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SHELL EO/EG PROCESS MEMORANDUM 102

SUBJECT : START-UP AND SHUT DOWN OF EO CATALYST

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INTRODUCTION

The current design is capable of running on both high selectivity catalyst and high activity catalyst. For practical purposes, this document shall refer to S-863 catalyst as a typical example of high activity catalyst and S-882 as a typical example of high selectivity catalyst. The object of this document is to outline the steps and procedures to be taken for successful start-up of EO catalyst in a commercial EO plant. Normally, experienced Catalyst vendor personnel will assist the plant with start-up of the catalyst. These procedures must be used in conjunction with the plant's operating and safety procedures.



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1. CATALYST PROTECTION AND BLANKETING AFTER CATALYST LOADING

- 1) During all stages of the catalyst loading and start-up, the catalyst and the reactor must be protected against moisture (including humid air) and catalyst poisons. Once the catalyst and inert loading has been completed and the reactor has been closed up, the reactor should be maintained under nitrogen pressure. Ensure that the nitrogen used is of good quality. Checking the nitrogen quality is especially important during periods of maintenance, when nitrogen or nitrogen lines have a higher risk of contamination. When possible, the nitrogen pressure in the reactor should be greater than the coolant pressure. Block valves on the reactor feed and product lines should normally remain closed until ready for start-up. A slight nitrogen purge across the catalyst bed in the normal direction of cycle gas flow is desirable.
- 2) Contact of the catalyst with liquid of any kind must be avoided. Liquids will cause rust formation in the reactor and irreversible catalyst damage. Sources of liquids include carryover from the absorbers, carryover from the CO₂ removal system, or exposure of the catalyst to a humid atmosphere. Water can also be introduced into the reactor when gas flow is initiated (e.g., at the start of the compressor) by entrained water that was initially left in dead or low pockets of the system piping. Therefore, a check of the low-point drains is required throughout the start-up procedure. Keep an eye on operations being conducted in the recovery and finishing sections of the plant. Avoid situations which could lead to contamination of the reactor feed lines or recycle loop with water or other material via leakage through "closed" valves.
- 3) Maintain the reactor coolant temperature between 50-60°C (120-140°F). Temperatures above 60°C (140°F) could begin evaporation of the ammonia compounds on the catalyst surface. These compounds could collect on cooler surfaces such as the outlet head and piping if no nitrogen purge is present.



2. GENERAL PRE-START-UP CHECKS

- 1) After catalyst and inert loading has been completed, maintain the reactors under nitrogen pressure greater than the pressure at the coolant side. The feed and product block valves must be closed and blinded if possible.
- 2) After the reactors have been closed up following the catalyst loading, and during the pre-start-up period, it is important to check periodically all low point drains on feed and product sides of the reactors. Check for accumulation of water or other liquid that might enter the reactors by some unforeseen means and damage the catalyst.
- 3) Check oxygen, ethylene, nitrogen, and methane feeds for impurity levels prior to bringing these streams into the unit and check them against feed specification requirements. Check to ensure the feed lines are clean, especially those lines which have been subject to maintenance activities.
- 4) If maintenance has been performed on the oxygen feed line, analyze for trichloroethane and trichloroethylene. These compounds, which are used as degreasing agents in oxygen service, must be below 10 ppb to avoid poisoning the catalyst.
- 5) Nitrogen or methane may be used for the initial purge of the catalyst, with nitrogen being preferred. Even though methane treatment facilities are installed for sulphur and heavy hydrocarbon removal, they are usually designed for the normal or design methane flow and may be "over-ranged" by high flow rates during periods of purging or pressurizing the system with methane. Impurities in the methane, such as hydrogen, may also concentrate to unacceptable levels in the cycle gas if the methane is added when there is no reaction taking place. If using methane for the purge step, the hydrogen concentration in the methane supply should be below 0.5%.
- 6) When nitrogen is used as the inert gas in place of methane, it should be remembered that nitrogen tends to lower the flammable limit. The design oxygen concentration in feed or product may not safely be attainable until the nitrogen has been displaced by methane. Since nitrogen is heavier than methane, it also reduces the compressor capacity, thereby reducing the GHSV through the reactors.
- 7) Calibrate oxygen analyzers and other analytical equipment (IR analyzers, gas chromatographs, mass spectrometers, etc.). Ensure that oxygen analyzers are properly lined up to the reactor feeds and products and are analyzing representative samples of these streams.
- 8) Many EO units are equipped with adjustable alarms and shutdowns for oxygen concentration and catalyst temperature. For these units, the initial set points for the alarm and shutdown levels should be 4.5 & 5% for inlet O₂, 2.5 & 3% for outlet O₂, and 280 & 285°C (535 & 545°F) for catalyst temperatures, respectively.



- 9) Keep an eye on the operations that are being conducted in the downstream sections of the plant. Avoid situations which could lead to contamination of the reactor feed lines or recycle loop with water or other material via leakage through "closed" valves.
- 10) Block valves on the reactor feed and product lines should normally remain closed until the nitrogen purge can begin. When preparing the reactors for nitrogen circulation, equalise the reactor pressure by opening the block valves sequentially to flow nitrogen in the design direction. If the reactor pressure is below the loop pressure, open the feed block valve first, followed by the product block valve to equalise the pressure. If the reactor pressure is above the loop pressure, open the product block valve first, followed by the feed block valve.



3. S-863 CATALYST

3.1 Nitrogen purge for fresh S-863 catalyst

The nitrogen purge (also called ammonia removal) step for S-863 catalyst is included to remove residual ammonia compounds from the catalyst prior to startup. The ammonia compounds on the catalyst are removed by heating the catalyst up to a temperature of 215-220°C while purging with nitrogen. The ammonia compounds leaving the catalyst need to be removed from the process by scrubbing them out in the EO absorber quench section.

- 1) Begin heating the reactor coolant to 215-220°C at a rate that is compatible with the unit equipment (usually the reactor has a maximum heating rate specified by the manufacturer).
- 2) Pressurize the reaction system with enough pressure to allow water circulation in the EO absorber quench section. Establish normal water flow through the quench section to prepare for ammonia compounds removal.
- 3) Prepare the reactors for cycle gas circulation. Gas should not be circulated through the reactors until the temperature reaches 65°C to prevent the possibility of moisture condensation inside the reactors. Equalize reactor pressure by opening the block valves sequentially to flow nitrogen in the direction of normal flow direction (if the reactor pressure is below the loop pressure, open the feed block valve first, followed by the product block valve. If the reactor pressure is above the loop pressure, open the product block valve first followed by the feed block valve.)
- 4) During the reactor heating, once the reactor temperature has reached about 65°C, start the nitrogen purge by first checking low point drains and ensuring no liquid is present, and then establishing cycle gas flow through the reactor. When the gas flow through the reactors is adjustable, the desired flow is 20-30% of the design flow rate, or the maximum rate at which the reactor heating system is able maintain the desired reactor coolant temperatures. Continue to heat up the catalyst to the desired temperature. As no steam is generated yet, the level in the HP steam drum will rise and the normal continuous blowdown to the MP steam drum is not sufficient to get rid of the additional condensate. During heating of the EO reactors the operators must periodically blowdown the condensate from the HP steam drum to the MP steam drum through the discontinuous blowdown operated by a handvalve.
- 5) During the heating of the reactor, ammonia compounds will be removed from the catalyst and absorbed in the EO quench water. Maintain a continuous purge and fresh makeup of the quench water. The ammonia concentration in the water may be monitored by titration, ion specific electrode or pH, to track ammonia removal progress.



