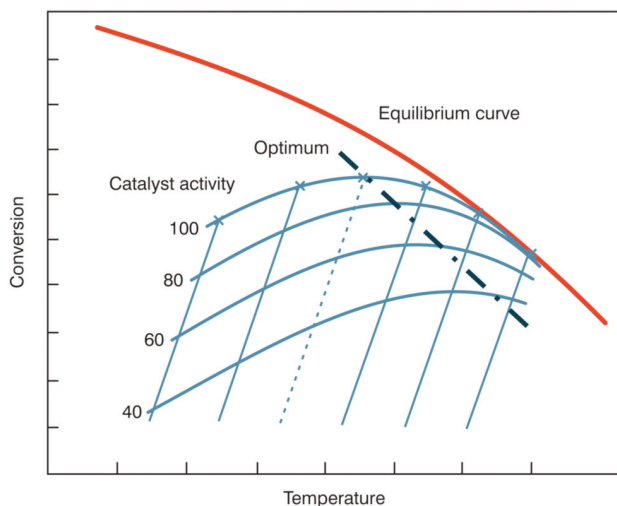Figure 1—Temperature optimization

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Figure 2—Temperature optimization due to catalyst deactivation

temperature is kept constant. The optima have been connected by the ·—·— line, which then shows how the optimum inlet temperature increases as activity decreases.

What is wrong with my plant?

The SO_2 emissions are increasing. Historical records show that the overall temperature rise is constant. Inlet temperature curves show no significant change for beds 1, 2 and 3. A slow drop of the inlet temperature to bed 4 is experienced; however, the temperature rise across bed 4 is almost constant. Figure 3 shows the SO_2 emission as function of inlet temperature to bed 4 and this figure illustrates the effect of non-optimum temperatures inlet bed 4. The basis is a plant with a 3+1 layout, 11.3% SO_2 and 9.7% O_2 in the feed gas and an overall conversion of 99.8% corresponding to 270 ppm SO_2. It can be seen from the figure that a non-optimum inlet temperature has a significant effect on the SO_2 emission: a difference of +/- 10°C from the optimum temperature of 420°C results in a 15–20% increase in SO_2 emission. So, even though the temperature rise across bed 4 is almost constant; the non-optimum inlet temperature to bed 4 is the reason for the increasing SO_2 emission.

Example 2: increased SO_3 level inlet bed 4

The presence of SO_3 at the inlet of the catalyst pass located after the intermediate absorption tower (IAT) can originate from either poor performance of the IAT or from leaking reheat-exchangers. In many double absorption plants the cold gas from the IAT is reheated with the exit gas from the third pass before entering the final catalyst pass(es). This means that SO_2 gas containing no SO_3 is reheated with the partly converted SO_2 gas containing high amounts of SO_3. The amount of SO_2 on an SO_3-free basis is the same in the two gas streams and the leak thus cannot be detected by a Reich's test. The gas coming from the IAT may contain acid carry-over and the result is corrosion and leaks in the hot and/or cold reheat-exchangers. Consequently an SO_3 increase will be experienced at the inlet of the final catalyst pass(es). This has a negative effect on the equilibrium and the equilibrium curve is pushed downwards, as illustrated in

Figure 4. The final result is a lower conversion in the catalyst passes after the IAT and consequently increasing SO_2 emissions.

When a gas containing SO_3 contacts humid air, white acid fume is formed immediately. This phenomenon can be used in detecting the presence and origin of SO_3 downstream the IAT. The gas leaving the IAT should be clear. If this gas is visible, too much SO_3 is slipping through the IAT. If the gas leaving the IAT is clear, but the gas entering the last pass(es) is visible there is a heat exchanger leak. If there is more than one heat exchanger between the IAT and the converter, the leaking exchanger can be determined by checking the gas inlet and outlet of each heat exchanger. The heat exchanger that has clear gas at the inlet and visible gas at the outlet is the leaking heat exchanger (Figure 5).

What is wrong with my plant?

