MARY KAY O'CONNOR PROCESS SAFETY CENTER
TEXAS A&M ENGINEERING EXPERIMENT STATION

21st Annual International Symposium
October 23-25, 2018 | College Station, Texas

Fire Incidents at Ethylene Oxide Reactors in Ethylene Glycol Plant

Kevin S. H. Hsueh
Assistant Vice President, Nan Ya Plastics Corporation
No.2, Formosa Industrial Complex, Mailiao, Yunlin, Taiwan, ROC
Email: kevinhsueh@npc.com.tw

Keywords: Spool piece flange leakage, bolt deformation, oxidation reaction, spontaneous combustion, reactor inlet pipeline, emergency vent, compressor oil pump, power supply panel, ground fault relay, ACB, MCCB, ethylene oxide, ethylene glycol

Abstract

In September 26, 2012 NYPC Mailiao Ethylene Glycol (EG-4) plant reported a fire incident on the spool piece flanges of inlet pipeline of both two Ethylene Oxide (EO) reactors, R-1/R-2, which were founded 43 minutes later after Recycle Compressor tripped.

1. The deformed bolts were founded on the Inlet pipeline spool piece flanges of both R-1 and R-2 reactors, which were caused by unexpected extra high temperature, leaded to the leakage of ethylene mixed gas and spontaneous combustion.
2. The insufficient and invalidated emergency vent, following the Recycle Compressor trip, triggered the abnormal oxidation reaction of ethylene/oxygen mixed gas at the front-end of both two reactors, 180 seconds after compressor trip, which gave rise to the extra high temperature in the reactor inlet pipeline and reactor dome.
3. The 6 inches valve of emergency vent kept open 90 seconds following the compressor trip, but the pressure drop was only 1.5 Bar, less than safety criterion 3.0 Bar. It indicated an insufficient vent quantity and created a possible pocket of gas of explosive concentration.
4. Recycle Compressor was tripped by low oil pressure while its affiliate main and auxiliary oil

pumps losing its 380V power supply at the same time.

5. The ACB(air circuit breaker) of 380V power panel, MCC-100/200, was tripped by ground fault relay protection resulted in stopping of power supply for all its distributed seventeen equipment, which included not only the main and auxiliary oil pumps of Recycle Compressor but also the air cooler fan motors of CO_2 stripper condenser.
6. The stator winding damage of air cooler fan motor caused an unexpected trip of the upstream ACB of 380V power distribution panel for its improper setting of ground fault relay protection. Tripping the MCCB(molded case circuit breaker) of motor itself to be treated a satisfactory way for protection of power supply system.

Process Description

Ethylene Glycol plant consists of two water-cooled ethylene oxide reaction systems plus recovery facilities, glycol reaction, evaporation and purification facilities.

1. Basic chemistry

Ethylene Oxide (EO) unit

Ethylene is oxidized by oxygen in the presence of a sliver catalyst to make ethylene oxide.

$$C_2H_4 + 1/2\ O_2 \longrightarrow C_2H_4O$$

ΔH @ 25°C = -25,550 kcal/kg-mole of C_2H_4

In addition, carbon dioxide and water are formed as by-products

$$C_2H_4 + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O$$

ΔH @ 25°C = -316,220 kcal/kg-mole of C_2H_4

Ethylene Glycol unit

The direct reaction of ethylene oxide and water is to form ethylene glycol. Other reactions take place since ethylene oxide also reacts with ethylene glycol and higher homologues.

$$C_2H_4O + H_2O \longrightarrow MEG$$

$$C_2H_4O + MEG \longrightarrow DEG$$

$$C_2H_4O + DEG \longrightarrow TEG$$

2. EO reactor unit description

Ethylene and oxygen enter from battery limits and are mixed with cycle gas. The gas mixture from the Gas-Gas Exchanger flows downward through the tube of two EO Reactors where a partial conversion of ethylene to ethylene oxide occurs over a solid catalyst. The heat of reaction is removed by boiling water in the shell of the Reactor and producing steam. The ethylene oxide is scrubbed from the Gas-Gas Exchanger shell side exit gas using EO lean cycle water, and EO rich cycle water is sent to the Ethylene Oxide Stripping and Reabsorption Section. A major portion of the lean (scrubbed) cycle gas is sent through the CO_2 contactor section to remove CO_2 made in the EO Reactors. EO reactor unit scheme is shown in figure 1. The Recycle Compressor provides the head necessary to circulate the large flow of cycle gas through the reactors and scrubber.