- 6) After reaching the target coolant temperature of 215-220°C, hold for 0-4 hours (or as advised differently by the Shell/Catalyst vendor start-up team) and then block in the feed gas to the reactors.
- 7) Sample the exit gas using a detection tube specific for ammonia 0-100 ppm. If the ammonia concentration is less than 10 ppm on two repeat samples the ammonia removal step is complete. If the concentration exceeds 10 ppm restart the hot nitrogen purge and repeat step 7 every two hours until the ammonia concentration is below 10 ppm.
- 8) Refresh the quench system with as much fresh water as possible to remove residual ammonia compounds from the process.
- 9) If start-up is not to proceed within six hours after the ammonia compounds removal step, it is recommended that the reactors be blocked in and maintained under nitrogen pressure until ready for start-up. If the reactors are blocked in, a small nitrogen purge should be introduced downward through the reactors until ready for start-up. Let reactors cool to 150°C or as advised by the Shell/Catalyst vendor start-up team. If the start-up is expected to be delayed for more than 24 hours, then cool to 100°C under 5-7 barg nitrogen pressure.

3.2 Start-up procedures for fresh S-863 catalyst

Once the nitrogen purge is completed the catalyst start-up may proceed. The first phase of the procedure is to add ethylene to the loop and conduct a chloride pre-soak. The purpose of the chloride pre-soak is to de-activate the catalyst since fresh S-863 is very active. Pre-soak should only be started when the plant is ready to proceed with oxygen addition immediately afterwards. The final phase of the start-up procedure is to achieve lined out operation at target feed rates and process conditions.

- 1) Check oxygen, ethylene, and methane feeds for impurity levels prior to bringing these streams into the unit.
- 2) Line up oxygen to the unit according to the normal safety procedures for cleaning and purging. If maintenance has been performed on the oxygen feed line, analyse for trichloroethane and trichloroethylene. These compounds, which are used as degreasing agents in oxygen service, must be below 10 ppb to avoid poisoning the catalyst.
- 3) Make sure that oxygen analysers and other analytical equipment (IR analysers, gas chromatographs, mass spectrometers, etc.) are calibrated. Set the initial alarm and trip settings for the oxygen and high temperature alarm and shutdown levels at 4.5 & 5% for inlet oxygen, 2.5 & 3% for outlet oxygen, and 280 & 285°C for catalyst temperatures or as advised by the Shell/Catalyst vendor start-up team.



- 4) Bring up the CO₂ recovery section, the EO removal and finishing sections, and have the back end of the plant on "hot standby" prior to unblocking the reactors. Target for SOC design conditions, which means that CO₂ in the reactor feed should be about 3-4 % after start up.
- 5) Maintain the reactors at or above 210-215°C throughout the chloride pre-soak and initial oxygen addition phases.
- 6) Check low point drains in the recycle loop for liquid prior to unblocking the reactors.
- 7) Establish (or re-establish) nitrogen gas through the reactors. Set the gas flow through the reactors at 20-25% of the normal flow or the maximum rate at which the temperature of at least 210-215°C can be maintained.
- 8) After verifying the quality of all feed streams, begin ethylene feed so that ethylene is passing through the catalyst bed. The start-up concentration of ethylene is set at 10-15% initially. Once the target ethylene concentration of 10-15% is reached in the loop, stop ethylene addition. Nitrogen is not used as ballast gas in order to keep the hydrocarbon inventory of the gas loop at minimum during initial start up of the catalyst.
- 9) Ensure that the tracing of the moderator lines is working properly in order to ensure proper evaporation of the moderator upon mixing with the loopgas. Line up the chloride feed system and the chloride analysers. Start chloride addition at the maximum controllable rate to each reactor, or as specified by the Shell/Catalyst vendor start-up team. Analyse the feed streams for chlorides during the chloride pre-soak with the chloride analyser, and adjust the chloride feed rate as advised by the Shell/Catalyst vendor start-up team. Continue the chloride pre-soak until the total amount of chloride fed to the reactors is ca 25 cc moderator/m³ catalyst (or as advised by the Shell/Catalyst vendor start-up team). When the chloride pre-soak is completed, stop or decrease chloride flow to the reactors until the start-up is ready to proceed. In case oxygen addition were to be postponed for more than 2 hours following the completion of the pre-soak, the moderator injection should be stopped.
- 10) During the chloride pre-soak, prepare the oxygen feed system for start-up. The time between the chloride pre-soak and the oxygen start should be minimised.
- 11) Add oxygen feed at the minimum controllable rate and hold for initial reaction to occur. Re-establish chloride flow at about 70% of the target flow rate or as advised by the Shell/Catalyst vendor start-up team. Watch the oxygen concentration in and out of the reactors. Also watch the outlet gas temperatures, the coolant temperatures, the peak temperature differences (PTD), and the reactor temperature profiles. Do not let the oxygen concentration in the inlet exceed 3%. When the oxygen flow is above the minimum flow requirement for the trip system the purge nitrogen must be cut off.



- 12) If essentially no reaction is occurring and the oxygen in the feed reaches 3%, decrease the feed gas flow and increase chloride addition as advised by the Shell/Catalyst vendor start-up team. If still no reaction occurs, stop oxygen addition and proceed as advised.
- 13) When the reaction starts as evidenced by a drop in the oxygen level in the product and rising catalyst temperatures (perhaps only a few degrees at first), increase the gas feed rate to the reactors in 10% increments (or as advised by the Shell/Catalyst vendor start-up team) as necessary to control the reaction. Keep the PTD below 25°C. Do not increase the cycle gas flow if the reaction rate is falling off. Raise the oxygen feed rate slowly in order to avoid generating high temperatures in the catalyst bed.
- 14) Adjust ethylene feed as necessary to maintain a target ethylene concentration of 10-15%.
- 15) Keep the delta oxygen concentration at or below 2% until significant chloride recycle is established. Place the reactors on coolant temperature control with a set point in the vicinity of the predicted initial temperature.
- 16) Adjust chloride addition as advised by the Shell/Catalyst vendor startup team. Initially the chloride addition rate can be 2-3 times the normal addition rate due to the high rate of chloride absorption onto the catalyst.
- 17) Begin methane addition at the maximum rate toward the target level (often 40-45%). Do not exceed the capacity of the methane purification systems.
- 18) Gradually increase the reactor cycle gas flow to design and slowly bring the oxygen concentration in the feed gas to about 2% delta oxygen (generally 50-70% of full oxygen feed). Initially, the oxygen concentration will remain low and oxygen conversion will be high (85-100%). At this point, the reactor(s) should be allowed to stabilize for a period of 12-24 hours. Stability is usually indicated by increasing oxygen concentration in the reactor outlet and/or significant levels of recycle chlorides (vinyl chloride level indicated at the reactor inlet.)

