

# GENERAL START-UP AND SHUTDOWN INSTRUCTIONS FOR A SPENT ACID (SAR) SULFURIC ACID PLANT CONVERTER CONTAINING MECS<sup>®</sup> CATALYST FOR SULFURIC ACID

## GENERAL

These instructions should be considered general guidelines for starting up the converter in a SAR sulfuric acid plant with MECS<sup>®</sup> Catalyst. Most SAR plants are equipped with indirect fired preheaters to heat the converter to operating temperature. Other plants are equipped with an indirect fired combustion air preheater which is also used to preheat the converter. Some plants have recuperators after the spent acid combustion furnace. In plants with recuperators, the recuperator heats the air to the converter in place of the typical gas /gas heat exchangers, and the hot converter gases are used to preheat the air to the combustion furnace. Heat up time is a function of the size of the preheater. Most plants can be heated to operating temperature within 24 hours. Plants with preheaters sized for the full design gas volume of the plant may be heated to operating temperature in as little as 12 hours.

Since there are many SAR configurations, specific issues such as valve positions, tower acid flows, gas bypass options, safety interlocks, preheater operation etc. are not included here. These instructions should be used in conjunction with the plant operating manual and any applicable manufacturers' specifications.

## PLANT START-UP

### HEATING THE CONVERTER

1. The heating of the converter should be carried out using dry air to minimize water condensation on the catalyst.
2. The air used to heat the plant usually comes in through the dilution air valve down-stream of the gas cleaning system. This point of entry minimizes the amount of water vapor in the gas. Air enters the drying tower, flows to the main compressor, typically passes through the cold heat exchanger, and then is heated in the start-up preheater, combustion air preheater, or other heat exchanger. The hot air flows through the remainder of the plant and either exits to the atmosphere or is recycled to the drying tower.
3. Adjust the gas valves, vents, bypasses, and blinds to the appropriate positions as described in the plant operating procedures.
4. Start the acid circulation over all towers.
5. Start the main compressor and adjust the flow rate to match the preheater size or plant operating instructions.
6. Start the fuel fire in the start-up preheater (or furnace combustion chamber) and adjust temperature in combustion chamber and at the hot air exit to meet plant requirements. Generally the plant heat-up rate should not exceed 55°C (100°F) per hour. For plants using a combustion air preheater, a start-up fan is necessary to provide combustion air, and the main blower is used to move the indirectly heated air through the plant.
7. Check the acid strength in the circulating systems and replace with strong acid as required. If the acid strength in the drying tower drops below 90%, stop the heat-up until the acid strength can be restored with strong acid imported from storage.
8. *During the heat up, MECS Inc. (MECS) recommends recycling the gas from the final tower to the drying tower inlet. This method requires a recycle duct with blinds and valves and is not available in all plants. Recycling the air through the start-up preheater or combustion air preheater greatly reduces the amount of acid that will be diluted during the heat-up and the amount of start-up emissions.*
9. Acid must be circulating through all of the towers. With the acid circulating, the drying tower will dry the ambient air and the absorbing towers will absorb SO<sub>3</sub> that is formed during the converter heat-up. If acid is not circulating in the towers, moisture from the air may damage the catalyst, and SO<sub>3</sub> not absorbed in the absorbing towers will cause a visible white plume in the stack.

## GENERAL START-UP AND SHUTDOWN INSTRUCTIONS FOR A SPENT ACID (SAR) SULFURIC ACID PLANT CONVERTER CONTAINING MECS<sup>®</sup> CATALYST FOR SULFURIC ACID

**CAUTION:** Note that the gas flows and gas temperatures to the converter passes should be adjusted as necessary to keep the temperatures within the manufacturer's specifications for mechanical integrity of the ductwork and converter, specifically the converter division plates. The manufacturer's specifications not only protect the structural integrity of the equipment, but also help maintain the gas-tight welds. For MECS-designed plants, the temperature in the converter inlet ducts should not exceed 600°C (1110°F) for stainless steel ducts and converters or 510°C (950°F) for carbon steel ducts and converters. The temperature differences across the division plates that separate the converter passes of MECS stainless steel converters should not exceed 120°C (250°F).

10. Start heating the plant with hot air around 150°C (300°F). Then slowly increase the preheater air outlet temperature to 600°C (1110°F) for stainless steel ducts and converters or 510°C (950°F) for carbon steel ducts and converters. Continue putting hot air through the converter until all passes of the converter are as close to 400°C (750°F) as possible. The first and fourth (or fifth) pass exit temperatures should be over 400°C (750°F), and the second and third pass inlet temperatures should be at least 420°C (790°F) before SO<sub>2</sub> conversion can begin. Note that passes containing cesium catalyst only need to be heated to 380°C (715°F) before SO<sub>2</sub> conversion can begin.