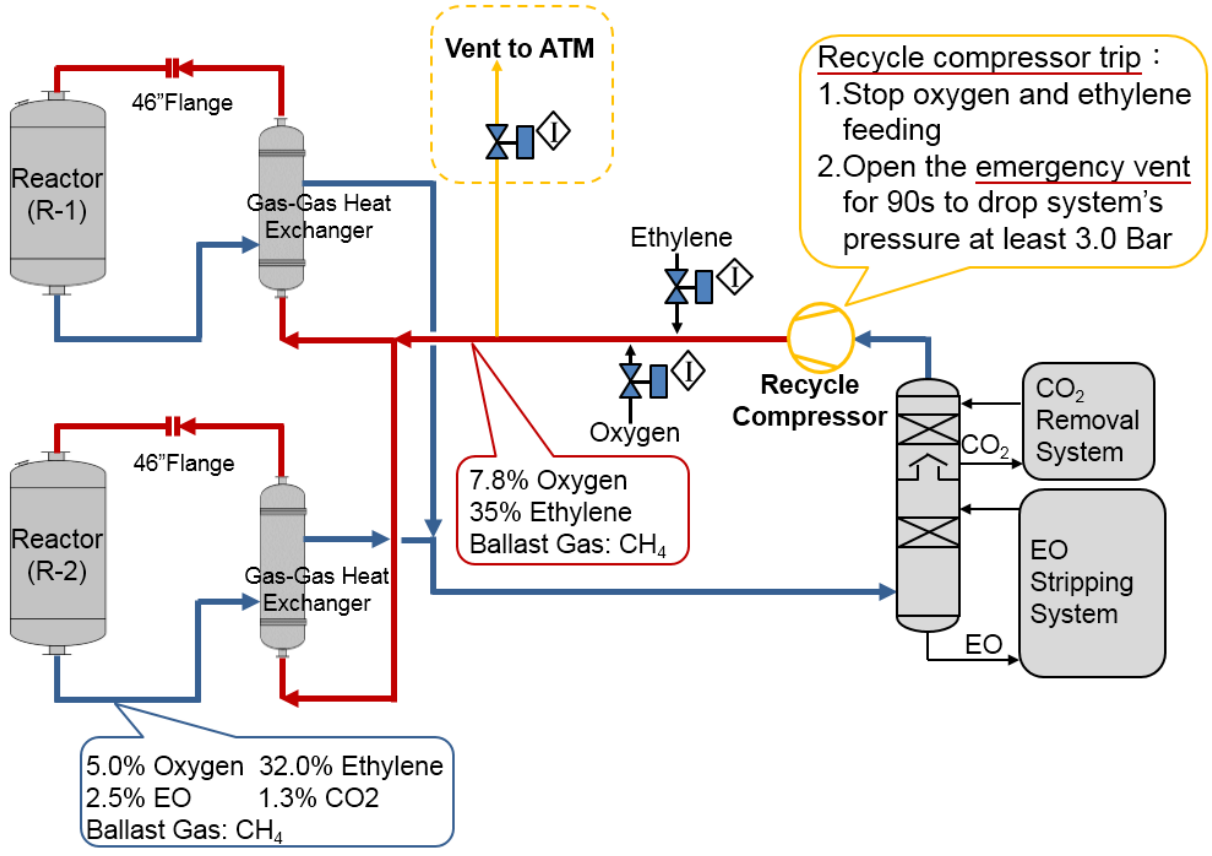

Figure 1. EO reactor unit Scheme

3. Emergency Vent Design

The Recycle Compressor may fail as a result of failure. Even though the automatic feed shutdown system has functioned correctly, there is the possibility that a pocket of gas of explosive concentration may have formed in the cycle gas pipe in the vicinity of the oxygen feed point.