3.3 Optimisation procedure for S-863 catalyst

- 1) After the reactors have stabilized and oxygen has begun to appear in the reactor outlet, begin raising the oxygen level in the feed at a rate of about 1.0-2.0% per 8-hour shift, or as advised by the Shell/Catalyst vendor start-up team. As the oxygen concentration is increased, adjust the alarm and trip settings for the inlet and outlet concentrations toward the target flammable limit approach. Typically, the alarm and trip settings are set at 0.7% and 0.5% away from the calculated flammable limit during normal operation.
- 2) Increase the ethylene concentration toward the design targets as advised by the Shell/Catalyst vendor start-up team. Monitor chloride levels during increases in ethylene concentration and changes in the amount of recycle



chlorides, and adjust chloride flow as necessary to maintain the target I-factor of 0.05 to 0.07.

- 3) The typical time to achieve full oxygen addition is about 60-72 hours. If methane ballast is used, do not go to the design oxygen concentration until the nitrogen and methane concentrations in the feed are near design, due to flammability constraints.

3.4 Guidelines for normal re-start of S-863

- 1) Establish gas flow in bypass mode, preferably with nitrogen.
- 2) After a thorough check of low point drains, bring in about 25% of full gas flow through reactors, or as high as can be established, while heating the reactor.
Caution: If the gas loop is not purged out during shutdown, it has been found that condensed water may accumulate in the feed valve and other cold parts of the reactor feed lines.
Caution: Make sure the gas flow is always in the correct direction.
- 3) Maintain or bring the catalyst temperature at near pre-shut temperatures or as high as the reactors can be heated.
- 4) Start oxygen at a low rate and watch for the reaction to occur. (The noticeable signs are increasing temperatures & oxygen conversion and decreasing oxygen concentration in gas loop).
- 5) Increase oxygen feed and gas feed to reactors in a stepwise manner, as the catalyst temperature profile allows. It should take about one hour to reach full gas.
- 6) Allow the catalyst bed temperatures to increase until they have reached approximately the pre-shutdown levels. The coolant system pressure should be set to control the catalyst bed temperatures at the target level.
- 7) The moderator feed may be started about 1-3 hours after the reaction has started. Both the time of moderator start and its flow rate would depend on the chloride concentration measurements. When the unit is brought to the pre-shut down conditions, the optimum moderator flow should be approximately the same.

3.5 Guidelines for normal shut-down of S-863

- 1) Cut off moderator supply about 30 minutes to 4 hours before oxygen trip.
- 2) Trip out oxygen.



- 3) Circulate the gases through reactors until oxygen concentration drops below 0.1%.
- 4) Block the reactors to retain heat and temperature at these levels, if the shutdown is planned for 24 hours or less. For longer shutdowns, circulate the gases until the exit gas temperatures have dropped to 150-170°C.
- 5) Maintain catalyst temperatures at 215-220°C for short (<24 hours) shutdown. For a longer shutdown, the temperatures need to be maintained at 150-170°C with a small nitrogen bleed through the reactors. For even longer shutdowns, keep the reactors well above the dewpoint, with a small nitrogen purge.
- 6) It is desirable to purge out the hydrocarbons from the gas loop in order to reduce possibility of water condensation in the loop at no flow conditions. In any case, periodic low point drain should be planned during the shutdown.



4. S-882 CATALYST

4.1 Introduction

In 2002, significant changes were made to the S-882 start-up procedure. The revised start-up procedure has been proven to result in the same initial performance as obtained with the old procedure, but in significantly less time and with fewer changes of plant conditions required. The major changes to the procedure were:

- 1) **Nitrogen Purge:** The recommended nitrogen purge time of 48 hrs has been reduced to 6-18 hrs. The shortened purge time is expected to be adequate to drive off the residual amines or other traces of volatile compounds on the catalyst surface. Repeated microreactor and pilot plant tests show that expected catalyst performance can be achieved without a nitrogen purge. But, a shortened purge is still recommended to avoid the possibility of foaming in the quench or EO absorber.
- 2) **Chloride Feed System Start-Up:** The chloride pre-soak has been replaced by a chloride feed system start-up step. The intent of this step is to verify that the chloride feed system is functioning properly and that chlorides will be introduced on demand at start-up. Pilot plant testing has demonstrated that S-882 will start up smoothly without a pre-soak as long as chloride feed is established at the time of oxygen addition. It was found that the moderator pre-soak employed previously caused excessive overmoderation, which necessitated a chloride strip to achieve optimal performance.
- 3) **Thermal Treatment:** The chloride strip has been replaced by a short (5 hrs) high temperature treatment at 268-272°C (514-522°F) catalyst temperature in the presence of oxygen throughout the entire catalyst bed. During this treatment step, chloride feed is maintained at normal operating levels at an I-factor of 0.08. If the catalyst has not been excessively overmoderated by an moderator presoak, or during the initial period of operation since O₂ feed was started, this high temperature treatment has proven to be the most rapid method to reach the maximum selectivity. If excessive overmoderation does occur, a conventional chloride strip may be required before the expected selectivity can be reached.
- 4) **Catalyst Optimization:** At the end of the heat treatment, catalyst operating conditions and performance are optimized by similar procedures as previously.

The previous method of start-up (with a chloride strip) continues to be listed as an optional method of start-up (see section 4.3), but the new method is preferred due to reduced time requirements.



4.2 Nitrogen purge for fresh S-882 catalyst

- 1) Prepare the reactors for cycle gas circulation. Equalize reactor pressure by opening the block valves sequentially to flow nitrogen in the direction of normal flow. (If the reactor pressure is below the loop pressure, open the feed block valve first, followed by the product block valve. If the reactor pressure is above the loop pressure, open the product block valve first, followed by the feed block valve.)
- 2) Begin heating the reactor coolant to 220-230°C (430-450°F) at a rate that is compatible with the unit equipment. (Usually the reactor has a maximum heating rate specified by the manufacturer.)

NOTE: For boiling coolant systems, set the coolant system pressure equivalent to the coolant vapour pressure at 255°C (491°F). For ISOPAR L coolant, the set point will be about 2.0 barg (29 psig). For water-cooled reactors, the steam drum pressure is about 43.2 barg (626 psig). The coolant system pressure should be kept high to avoid boiling the coolant during the purge.