**CAUTION:** Keep the ductwork temperatures and differential temperature across the converter division plates within the manufacturer's specifications.

11. If a superheater is present after a pass, the outlet temperature of the pass should not exceed 510°C (950°F) during the heat-up. This will prevent damage to the superheater in case there is no steam flow.
12. **FOR PLANTS NOT RECYCLING THE HEAT-UP GASES:** As the converter is heating, the vent gases in the start-up vents (typically before the absorbing towers) may become cloudy as SO<sub>3</sub> gas is evolved from the catalyst when it reaches approximately 250 - 300°C (480 - 570°F). If these emissions are not acceptable, then the gases must be routed through the final tower and to the stack. This requires shutting down the start-up preheater and main compressor to allow the duct blinds to be changed accordingly. Restart the main compressor and start-up preheater to continue the heating process. When the vent gases are flowing through the absorbing towers, the acid becomes dilute due to absorption of the water from the ambient air. It is important to carefully monitor the acid strength when the vent gases are flowing through the towers to avoid circulating weak acid (<93 weight %). Weak acid must be pumped to storage and the volume replaced with strong acid (98%) to maintain acid strength above 93%. In some plants a start-up bypass duct is provided to bypass gas around the interpass tower to avoid cooling the gas as it passes through the tower and subsequent heat exchangers.
13. For those plants using a separate indirectly fired preheater, use the start-up fan to preheat the decomposition furnace combustion chamber so the furnace will be ready to process spent acid when the converter is at operating temperature.
14. After the catalyst has reached the specified temperatures, the plant is ready to receive SO<sub>2</sub> gas from the furnace / gas cleaning system.
15. Make sure the decomposition furnace and gas cleaning system are ready to supply SO<sub>2</sub> gas before stopping and isolating the air preheater. Otherwise, the converter beds may cool off before sufficient heat can be generated in the converter beds to keep the plant at temperatures to convert the SO<sub>2</sub>. (In some plants the start-up preheater is also designed to heat SO<sub>2</sub> gas and is equipped with isolation valves. In this case the preheater can remain online during the initial flows of SO<sub>2</sub> gas.)

# GENERAL START-UP AND SHUTDOWN INSTRUCTIONS FOR A SPENT ACID (SAR) SULFURIC ACID PLANT CONVERTER CONTAINING MECS<sup>®</sup> CATALYST FOR SULFURIC ACID

## STARTING THE SO<sub>2</sub> GAS FLOW TO THE PLANT

16. Reposition duct blinds and valves as necessary.
17. Adjust acid flow to all towers to design rates and strength.
18. Verify that the stack gas oxygen and SO<sub>2</sub> analyzers are ready for service.
19. Start the main compressor and, as soon as practical, start the spent acid / H<sub>2</sub>S gas feed and fuel to the decomposition furnace. Keep the oxygen levels in the furnace at or above 2% to prevent sulfur sublimation.
20. Initiate SO<sub>2</sub> production at approximately 40 to 50% of full rate. It is recommended that this be done using approximately 7 to 9% SO<sub>2</sub> gas feed at a reduced blower rate. Maintain this rate until the converter passes start to show conversion (a rise in exit temperature above the inlet temperature).
21. A gradual temperature rise will be observed in the first pass within a few minutes of catalyst being in contact with sulfur dioxide. For the initial start-up with new catalyst, this temperature rise (measured at the first pass outlet) should peak within forty five minutes at a maximum of 20 to 50°C (35 to 90°F) above the expected outlet operating temperatures for a given gas strength. This temperature maximum will begin to drop after approximately thirty minutes to eventually line out at the expected operating temperature for a given SO<sub>2</sub> strength gas stream.
22. Slowly increase the gas flow, and then match with a proportional increase in the spent acid / H<sub>2</sub>S gas feed rate to the furnace. Maintain stack oxygen concentration at or above 4.0% O<sub>2</sub>. Hold this gas flow and strength until the inlet temperatures to each pass of catalyst are near the design temperatures. The pass 1 outlet temperature should not exceed 650°C (1200°F) to prevent damage to the catalyst.
23. The plant should be stabilized before attempting to increase the plant rate. Then the plant rate can slowly be increased by adjusting the main compressor with a proportional increase in the spent acid / H<sub>2</sub>S gas feed rate to the furnace. The rate of feed adjustment should be dictated by the SO<sub>2</sub> emissions and the bed inlet temperatures. Raising the rate slowly minimizes process upsets and helps to keep everything under control. The feed rate increase will not generate a large temperature rise during the initial start-up with new catalyst since the catalyst is almost completely sulfated prior to operation.