The SO_2 emissions are increasing. Historical records show that the overall temperature rise is almost constant. Inlet temperature curves show no changes for beds 1, 2, 3 and 4. The operating data show no signs of changes in the SO_2 concentration in the feed gas or pressure drop across the individual beds.
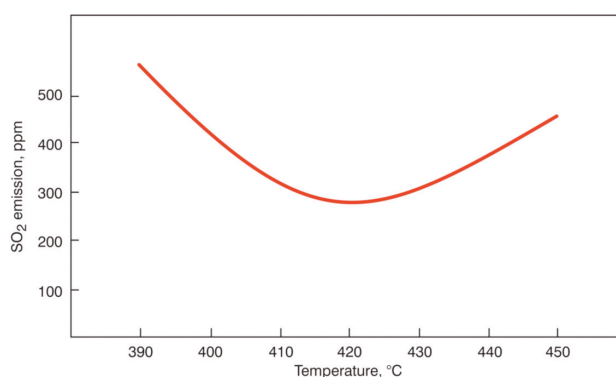

Figure 3—Effect of non-optimum inlet temperature to bed 4. Basis: 3+1 layout, 11.3% SO_2 and 9.7% O_2 in the feed gas. SOR conversion = 99.8% corresponding to 270 ppm SO_2
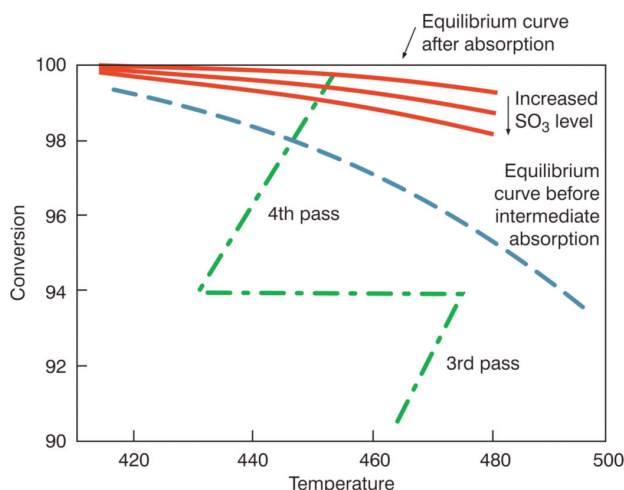

Figure 4—The SO_3 concentration effect on the equilibrium curve after IAT
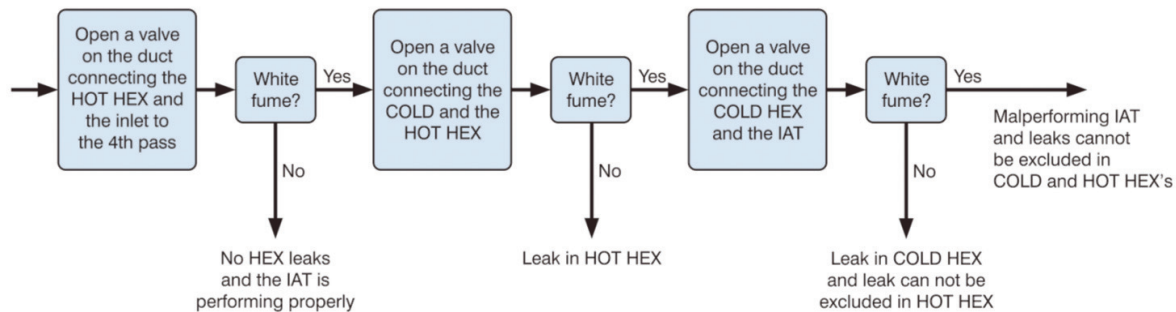
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Figure 5—Visual detection of SO₃ leaks

The next step is to check the inlet gas to the catalyst pass after the IAT for visible gas. Figure 6 shows the SO_2 emission as function of IAT efficiency and this figure illustrates the effect of increased SO_3 levels inlet bed 4. The basis is a plant with a 3+1 layout, 11.3% SO_2 and 9.7% O_2 in the feed gas, an IAT efficiency of 99.9% and an overall conversion of 99.8% corresponding to 270 ppm SO_2. It can be seen from the figure that a poor working IAT or leaking reheat-exchangers illustrated as low IAT efficiency has a significant effect on the SO_2 emission.

Example 3: channelling

Uneven gas flow distribution through the catalyst bed or channelling may be caused by: a collapsed grid causing a hole in the catalyst bed; high gas velocities inlet the converter may cause catalyst movements and possible 'holes' in the catalyst bed; and dust build-up in the top of the catalyst bed will reduce the 'available' catalyst area.