- 3) Pressurize the reaction system with enough pressure to allow water circulation in the EO absorber. Establish normal water flow through the absorber to prepare for ammonia compound removal. For absorbers equipped with a quench section, water flow need only be established in the quench section.
- 4) During the reactor heating, once the reactor temperature has reached about 65°C (150°F), start the nitrogen purge by first checking low point drains and ensuring no liquid is present, and then establishing cycle gas flow through the reactor. When the gas flow through the reactors is adjustable, the desired flow is 20-30% of the design flow rate, or the maximum rate at which the reactor heating system is able to maintain the desired reactor coolant temperatures. **Gas should not be circulated through the reactors until the temperature reaches 65°C (150°F) to prevent the possibility of moisture condensation inside the reactors.** Continue to heat up the catalyst to the desired temperature.
- 5) During the initial phase of the nitrogen purge, ammonia compounds will be removed from the catalyst and absorbed in the EO absorber water. Maintain a continuous purge and fresh makeup of the lean absorbent (also called scrubber water or lean cycle water).
- 6) After reaching the target coolant temperature of 220-230°C (430-450°F), continue the nitrogen purge for 6-24 hours (as advised by the Catalyst vendor/Shell Start-up Team) to ensure adequate removal of residual amine compounds and prevent foaming in the EO absorber.
- 7) Progress of the ammonia compound removal can be monitored by checking for ammonia in the water purged from the EO absorber by titration, by use of



an ion specific electrode, and/or by pH. Once the ammonia concentration in the quench or absorber solution is below 70 ppm, the purge step can be considered complete.

- 8) Once the nitrogen purge is complete, check the quality of the quench and lean cycle water to assure proper pH and foaming characteristics. If necessary, continue to purge water and add fresh until quality is acceptable. Maintain the cycle gas flow at 20-30% of the normal design flow and reactor temperatures at 220-230°C (430-450°F). Once water quality is determined to be acceptable, the plant can proceed directly from this step into the Chloride Feed System start-up.

If start-up is not to proceed immediately after the nitrogen purge, the reactor(s) can be maintained at the start-up temperatures of 220-230°C (430-450°F) or the temperatures can be reduced if energy conservation by the plant is desired. If the temperature is reduced, a minimum temperature of 100°C (210°F) is recommended to assure the reactor remains above the dew point. During the time between the nitrogen purge and actual start-up, a nitrogen blanket and purge should be maintained on the catalyst.

At this point, two options are given for start-up:

- The traditional chloride pre-soak and strip procedure is covered in section 4.3,
- The preferred heat treatment procedure is covered in section 4.4.

4.3 Traditional chloride pre-soak and strip for S-882 catalyst

4.3.1 Chloride pre-soak

- 1) Check the low point drains in the recycle loop for liquid prior to unblocking the reactors.
- 2) Establish (or re-establish) cycle gas flow through the reactors. Where the gas flow through the reactors is adjustable, set the flow at 20-30% of the design flow rate, or at the maximum rate at which the reactor heating system is able to maintain the desired reactor coolant temperature of at least 220°C (430°F).
- 3) Heat the reactor coolant back up to start-up temperatures of $230 \pm 10^\circ\text{C}$ ($450 \pm 20^\circ\text{F}$). Maintain the reactors at or above 220°C (430°F) throughout the chloride pre-soak and initial oxygen addition phases. For boiling coolant systems, set the pressure control high enough to prevent coolant boiling.
- 4) Prepare the chloride addition system. Verify chloride analyzer is calibrated and in service. Check the chloride addition point. If possible, inject chlorides downstream of the reactor bypass. For systems where the chloride addition



point is upstream of the reactor bypass valve, it may be necessary to adjust the target chloride addition level to compensate for chloride loss in the absorber during the presoak.

- 5) Re-establish levels and circulation in the EO absorber system. Bring up the CO₂ recovery section, the EO removal and finishing sections, and have the back end of the plant on "hot standby" prior to unblocking the reactors. The chloride presoak will take approximately 4-6 hours, after which oxygen addition can begin. The time delay between the chloride presoak and the addition of oxygen should be minimized.
- 6) After verifying the quality of all feed streams, begin ethylene feed to the cycle gas loop. Continue ethylene addition to the loop until a concentration of 10-15% is reached. Once the target ethylene concentration is established, stop ethylene addition.
- 7) Ensure that the reactor feed gas temperature is at least 120°C (250°F) and that steam tracing is on and hot along all chloride feed lines to reduce the potential of putting liquid chloride onto the catalyst.
- 8) Start chloride addition at a rate specified by the Catalyst vendor Start-up Team. Continue the chloride pre-soak until the total amount of chloride fed to the reactors is equivalent to 64 cc/m³ (1.8 cc/ft³) for ethyl chloride, or 32 cc/m³ (0.9 cc/ft³) for ethylene dichloride. Target addition time is 4-6 hours. Analyze the reactor feed streams for chlorides during the pre-soak, and adjust the chloride feed rate as advised by the Catalyst vendor Start-up Team.
- 9) When the chloride pre-soak is completed, reduce (or stop) the chloride addition until the start-up is ready to proceed, as advised by the Catalyst vendor start-up team.

4.3.2 Catalyst start-up / oxygen addition

- 1) While completing the chloride pre-soak, prepare the oxygen feed system for start-up. Line up oxygen to the unit according to the normal safety procedures for cleaning and purging.
- 2) Prepare the carbonate system for maximum CO₂ removal to keep CO₂ in the recycle loop low and at preferably below 4% following start-up.
- 3) Prepare the reaction system for start-up. Verify ethylene concentration is 10-15%. Verify the oxygen concentration alarms and shutdowns are at desired levels. Verify reactor coolant temperatures are 230 ± 10°C (450 ± 20°F).
- 4) With the cycle gas flow through the reactors, re-establish chloride flow at about 70% of the target flow rate, or as advised by the Catalyst vendor start-up team. It is advisable to have the feed chloride concentration at 1-3 ppm as the reaction starts.