To ensure that gas does not reach the Gas-Gas Exchanger or Reactors, the vent valve downstream of the oxygen feed station will open immediately. This will vent gas away from Reactors. Venting will be continuing for 90 seconds.

4. Reactor Inlet Pipeline Design

The 46 inches top outlet pipeline of Gas-Gas exchanger (the other word is inlet pipeline of Reactor) must be removed while perform the internal inspection based on the local government rule. In order to perform the crane job easier that the pipeline was designed with a spool piece on the Gas-Gas Exchanger side.

5. Power Supply Scheme

(1) High voltage: 13.2KV
Recycle Compressor motor power (13.2KV) is supplied from 3.3KV feeder LINE #1, and the system's power supply scheme is shown in figure 2.

(2) Middle/Low voltage: 3.3KV/380V

A. Pump/fan motors are supplied from 3.3KV feeder LINE #2 and divided into two groups.

B. The 380V power of main and auxiliary oil pumps of Recycle Compressor comes from the MCC-100/200 panel, same as CO_2 stripper air cooler fans.

C. Power Panel Protection Trip Design:

ACB (Air Circuit Breaker):

Grounding Fault Relay (0.3s)
Over Current delay
Short Circuit delay

MCCB (Molded Case Circuit Breaker):

Rated Current Protection (10s)
Short Circuit delay

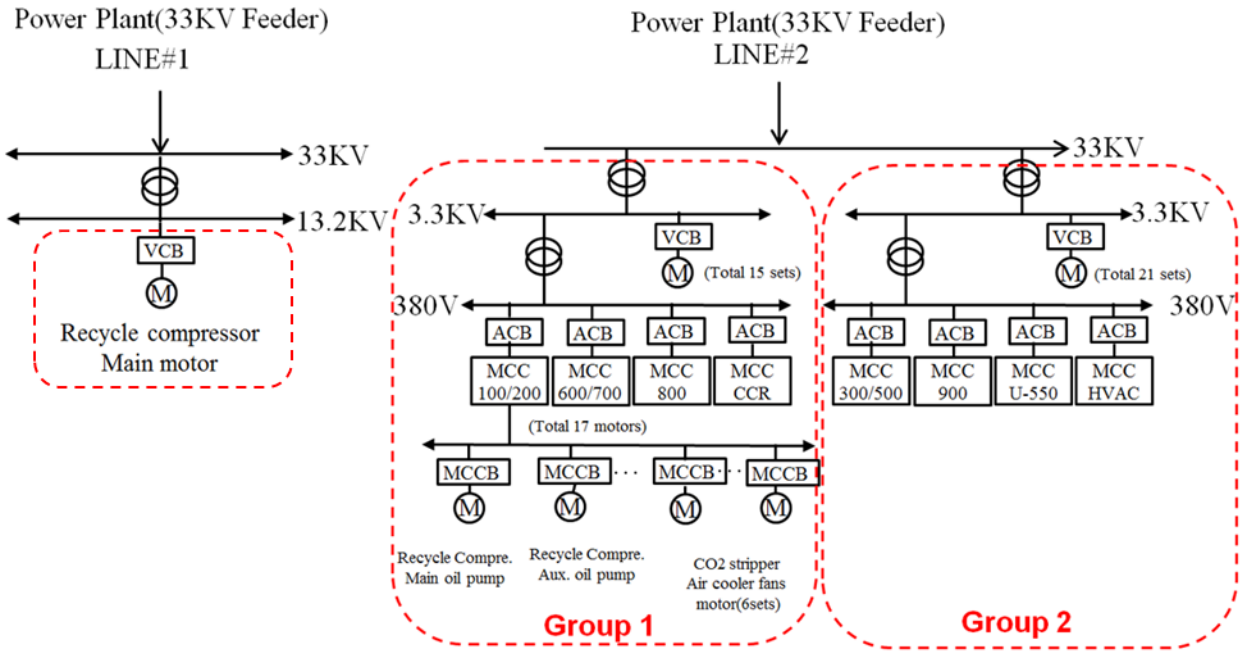

Figure 2. Power Supply Scheme