Channelling will cause non-uniform temperature and concentration profiles at the exit of the bed. A drop in the outlet temperature will be detected only if the thermo-couple(s) are located right below the 'channelling' area(s). Sometimes the temperature rise is apparently as expected and sometimes an average temperature rise is seen corresponding to a mixture of converted and partly unconverted gas. The average conversion taking place in the bed will be lower than expected, i.e. a higher concentration of SO_2 will enter the following bed and give a temperature rise in the following beds, which is higher than expected.

Figure 7 illustrates the effect on temperature rise in a four-bed converter with and without channelling. The red colour illustrates the temperature rise across each bed during a three-year period in case of no channelling. A slightly decrease in the temperature rise across each bed is caused by the normal catalyst deactivation. The blue colour illustrates the temperature rise across each catalyst bed during a two-year period in case of channelling caused by dust build-up in the top of the first bed. The figure clearly shows that as the dust deposition develops in bed 1 and the degree of channelling increases the missing conversion in the first bed (shown as a drop in the temperature rise) will show up as increasing temperature rises in the lower beds.

To distinguish between the different channelling reasons it is important to study the speed of the change in temperature rise: is it developing over time or is it a sudden change taking place overnight? In addition, pressure drop measurements may support such investigations: is the pressure drop increasing due to dust deposition or does it decrease due to a 'hole' in the catalyst bed or a dropped grid?

What is wrong with my plant?

The SO_2 emissions are increasing. Historical records shows that the overall temperature rise has increased and that $\Delta T_{total, actual} > \Delta T_{theoretical}$. The records also show that the
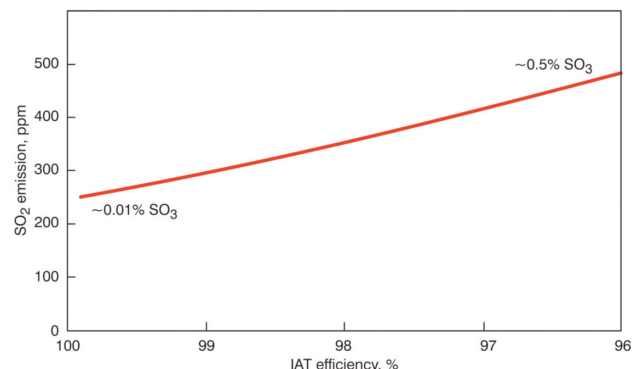

Figure 6—SO₂ emission as function of IAT efficiency. Basis: 3+1 layout, 11.3% SO₂ and 9.7% O₂ in the feed gas. 99.9% IAT efficiency. Start-of-run conversion = 99.8% corresponding to 270 ppm SO₂
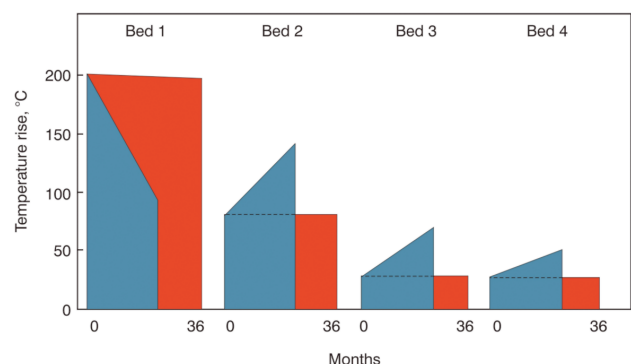

Figure 7—The effect of channelling in bed 1 on temperature rises. Dark grey: no channelling. Light grey: channelling due to dust deposition. Basis: 3+1 layout, 11.3% SO₂ and 9.7% O₂ in the feed gas. SOR conversion = 99.8% corresponding to 270 ppm SO₂

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temperature increase across bed 2 has increased and historical pressure drop curves across each bed show a sudden decrease in pressure drop across bed 1. These signs indicate that a grid has dropped in bed 1 causing low conversion in bed 1, which is partly compensated for in bed 2.