- 5) Establish oxygen feed at the **minimum controllable rate and hold for initial reaction to occur**. Watch the O₂ concentration in and out of the reactors. Also watch the outlet gas temperatures, the coolant temperatures, the peak temperature differences (PTD), and the reactor temperature profiles. Do not let the O₂ concentration in the inlet exceed 3%.
- 6) If essentially no reaction is occurring and the oxygen concentration in the reactor feed reaches 3%, stop oxygen addition and proceed as advised by the Catalyst vendor start-up team.
- 7) When the reaction starts as evidenced by a drop in the oxygen concentration in the reactor outlet and rising catalyst temperatures (perhaps only a few degrees at first), increase the cycle gas flow to the reactors as advised by the Catalyst vendor Start-up Team to control the reaction. Target to keep the PTD (Peak Temperature Difference) below 25°C (45°F). Do not increase the cycle gas flow if the reaction rate is falling off. Raise the oxygen feed rate slowly in order to avoid generating high temperatures in the catalyst bed.
- 8) Adjust ethylene feed as necessary to maintain a target ethylene concentration of 10-15%.
- 9) Maintain the inlet oxygen concentration at 2-3% (3% maximum). Allow the heat of reaction to heat up the reactor coolant during this period toward a target temperature of 240-250°C (465-485°F). Once the target temperature is reached, and significant reaction is taking place (Δ -O₂ approximately 2% or greater), place the reactor(s) on coolant temperature control.
- 10) Continue chloride addition as advised by the Catalyst vendor start-up team. Initial I-factor target will be 0.15 or greater. Allow the ethylene concentration to increase to 20%.
- 11) Begin methane addition at the maximum rate toward the target level (often 40-45% in recycle gas). Do not exceed the capacity of the methane purification systems in order to maintain its required purity (sulphur, HHC, etc.).
- 12) Once the reactor coolant has achieved the target temperature, and reactor coolant control is stable, begin raising oxygen feed as advised by the Catalyst vendor Start-up Team. Typically, 100% of the target oxygen addition rate can be achieved within the first 24-36 hours of operation. Initially, the oxygen concentration will remain low (2-4%), and oxygen conversion will be high (85-100%).
- 13) Continue to monitor chloride addition and I-factor. Once target oxygen feed rates, I-factor, and catalyst temperatures are reached, and the Catalyst vendor team has verified the catalyst is over-moderated, the start-up may proceed to the chloride stripping stage of the start-up.



4.3.3 Chloride stripping

- 1) Close and isolate the chloride feed to the reaction system. With no chloride addition, maintain oxygen feed rates at the target level and the reactor coolant temperatures at 245-250°C (475-485°F). The strip will last for approximately 24 to 72 hours.
- 2) For units with adjustable set-points, adjust the ESD and alarm set-points for the inlet and outlet concentrations toward at the normal approach from the flammable limit.
- 3) Shortly after isolating the chloride feed, a number of operating conditions can be considered in order to quicken the process of chloride stripping: (a) increase the ethylene concentration in the loop up to target concentrations (typically 25–30%); (b) increase operating temperature (255°C max); (c) shut down residual compressor; or (d) shut down ethylene recovery system.
- 4) As the chloride levels in the system slowly drop, the catalyst will deactivate at constant temperature, the oxygen conversion across the reactors will decrease, and oxygen concentrations will increase. Towards the end of the strip, if necessary, the reactor coolant temperatures can be increased as needed to control the oxygen concentration below the flammable limit, up to a maximum coolant temperature of 255°C (490°F). If oxygen concentrations continue to increase and the maximum coolant temperature is reached, reduce the oxygen feed rate as necessary to control oxygen concentration at desired levels.
- 5) The chloride strip is complete when the I-factor drops below 0.05, the oxygen conversion show a significant drop (>30%), the reactor outlet EO concentration drops by 20-30%, the reactor selectivity indicates a significant decline (of 5-7%), and the coolant temperature is at the desired level (250-255°C). At this time, chloride flow should be re-established at a rate recommended by the Catalyst vendor start-up team. The initial I-factor target (0.04-0.06) will be well below the expected optimum I-factor.
- 6) It is important that a proper chloride strip be performed. When the chloride strip is not sufficient, the catalyst may not reach the expected selectivity during the chloride optimization step, forcing the chloride-stripping step to be repeated.
- 7) Proceed to section 4.5, Catalyst Optimization.



4.4 Preferred heat treatment procedure for S-882 catalyst

4.4.1 Chloride feed system start-up

The purpose of the chloride feed system start-up is to verify that the chloride feed system and analyzers are working properly and there will be no delay in introduction of chlorides during the oxygen addition step.

- 1) Check once again the low point drains in the recycle loop for liquid prior to unblocking the reactors.
- 2) Establish (or re-establish) cycle gas flow through the reactors. Where the gas flow through the reactors is adjustable, set the flow at 20-30% of the design flow rate, or at the maximum rate at which the reactor heating system is able maintain the desired reactor coolant temperature of at least 220°C (430°F).
- 3) Maintain the reactors at or above 220°C (430°F) throughout the chloride feed system start-up and initial oxygen addition phases. For boiling coolant systems, set the pressure control high enough to prevent coolant boiling, as advised by Catalyst vendor start-up team.
- 4) Prepare the chloride addition system. Verify chloride analyzer is calibrated and in service. Check the chloride addition point. If possible, inject chlorides downstream of the reactor bypass.
- 5) Re-establish levels and circulation in the EO absorber system. Bring up the CO₂ recovery section, the EO removal and finishing sections, and have the back end of the plant on "hot standby". The chloride feed system start-up should take only 1–2 hours, after which oxygen addition can begin.
- 6) After verifying the quality of all feed streams, begin ethylene feed to the cycle gas loop. Continue ethylene addition to the loop until a concentration of 10–15% is reached. Once the target ethylene concentration is established, stop ethylene addition.
- 7) Ensure that the reactor feed gas temperature is at least 120°C (250°F) and that steam tracing is on and hot along all chloride feed lines to reduce the potential of putting liquid chloride onto the catalyst. For liquid chloride feed systems, verify that the feed lines are packed (liquid full) up to the injection point(s).
- 8) Start chloride addition at a rate specified by the Catalyst vendor Start-up Team. The initial target I-factor is 0.08–0.10. The target ethyl chloride feed concentration will depend on the ethylene and ethane concentrations, but is expected to be in the range of 1–2 ppm. The chloride addition rates should be adjusted as specified by the Catalyst vendor start-up team. Because there is no reaction occurring and the fresh catalyst has no chloride on the surface **there will be no recycle chlorides during the chloride feed system start-up. Typically, the chloride feed rate necessary to attain**



the desired chloride feed concentration can be estimated based on the recycle gas flow to the reactors. It is usually desirable to start with 2–3 times the normal chloride feed rate at least until feed lines are packed and chlorides appear in the reactor feed gas analyses.

- 9) Analyze the reactor feed streams for chlorides, and adjust the chloride feed rate as advised by the Catalyst vendor Start-up Team.
- 10) When the two or more consecutive chloride analyses verify that the feed system is working properly, the chloride feed start-up is complete. Continuation of the chloride feed for 1-2 hours with I factor at 0.08-0.10 will facilitate smooth start-up without causing catalyst over-moderation.
- 11) Stop the chloride addition if the plant is delayed in starting of oxygen addition or when the total moderator injected exceeds 50 cc/m³.