Description of Event

In September 26, 2012 NYPC Mailiao Ethylene Glycol (EG-4) plant reported fire incidents on the spool piece flanges of inlet pipeline of both two Ethylene Oxide (EO) reactors, R-1/R-2, which were founded 43 minutes later after Recycle Compressor tripped. Events sequence shown as figure 3 and line-up during pipeline flange fire shown as figure 4.

00′ 00″ Stator winding damage of air cooler fan motor (40 hp, 380V) caused over-current

00′ 01″ Ground fault protection relay worked, and caused a trip of 380V power panel

00′ 02″ Both main/aux. oil pumps lost power, and recycle compressor(14,750 hp, 13.2KV) tripped

00′ 02″ Emergency vent worked 90 sec., but wrong sizing
01′ 32″ caused insufficient vent quantity

03′ 00″ Internal active reactions occurred at the inlet zone of both reactors

43′ 00″ High temp. stress in pipeline leaded spool piece flanges as the breaking points and got external fires

Figure 3. Events Sequence

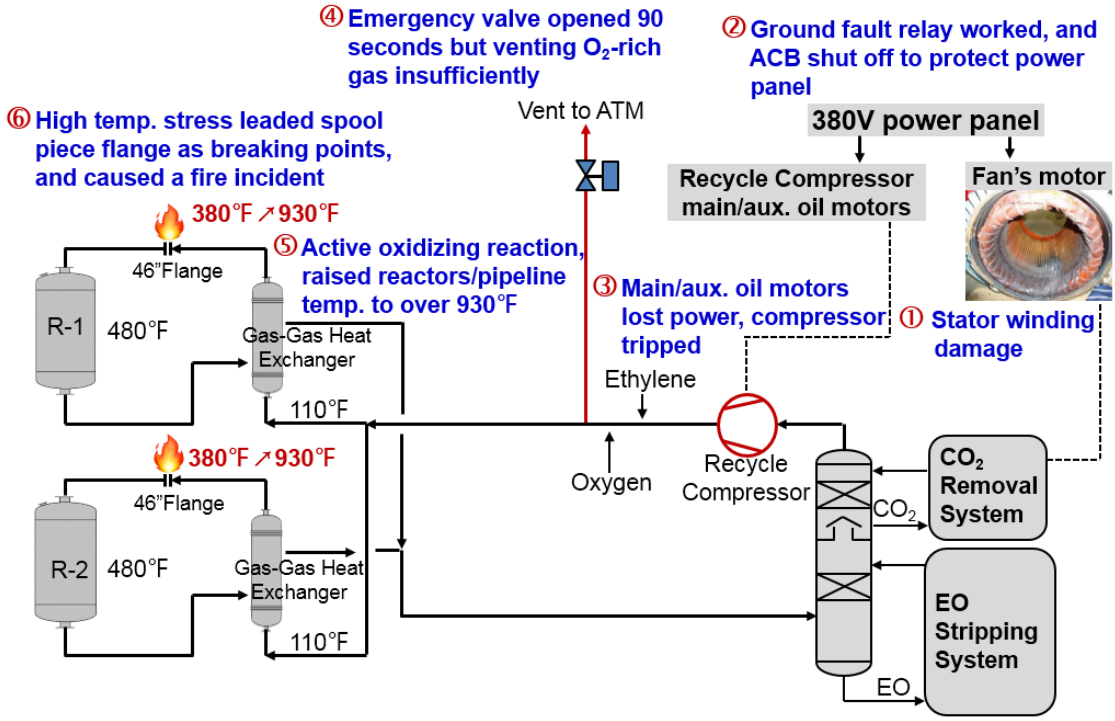

Figure 4. Line-Up during Pipeline Flange Fire

Root Cause Investigation

1. Bolt Deformation

The bolt deformation on the Inlet pipeline spool piece flanges of both R-1 and R-2 reactors, caused by unexpected extra high temperature(>930°F), leaded to the leakage of ethylene mixed gas and spontaneous combustion.