Example 4: heat exchanger leak after final catalyst bed

In many metallurgical plants the cold feed gas from the drying tower is as a first step heated with the exit gas from the final catalyst pass. This means that strong unconverted SO_2 feed gas is heat exchanging with highly converted gas from the final catalyst pass containing only a few hundred ppm SO_2 or less. The feed gas is coming directly from the drying tower and often acid carry-over problems are experienced. The result is corrosion and tube leaks in this very critical cold-gas-heat-exchanger. The higher pressure SO_2 rich feed gas will leak into the lower pressure SO_2 lean exit gas, causing an increase in SO_2 emissions which very often increase over time.

What is wrong with my plant?

The SO_2 emissions are increasing. Historical records show no changes in temperatures, SO_2 concentration in the feed gas or pressure drop that can explain this increase. Also the test for visible gas at the inlet of the catalyst pass after the intermediate absorption tower is negative. The only development in the operating data is the increasing SO_2 emission, indicating that the root of the problem must be found downstream from the converter. In order to locate the problem, SO_2 measurements are carried out simultaneously on the lean SO_2 gas at the inlet and outlet of the cold-gas-heat exchanger. An SO_2 concentration at the inlet of the heat-exchanger corresponding to the outlet of bed 4 pinpoints a leaking heat exchanger.

Good catalyst record keeping

When loading the catalyst, it is important to calculate the depth of the catalyst layer(s) and supporting material for each bed and to mark the converter wall plainly. Good record keeping is invaluable in connection with future screening and catalyst sampling activities especially when a catalyst bed consists of several catalyst layers of different type or age. Precise knowledge about the interface between two catalyst layers, e.g. standard catalyst and a more expensive caesium catalyst or new and old catalyst, will ease the unloading and prevent mixing of the two catalyst types, which would reduce the effect of the caesium catalyst. In addition, this knowledge is essential when collecting catalyst samples as otherwise wrong and expensive conclusions about future replacement strategies may be drawn. We also recommend that all inspections in the converter and all phenomena observed are documented with photos and/or videos, which can aid in troubleshooting and operator training programmes.

Spent catalyst samples

Activity testing of spent catalyst samples in combination with evaluations of the catalyst performance based on operating data is a very efficient tool to follow the catalyst history. However, as described above activity information will have value only if exact knowledge about catalyst type, age and location are known for each sample.

In order to obtain representative catalyst samples from the converter beds, we recommend collecting samples according to the guidelines below.

As the first pass has been exposed to the highest ΔT as well as possible contaminants in the feed, it is recommended to sample from three depths down through the catalyst bed for characterizing the performance of the bed.

Four samples should be collected from each of the layers: top, middle and bottom. The top samples should be collected from a depth of 5–10 cm (not including the inert material). Likewise, the bottom samples should be collected 5–10 cm from the bottom. The four samples from each layer should be collected 90°C apart, e.g. in the directions: N, E, S and W and then combined to one sample for testing, i.e. three composite samples representing the top, middle and bottom layers of bed 1 are sent for testing.

For the second pass it is adequate to test composite samples representing the top and bottom layers. For the lower passes a single composite sample from each pass is sufficient. This sample should be collected 5–10 cm from the top of the catalyst bed.

It is important that the sample containers are marked to identify the sample location (bed number and layer) and that each sample is followed by information on catalyst type, age and any possible observations or pictures about dust depositions, etc.

Conclusion

Reliable operating data are required for all performance analyses. The operating data should be measured and monitored on a regular basis. If any discrepancy exists between $\Delta T_{total,\ actual}$ and $\%SO_{2,\ inlet}$ it is important that the reason for this inconsistency is pinpointed and rectified.

When reliable operating data are obtained a more detailed analysis of the converter operation can begin: all data should be recorded and plotted to better illustrate possible trends in the performance and to provide the best basis for troubleshooting and optimization. Any changes in temperature rise, SO_2 emissions, and pressure drop should be investigated thoroughly and in most cases it will reveal the root cause of changes in the plant performance.

Good catalyst record keeping is invaluable for planning future catalyst screening and sampling activities, especially when a catalyst bed consists of various catalyst layers of different type or age.

Activity testing on spent catalyst samples in combination with evaluations of the catalyst performance is a very efficient tool for catalyst management. However, activity information will have value only if exact knowledge about catalyst type, age and location is available for each sample.

A deeper understanding of the actual status of the catalyst in each pass of a sulphuric acid converter is important knowledge when troubleshooting, optimizing plant performance and developing the most cost-effective replacement strategy. ◆