4.4.2 Catalyst start-up / oxygen addition

- 1) While conducting the nitrogen purge and the chloride feed system start-up, prepare the oxygen feed system for start-up. Line up oxygen to the unit according to the normal safety procedures for cleaning and purging.
- 2) Prepare the carbonate system for maximum CO₂ removal.
- 3) Prepare the reaction system for start-up. Verify ethylene concentration is 10-15%. Verify the oxygen concentration alarms and shutdowns are at desired levels. Verify reactor coolant temperatures are 230 ± 10°C (450 ± 20°F).
- 4) With the cycle gas flow through the reactors, re-establish chloride flow at about the target flow rate, or as advised by the Catalyst vendor start-up team. It is advisable to have the feed chloride concentration at 1-3 ppm as the reaction starts.
- 5) Establish oxygen feed at the **minimum controllable rate and hold for initial reaction to occur**. Watch the O₂ concentration in and out of the reactors. Also watch the outlet gas temperatures, the coolant temperatures, the peak temperature differences (PTD), and the reactor temperature profiles. Do not let the O₂ concentration in the inlet exceed 3%.
- 6) If essentially no reaction is occurring and the oxygen concentration in the reactor feed reaches 3%, stop oxygen addition and proceed as advised by the Catalyst vendor start-up team.
- 7) When the reaction starts as evidenced by a drop in the oxygen concentration in the reactor outlet and rising catalyst temperatures (perhaps only a few degrees at first), increase the cycle gas flow to the reactors as advised by the Catalyst vendor Start-up Team to control the reaction. Target to keep the PTD below 25°C (45°F). Do not increase the cycle gas



flow if the reaction rate is falling off. Raise the oxygen feed rate slowly in order to avoid generating high temperatures in the catalyst bed.

- 8) Adjust ethylene feed as necessary to maintain a target ethylene concentration of 10-15%.
- 9) Begin methane addition at the maximum rate toward the target level (often 40-45%). Do not exceed the capacity of the methane purification systems.
- 10) Once the reaction has stabilized, as evidenced by PTD's reliably less than 25°C, begin to move the reactors toward full gas flow rate and full oxygen feed rates. During this process the inlet oxygen may be allowed to increase above 3%. Watch the oxygen concentrations to ensure that the reactors are converting all of the oxygen being fed. A steadily increasing oxygen concentration after an oxygen feed increase indicates that the reactors are not converting all the oxygen. If this occurs, the inlet oxygen concentration should be controlled by 1) increasing gas flow to the reactors, 2) increasing separator/steam drum pressure and 3) controlling or reducing the rate of oxygen addition.
- 11) Continue chloride addition as advised by the Catalyst vendor startup team. The initial I-factor target will be 0.08 – 0.10. During the start-up, the catalyst will adsorb chlorides at progressively deeper locations in the bed. When the entire bed has been exposed, chloride "breakthrough" occurs. This should occur after a few hours. After breakthrough, chlorides will begin showing up in the recycle gas. As this occurs, it will be necessary to reduce chloride feed to maintain the target I-factor. **It is important to avoid overmoderation of the catalyst at this stage. If the I-factor becomes too high, a chloride strip may be required rather than the shorter and simpler thermal treatment.**
- 12) Initially, the oxygen concentration will remain low (3-4%), and oxygen conversion will be high (60% or greater).
- 13) Full oxygen feed rate can be typically reached in 12-36 hours of the start-up.

4.4.3 Thermal treatment

- 1) Continue to increase oxygen feed rate, gas flow to reactors, and coolant separator pressures (kero-cooled reactors) or steam drum pressures (water-cooled reactors) to achieve the following conditions within ~24 hours:

Gas Flow: max

Catalyst Temperature: $270 \pm 2^{\circ}\text{C}$ ($518 \pm 5^{\circ}\text{F}$)

I-factor: 0.08–0.10

Oxygen Feed Rate: full desired rate for start-up



Ethylene Concentration: 10–15%

Oxygen in Reactor Outlet(s): at least 0.5%

- 2) In some cases (especially low work rate plants) it may be necessary to reduce ethylene concentration and/or increase CO₂ concentration in order to obtain at least 1% outlet O₂. However, it is important to achieve this minimum outlet oxygen concentration so that the catalyst bed is conditioned uniformly during the thermal treatment.
- 3) Once the average catalyst temperature reaches 270°C (518°F), the thermal treatment should continue at this temperature for 5–8 hours or as advised by Catalyst vendor start-up team. This step is necessary for optimal performance of the catalyst, but it is important to minimize the additional time the catalyst is operated at high temperatures. Pilot plant tests have shown that excessive operating time at high temperatures can result in loss of catalyst activity. However, lower temperatures will require longer time for achieving the target catalyst chemistry.
- 4) For units with adjustable set points, adjust the ESD and alarm set points for the inlet and outlet concentrations to the normal approach from the flammable limit. During the thermal treatment, the selectivity is expected to rise gradually and the O₂ conversion may decline.
- 5) After completing the thermal treatment, and after consulting with the Catalyst vendor start-up team, the plant may proceed to section : Catalyst Optimization.

4.5 Catalyst Optimization for S-882 catalyst

- 1) Once the thermal treatment (section 4.4.3) or the alternative chloride strip procedure (section 4.3.3) is complete, the reactor feed gas (ethylene, O₂, CO₂, CH₄) and operating conditions should be brought to target conditions and the catalyst optimization step started.
- 2) The reactor coolant temperature(s) should be lowered as necessary to achieve the desired oxygen feed concentration (typical flammable approach = 0.5-1.0%). For multi-reactor systems, the reactor coolant temperatures should be adjusted so that the oxygen conversion across the reactors is balanced (all reactors should have the same outlet oxygen concentration.)
- 3) The ethylene feed concentration should be brought to the normal operating target (typically 25-35%).
- 4) The I-factor should be allowed to decrease to 0.06 or as advised by the Catalyst vendor start-up team. The I-factor target at the start of the optimization should be at a value lower than the expected optimum. Note, this does not mean that chloride feed rates should be reduced. The I-factor will decrease as a direct result of the increase in ethylene concentration at constant chloride addition rates.



- 5) Initially, during the optimization process, expect the selectivity to increase rapidly. This will result in significant increases in EO production that the downstream equipment must be prepared to process.
- 6) The oxygen feed rates should be adjusted so that the production target will be achieved at the expected optimum selectivity.
- 7) After plant operation and catalyst performance have stabilized at the initial I-factor target, increase chloride flow to the reactors in a stepwise manner every 8-12 hours. At each moderator flow set point (or I-factor), adjust reactor coolant temperatures as necessary to maintain oxygen concentration at the target level and to keep the reactor outlet oxygen concentration balanced.
- 8) Note the average selectivity as the reaction stabilizes after every chloride feed increase.
- 9) If the reactor selectivity has increased, repeat steps 6 and 7. Continue to increase the I-factor (repeating step 6 and 7) until there is no further increase of the selectivity. At this point, the optimization is complete. If the selectivity has decreased, go to step 10.
- 10) If the reactor selectivity has decreased after Steps 6 and 7, reduce the chloride feed back to the previous value. Record the selectivity after the catalyst has lined out (note the catalyst may take longer to recover from over-moderation. When decreasing I-factor, it may take up to 48 hours before the selectivity reaches a new steady-state value.) At this point, the optimization is complete.
- 11) Once the optimum is determined, the catalyst performance test run can be initiated.