(1) According to Table 1, the strength of bolting materials will reduce to 34% at 950°F.

(2) Unequal thermal expansion across the pipeline at 930°F causes higher stress on spool piece flange, which simulation result is shown in figure 5.

ASME B31.3

Nominal Composition	Spec. No.	Type/ Grade	Min. Temp., °F (6)	Specified Min. Strength, ksi		Min. Temp. to 100	200	300	400	500	600	700	800	850	900	950	1,000	1,050	1,100	1,150
				Tensile	Yield															
Ni–Cr–Mo	A320	L43	−150	125	105	25.0	25.0	25.0	25.0	25.0	25.0	25.0	...	...	...	...	...	...	...	...
Cr–Mo	A320	L7	−150	125	105	25.0	25.0	25.0	25.0	25.0	25.0	25.0	...	...	...	...	...	...	...	...
Cr–Mo	A320	L7A	−150	125	105	25.0	25.0	25.0	25.0	25.0	25.0	25.0	...	...	...	...	...	...	...	...
Cr–Mo	A320	L7B	−150	125	105	25.0	25.0	25.0	25.0	25.0	25.0	25.0	...	...	...	...	...	...	...	...
Cr–Mo	A320	L7C	−150	125	105	25.0	25.0	25.0	25.0	25.0	25.0	25.0	...	...	...	...	...	...	...	...
Cr–Mo	A193	B7	−55	125	105	25.0	25.0	25.0	25.0	25.0	25.0	25.0	21.0	17.0	12.5	8.5	4.5	2.4	...	...
Cr–Mo–V	A193	B16	−20	125	105	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	23.5	20.5	16.0	11.0	6.3	2.8	1.2
...	A354	BD	−20	150	130	30.0	30.0	30.0	30.0	30.0	30.0	30.0	...	...	...	...	...	...	...	...

Table 1.Strength of Bolts in Different Temperature

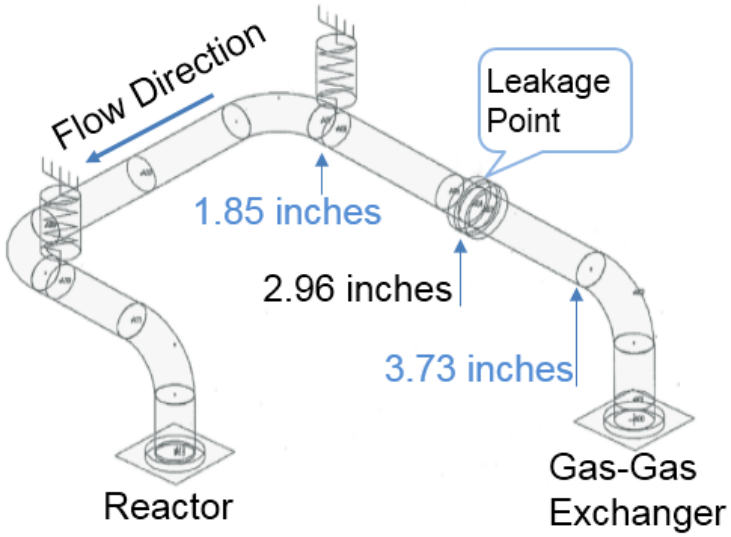

Figure 5. Simulation of heat expansion of pipeline at 930°F

Action

(1) Eliminate the spool piece design of the reactor inlet pipeline to strengthen its high temperature endurance, shown as figure 6. Use the bigger crane to lift up the whole pipeline to perform the internal inspection during overhaul