## PLANT SHUTDOWN

Condensed moisture or acid may decrease the physical strength and/or cause a loss of vanadium or active salts in the catalyst, leading to high pressure drop and a possible permanent decrease in conversion efficiency. The catalyst is hygroscopic (attracts moisture), especially if SO<sub>2</sub> or SO<sub>3</sub> gas has been in contact with the catalyst. Therefore, during a plant shutdown, moist air must be avoided and eliminated, to the maximum possible extent, from the catalyst and the converter / heat exchanger system. Before a shutdown SO<sub>2</sub> and SO<sub>3</sub> should be purged from the plant to reduce the sulfuric acid dew point temperature should any moisture enter the plant during the shutdown.

For any planned shutdown, especially if it is to be of such length that the catalyst temperatures will fall below the dew point of sulfuric acid (i.e. the point where moisture or acid would condense), the converter system should be thoroughly purged with dry air to remove the SO<sub>2</sub> and SO<sub>3</sub> prior to shutdown.

For an unplanned shutdown, such as a plant shutdown due to an interlock, the plant should be purged with dry air to remove the SO<sub>2</sub> and SO<sub>3</sub> as soon as practical if the plant cannot be restarted quickly.

# GENERAL START-UP AND SHUTDOWN INSTRUCTIONS FOR A SPENT ACID (SAR) SULFURIC ACID PLANT CONVERTER CONTAINING MECS<sup>®</sup> CATALYST FOR SULFURIC ACID

## PLANNED, SHORT TERM SHUTDOWN

Prior to the shutdown, coordinate shutdown with steam users. Adjust heat exchanger bypasses to raise the inlet temperatures in the converter by 10°C (18°F) in each pass and operate the plant at the higher temperatures for an hour or two to let the heat build in the catalyst beds. This will increase the length of time the plant may remain shut down without requiring the use of the start-up preheater to start up.

Note that if the catalyst bed temperatures fall below 400°C (750°F) for standard catalyst or 380°C (715°F) for cesium catalyst, the start-up preheater will be needed to reheat the beds prior to processing SO<sub>2</sub> gas again. It is very important to keep Pass 1 above this temperature. If conversion stops in pass 1 because of low temperature, eventually over the next 12 to 24 hours conversion will stop in all beds, and SO<sub>2</sub> emissions will continue to increase. The only way to restore conversion is to restart the preheater and heat up the first pass.

Reduce the plant rate to about 50% of design rate. Shut off the spent acid and H<sub>2</sub>S gas feed to the furnace, but continue to operate the main compressor at approximately 50% volume.

Purge the converter / heat exchanger system with dry air until the SO<sub>2</sub> and SO<sub>3</sub> are purged from the catalyst passes (approximately 20-30 minutes for a purge prior to a short shutdown).

## PLANNED, LONG TERM SHUTDOWN

Reduce the plant rate to about 50% of design rate. Shut off the spent acid and H<sub>2</sub>S gas feed, but continue to operate the main compressor at approximately 50% volume.

Purge the converter / heat exchanger system with dry air until all the equipment is cooled down and the SO<sub>2</sub> and SO<sub>3</sub> are purged from the catalyst passes (approximately 24 hours for a purge prior to a shutdown to cold conditions).

After purging the system, care should be taken to prevent moist air from reaching the catalyst. Natural draft will bring in moist air through the plant stack and the air inlet. The main valve in the discharge of the main compressor should be closed and all other valves that would otherwise allow ambient air to enter the plant should be shut and blanks installed to prevent moist air intrusion. If maintenance work is performed on the converter, the length of time that the manways are open should be minimized. Polyethylene sheeting secured with rope or wire should be used to cover the open converter manways when personnel are not inside the vessel. Polyethylene sheeting should also be used to cover other open manways within the gas system of the plant.

If the shutdown plans require the plant to be down for a long period, in excess of several months, sulfuric acid must be circulated through the towers on a regular basis (once or twice per week for an hour). Even with this precaution, it will be very difficult to maintain a dry environment for the catalyst. It is recommended that the catalyst is removed from the converter and stored in dry, closed waterproof bags or drums until the plant is ready to start up again. The drums or bags should be clearly labeled with the catalyst pass number and the catalyst location in the bed (top, middle, or bottom) so that the catalyst can be replaced in the same location later. Catalyst bags or drums should be stored indoors in a dry warehouse facility on wooden pallets to prevent exposure to free-standing water. If the catalyst needs to be stored outside of warehousing facilities, it must be stored in waterproof drums that are elevated on pallets to minimize exposure to free-standing water and must be covered with water-impermeable plastic to eliminate moisture exposure.

Catalyst should be reloaded in its previous location in the converter only a few days prior to the planned restart of the plant. Care should be taken so that moist air does not reach the catalyst between the time of catalyst loading and the plant restart.

Copyright © 2014. MECS, Inc. All rights reserved. The DuPont Oval Logo, DuPont™, The Miracles of Science™ and all products denoted with a ® or ™ are trademarks or registered trademarks of E. I. du Pont de Nemours and Company or its affiliates.