4.6 I-Factor for S-882 catalyst

S-882 catalyst is unique in its response to chloride levels, or I-Factor. Conventional or high activity catalyst requires higher operating temperatures with increases in I-Factor. In addition, the desired I-Factor remains nearly constant throughout the life of a high activity catalyst. For S-882 and other high selectivity catalysts, the response is reverse. In other words, increases in I-Factor give decreases in operating temperature. Also, there is an optimum I-Factor for the catalyst, a value where the selectivity is maximized. This optimum I-Factor changes throughout the life of the catalyst, and in general the I-Factor needs to be increased as the operating temperatures increase due to catalyst aging. More information on the I-Factor can be found in Appendix A.



4.7 Catalyst start-up for S-882 catalyst

While the initial start-up of S-882 catalyst involves many unique steps, routine start-ups are shorter and do not require as many steps. Routine start-ups of S-882 catalyst can take as little as 2-8 hours to achieve full production rates.

- 1) Bring up the CO₂ recovery section, the EO removal and finishing sections, and have the back end of the plant on "hot standby" prior to unblocking the reactors.
- 2) Heat the reactor coolant to the temperature of operation experienced prior to the last shutdown, or to the maximum temperature of the heating system, whichever is lowest.
- 3) Check low point drains in the recycle loop for liquid prior to unblocking the reactors.
- 4) Establish cycle gas flow through the reactors. Set the gas flow through the reactors at 20-25% of the normal flow or the maximum rate at which the temperature of the reactors can be maintained.
- 5) After verifying the quality of all feed streams, begin ethylene feed to establish a baseline ethylene concentration in the loop. An ethylene concentration of 10% or greater is desirable before oxygen addition. Towards the end of the catalyst life, when the catalyst activity has significantly declined, higher ethylene concentrations (up to normal operating concentrations) may be desirable to help catalyst activity during start-up.
- 6) Line up oxygen to the unit according to the normal safety procedures for cleaning and purging. If maintenance has been performed on the oxygen feed line, analyze for trichloroethane and trichloroethylene. These compounds, which are used as degreasing agents in oxygen service, must be below 10 ppb to avoid poisoning the catalyst.
- 7) Add oxygen feed at the minimum controllable rate and hold for initial reaction to occur. Watch the O₂ concentration in and out of the reactors. Also watch the outlet gas temperatures, the coolant temperatures, the peak temperature differences, and the reactor temperature profiles. Do not increase oxygen flow if no sign of reaction is indicated. Reaction is indicated by increasing catalyst bed temperatures and a reduction in reactor outlet oxygen concentration.
- 8) Establish chloride flow. Target an I-factor slightly lower than the I-factor experienced during the last shutdown. For example, if at the time of shutdown the I-factor was 0.09, the target I-factor for start-up should be 0.08-0.085.



- 9) If essentially no reaction is occurring and the oxygen concentration in the feed reaches 3%, decrease the cycle gas flow to the reactors and increase chloride addition.
- 10) Once reaction is indicated and the temperatures of the reactors are increasing, gradually increase cycle gas flow to the reactors. Increase the oxygen feed flow with the increases in cycle gas flow.
- 11) Begin ethylene addition and increase ethylene flow as necessary to bring ethylene concentration to the target level.
- 12) Once oxygen flow is high enough to stop the nitrogen purge through the oxygen mix nozzle, begin methane addition at the maximum rate toward the target level.
- 13) Bring the cycle gas flow to the reactors to maximum. Continue to increase oxygen flow to the target level, whilst maintaining a close watch on the level in the EO stripper tops surge drum. Adjust reactor temperature as necessary to control oxygen concentration at the desired level.
- 14) Once the reaction feed rates and compositions are at the design conditions, perform an I-factor optimization to obtain maximum selectivity. If the design conditions are near to those experienced at the time of shutdown, the optimum I-factor should be approximately equal to the optimum I-factor before the shutdown.

4.8 Catalyst Shutdown for S-882 catalyst

- 1) For planned catalyst shutdowns, stop chloride addition approximately 15 minutes before the stoppage of oxygen addition.
- 2) Trip the oxygen feed supply. Circulate the cycle gas through the reactors until the oxygen concentration drops below 0.1%.
- 3) Stop the cycle gas flow through the reactors and close the inlet and outlet reactor isolation valves.
- 4) If the shutdown will be short in duration (less than 24 hours), maintain the catalyst temperatures at 230-240°C. For extended shutdowns, this temperature may be reduced even further, but should always be kept above the dew point to prevent any chance of water condensing on the catalyst surface.
- 5) Establish a small nitrogen bleed through the reactors to maintain an inert atmosphere.



4.9 Chloride re-optimization for S-882 catalyst

Chloride re-optimizations should be performed periodically (every 4-5 weeks), after significant changes in operating conditions such as production rate increases, or when significant changes are observed in catalyst selectivity.

Unlike conventional catalyst, the optimum I-factor will change throughout the life and at different operating conditions for S-882 catalyst. To maximize catalyst selectivity, a chloride re-optimization should be performed from time to time. The re-optimization involves making small adjustments to the I-factor and monitoring selectivity.

In general the optimum I-factor increases with the catalyst life as the catalyst activity declines. Higher coolant temperatures usually require a higher I-factor to remain at optimum. Therefore, changes in process conditions that require the temperatures to be increased (for example, an increase of workrate or a decrease in ethylene concentration) will typically require an increase in I-factor.

Typically the re-optimization process begins with the catalyst in an under-moderated state, since catalyst temperatures increase with catalyst age. With this situation, the optimization will start with small increases in I-factor. However, there are situations where the catalyst can be over-moderated, such as when there is a significant decrease in workrate. For these situations, it is recommended that a significant decrease be made in the I-factor to take the catalyst to an under-moderated condition. This is because the catalyst responds slower to decreases in I-factor when over-moderated than it does to increases in I-factor when under-moderated. During the optimization process, it is important that small steps be made in the I-factor (0.005 - 0.01) and that sufficient time be allowed for the catalyst and chloride to equilibrate.

To help the re-optimization process, it is recommended that a plot be made of the measured selectivity verses the measured I-factor. The response should give a catalyst response shown above. The plant will help to monitor the progress of the re-optimization procedure and help identify the optimum I-factor.

- 1) Bring the unit to the desired conditions for ethylene and oxygen concentration and production rate. For multi-reactor systems, the reactor temperatures should be adjusted so that the oxygen conversion across the reactors is balanced (all reactors should have the same outlet oxygen concentration.)
- 2) If it is believed the catalyst is over-moderated, reduce the I-factor enough to bring the catalyst to an under-moderated condition.