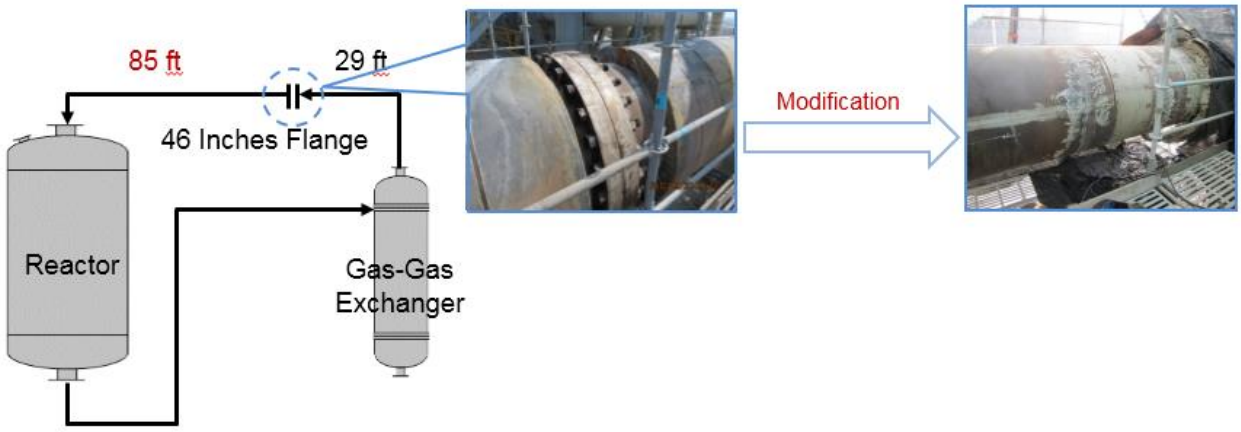

Figure 6. Eliminate the spool piece design of the reactor inlet pipeline

(2) Cr-Mo alloy bolts of inlet flange of reactors are replaced by Cr-Mo-V alloy bolts to improve its high temp. stress endurance. Strength of bolts in different temperature shown as figure 7.

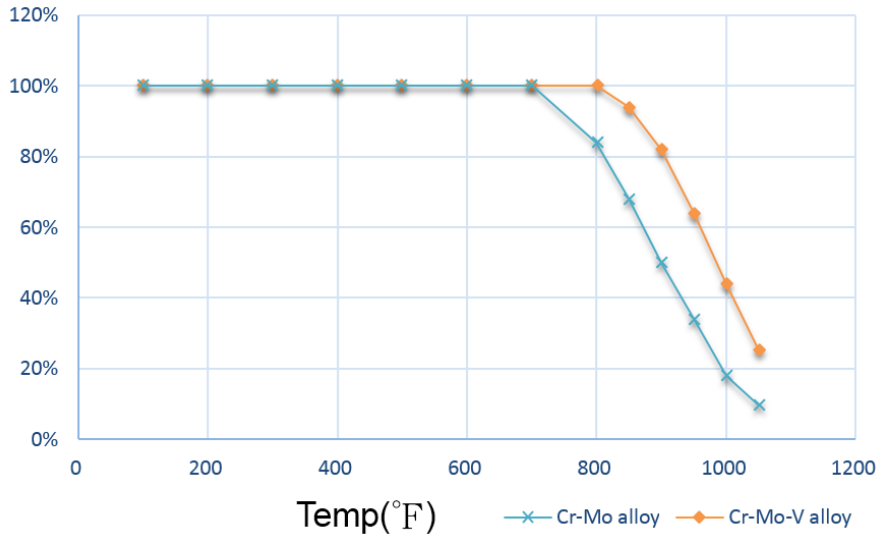

Figure 7. Strength of bolts in different temp. with Cr-Mo and Cr-MO-V alloy

(3) One of HAZOP and MOC team member must be proficient at material science to evaluate and recognize the impact correctly and properly.

2. Insufficient Emergency Vent

The insufficient emergency vent, following the Recycle Compressor trip, triggered the abnormal oxidation reaction of ethylene/oxygen mixed gas at the front ends of both two reactors, 180 seconds after compressor trip, and leaded the temperature to above 930°F in the reactor inlet pipeline and reactor dome.