- 3) Increase chloride flow to the reactors in a stepwise manner every 8-12 hours. Adjust reactor coolant temperatures as necessary to maintain oxygen concentration at the target level and also to keep the reactor outlet oxygen concentration balanced.
- 4) Note the average selectivity as the reaction stabilizes after every chloride feed increase.
- 5) If the reactor selectivity has increased, repeat step 3 and 4 above. If the selectivity has decreased, go to step 6. Continue to increase the I-factor (repeating step 3 and 4) until there is no further increase of the selectivity, or until the point where selectivity decreases. Once a decrease is noted (the optimum has been passed), reduce the I-factor to the previous value where the selectivity was at optimum. At this point, the optimization is complete.
- 6) If the reactor selectivity has decreased in Steps 3 and 4, reduce the chloride feed back to the previous value. Record the selectivity after the catalyst has lined out. (Note the catalyst may take longer to recover from over-moderation. When decreasing I-factor, it may take up to 48 hours before the selectivity reaches its new steady-state value.) At this point, the optimization is complete.



5. CATALYST PROTECTION AND BLANKETING

- 1) Contact of the catalyst with liquid of any kind must be avoided. Liquids should be kept out of the reactor catalyst bed. Sources of liquids include carry over from the absorbers, carry over from the CO₂ removal system, or exposure of the catalyst to a humid atmosphere.
- 2) For long term reactor outages, the reactor temperature should be maintained at a minimum of 50-60°C. A slight nitrogen purge should be maintained across the catalyst bed in the normal direction of cycle gas flow.
- 3) The reactor inlet and outlet isolation valves should remain closed. Cycle gas must not be circulated through the reactors until the temperature reaches 65°C or greater to prevent the possibility of moisture condensation inside the reactors.



6. PERFORMANCE TEST

The objective of this test is to measure and document the initial performance of the catalyst. The duration of the performance test is specified in the catalyst sales contract, and is typically a period of 24 hours. The total time for the performance test depends on the number of reactors and the number of streams that can be monitored at the same time. The duration of the test can be reduced or increased as needed to accommodate customer needs/preferences. During the performance test, the unit must be under steady operation, with no significant changes to process parameters.

- 1) The operating conditions for the performance test are normally specified in the catalyst sales contract. Typically, these conditions are unique to each production unit. Deviations from the contract conditions can be accounted for by using Catalyst vendor's catalyst performance model.
- 2) Prior to start of the performance test, the reactors must be stable and at the target parameters.
- 3) Reactor selectivities and chloride levels will be determined through use of the Catalyst vendor's mobile analytical laboratories when available. Customer analyzer values will also be used. Suspect data, such as values with poor oxygen closures, will be discarded and not used for determining average selectivity.



APPENDIX A. MODERATION OF SHELL EO CATALYST: I-FACTOR

For conventional catalyst, chlorides inhibit both the combustion reaction and the reaction to form EO. However, they slow down the combustion reaction much more. Therefore, the catalyst selectivity is increased by the addition of chlorides. These halogenated hydrocarbons are called inhibitors because they inhibit the reaction or reduce the catalyst activity (the temperature needed to maintain a constant conversion is increased).

However, hydrocarbons in the feed, particularly ethylene and ethane, tend to strip adsorbed chlorides from the catalyst surface. This competition between chlorides adsorbing onto the catalyst surface and being stripped off by hydrocarbons is combined into one single expression: the I-factor.

The I-factor is defined as:

$$\frac{\text{total Cl (ppm mol)}}{[\text{ethylene}] (\% \text{ mol}) + 85 \times [\text{ethane}] (\% \text{ mol})}$$

This expression adequately normalizes chloride and hydrocarbon interactions with the catalyst surface.

However, chlorides affect S-882 type high selectivity catalysts differently than they do S-863 type high activity catalysts:

- 1) Chlorides do NOT inhibit S-882; chlorides activate S-882 or speed up the reaction (the temperature required to maintain a constant conversion is decreased). For this reason, we generally refer to chlorides as moderators, because they can inhibit S-863 catalyst, and they can activate S-882 catalyst.
- 2) S-882 catalyst also displays an optimum selectivity response to the I-factor. Variations above or below the optimum I-factor will result in lower catalyst selectivity.
- 3) S-882 catalyst also responds differently to changes in the I-factor caused by chloride concentration and/or ethylene and ethane changes. The chloride interaction on the catalyst surface is different. In general, the response of S-882 to changes of this kind is slower than for S-863. Thus, it is more difficult for chlorides to adsorb onto the catalyst surface and to be stripped off in particular. As a result, line out times during chloride/ethane changes or upsets are generally longer for S-882 than for S-863.



- 4) For optimum catalyst performance over life, the advised I-factor for S-863 is in the range 0.06 - 0.07. A too high I-factor will result in initial high selectivity, but a faster selectivity decline over catalyst life. A too low I-factor results in loss of selectivity.
- 5) In addition, the optimum I-factor for S-882 increases with age. Therefore, it is often difficult to know for certain if the current operation is at the optimum selectivity without frequent optimisation of the catalyst.



APPENDIX B. INFLUENCE OF OPERATING VARIABLES FOR EO CATALYST

Table 1 Typical operating parameters influencing selectivity and activity for high activity catalyst (S-863)

Operating parameter	Unit	Typical value	Catalyst Selectivity	Catalyst Activity *)
Increase in:			results in:	
O ₂ concentration in feed	%mole	7.5 – 8.5	++	++
C ₂ = conc. in feed	%mole	25 - 30	+	+
CO ₂ concentration in feed	%mole	3-5	-	--
GHSV	hr ⁻¹	3500	+	-/o
Workrate	kg EO/m ³ .hr	180	-	-
Oxygen conversion	%	30-40	-	-
Reactor pressure	barg	16.5	-	+
I-factor	-	0.06-0.07	+	-

*) Increase in activity results in a decrease in coolant temperature to achieve the same EO production.



Table 2 Typical operating parameters influencing selectivity and activity for high selectivity catalyst (S-882)

Operating parameter	Unit	Typical value	Catalyst Selectivity	Catalyst Activity *)
Increase in:			results in:	
O ₂ concentration in feed	%mole	7– 8	++	+
C ₂ = conc. in feed	%mole	25 - 35	+	+
CO ₂ concentration in feed	%mole	1	-	--
GHSV	hr ⁻¹	3500	++	+
Workrate	kg EO/m ³ .hr	180	-	--
Oxygen conversion	%	30-45	-	-
Reactor pressure	barg	16.5	-	+
I-factor(**)	-	0.06-0.15	optimum	+

*) An increase in activity results in a decrease in coolant temperature to achieve the same EO production.

**) The optimum I-factor changes over time