The six inches valve of emergency vent kept open 90 seconds following the compressor trip, but the pressure reduce was only 1.5 Bar, less than the safety criterion 3.0 Bar, that indicated an insufficient vent quantity and created a possible pocket of gas of explosive concentration. On the other hand, PHA failed to confirm whether or not the amount of emergency discharge reached safety limitation.

Action

(1) Emergency vent valve and line size is replaced from 6 to 8 inches, and interlock logic is modified to take into account not only venting time (90 seconds) but also process pressure drop (>3.0 Bar), the modification shown as figure 8.

(2) All the safeguards, included emergency vents and pressure relief valves, must be reviewed not only the mechanical function but also its discharge quantification.

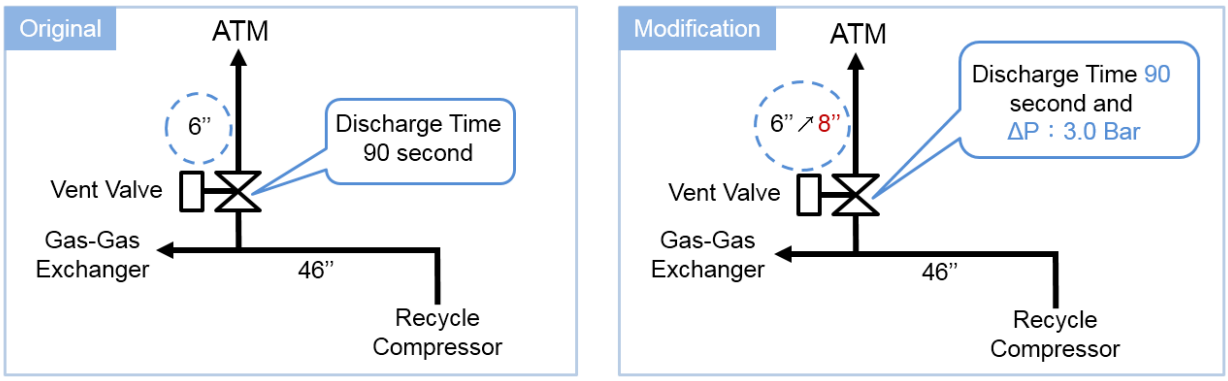

Figure 8. Emergency Vent and Interlock Modification

3. Recycle Compressor Tripped by losing power of oil pumps

Recycle Compressor was tripped by low oil pressure while its affiliate main and auxiliary oil pumps losing 380V power supply at the same time.

Action

(1) The main oil pump and auxiliary oil pump of Recycle Compressor comed from the MCC-100/200 panel which was belonging to middle/low voltage GROUP #1 originally. In order to reduce the risk that the auxiliary oil pump is modified to relocate to another MCC-300/500 panel, belonging to middle/low voltage GROUP #2, to reduce the risk of losing both oil pumps at the same time. The modification is shown in figure 8.

(2) Other affiliated oil pumps and blowers of major equipment, such as incinerator…etc., are also modified to be supplied from different power supply panels.

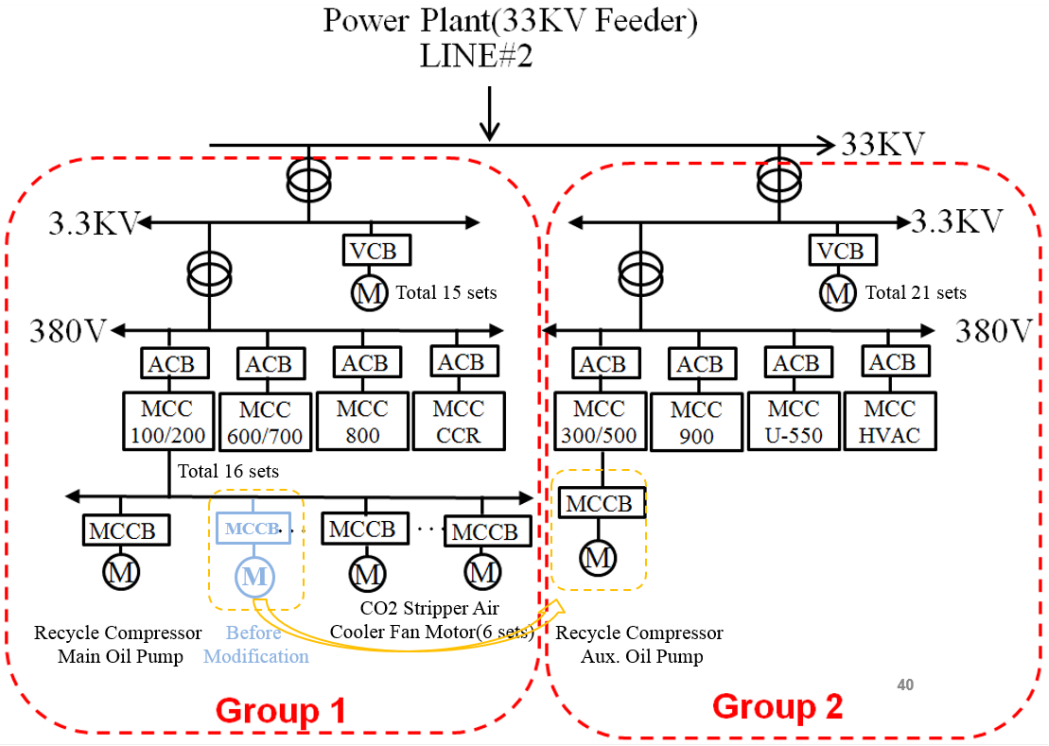

Figure 8. Power Supply Scheme Modification

4. Power Supply Panel Tripped by the Improper Ground Fault Trip Setting

The ACB(air circuit breaker) of 380V power panel, MCC-100/200, was tripped by ground fault relay protection resulted in the losing power for all its distributed seventeen equipment, which included not only the recycle compressor's main and auxiliary oil pumps but also the CO_2 stripper condenser air cooler fan motors.

The stator winding damage of air cooler fan motor was expected to be protected by its own MCCB. However, it tripped the upstream 380V power supply panel for the improper protection setting of ground fault relay of ACB.

(1)The insulation and ground resistance tests of fan motor were performed three months before the incident. Its insulation resistance >100MΩ@500V and ground resistance 0.12Ω showed that the motor was at good condition.

(2)The failed motor is analysis by TUV that the root cause is insulation failure between layers of stator which could be the manufacture defect or maintenance non-conformity. The insulation failure result is shown in figure 9.

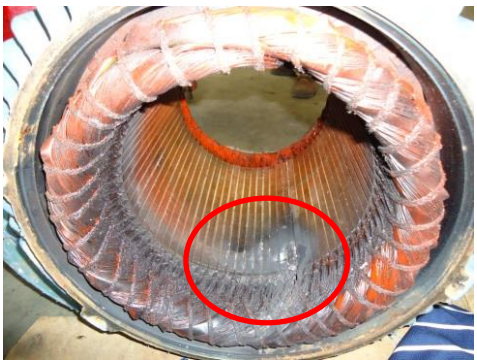

Figure 9. Insulation failure between layers of stator

Action

Because of the motor can be protected by its own MCCB with rated current protection and short circuit delay, that Protection Trip Design of ACB is modified to delete the ground fault relay.

ACB Protection Setting Modification

ACB (Air Circuit Breaker):

~~Ground fault relay (0.3s)~~ (deleted)
Over current delay
Short circuit delay

MCCB (Molded Case Circuit Breaker):

Rated current protection (10s)
Short circuit delay

Conclusions

1. The spool piece for the potential oxidation pipeline must to be eliminated to strengthen its high temperature endurance.
2. Emergency vent must be validated and confirmed.
3. Separated power supply scheme must be considered for the main and auxiliary oil pumps of major compressor.
4. The coordination of protection settings between ACB of power supply panel and MCCB of downstream terminal motors must be reviewed.
5. PHA group to assign a member specialized in materials to recognize the impact of process deviation.