Report on the overview of the high pressure gas accident

Reference No. 2011-386	**Name of the accident:** Explosion and fire at vinyl chloride monomer production plant.		
Date and time of occurrence: Around 15:15 on November 13, 2011		**Place of the accident:** Shunan-city, Yamaguchi Prefecture, JAPAN	
Plant name: Vinyl chloride monomer production plant unit 2	**Equipment name:** 1. Hydrochloric acid removal column 2. Reflux tank of the hydrochloric acid removal column 3. Liquid hydrochloric acid buffer tank	**Main structural materials:** 1. JIS SLA325A, JIS SPV315 2. JIS SLA325A 3. JIS SLA325A	**Summary of dimensions (mm):** 1. Overall length $28,000^{TL}$ Upper stage $1,900^{ID}$ x $11,600^{TL}$ Middle stage $1,900^{ID}$ x $2,800^{ID}$ x 800^{TL} Lower stage $2,800^{ID}$ x $15,600^{TL}$ 2. $2,800^{ID}$ x $6,600^{TL}$ 3. $2,700^{ID}$ x $5,600^{TL}$
Contents: Hydrochloric acid(HCl) Vinyl chloride monomer(VCM) Ethylene dichloride(EDC)	**Capacity to produce high-pressure gas:** $31,169,350m^3$(Normal)/day	**Normal operating pressure:** 1. 1.90MPa 2. 1.90MPa 3. 1.90MPa	**Normal operating temperature:** 1. -25°C/120°C 2. -25°C 3. -25°C

Damage situation:

On account of the failure of the emergency relief valve in the oxy chlorination process A series at the vinyl chloride monomer production plant unit 2, the plant was shut down according to emergency procedures. When the work to extract the liquid was underway, thereafter, gases such as HCl, VCM leaked from the liquid hydrochloric acid buffer tank, and about ten minutes later, two explosions occurred in the vicinity of the reflux tank of the hydrochloric acid tower. As a result, a wide area of the plant burst into flames and one operator was killed.

Overview of the accident:

1. At 3:39, the emergency relief valve connected to the detoxifying equipment of the oxy chlorination process A series (hereinafter, called “Oxy A series”) at the vinyl chloride monomer production plant unit 2 under normal operation was broken and was suddenly opened leading to a rapid drop of the system pressure.
2. At 3:52, the Oxy A series automatically was shut off by interlocking.
3. At 3:53, the cracking furnaces A series and B series went into emergency shutdowns to adjust the capacity utilization rate of the cracking furnaces to that of the Oxy B series.
4. At around 4:10, due to the emergency shutdowns of the cracking furnaces A series and B series, the production amount of hydrochloric acid (HCl) and vinyl chloride monomer (VCM) as well as the amount of unreacted 1,2-ethylene dichloride (1,2-EDC) dropped significantly, and the temperature of the middle stage (18th stage) of the hydrochloric acid removal column dropped from 80°C (the normal working temperature) to 57°C. In order to recover the temperature of the 18th stage to 80°C, the operator increased the amount of steam of the heater of the hydrochloric acid removal column and decreased the reflux volume.
5. At 4:40, the temperature at the column top (50th stage) of the hydrochloric acid removal column increased to 38°C, which should be -24°C in the normal state, and VCM got mixed into HCl in both the upper part of the hydrochloric acid removal column and its reflux tank.
6. At 5:57, owing to the contamination of VCM in the reflux tank of the hydrochloric acid removal column, the mass-balance was lost and the oxygen concentration of the Oxy B series increased. As a result, the whole production facility including the Oxy B series was shut down.
7. Subsequently, operations were conducted according to the shutdown manual of the hydrochloric acid removal column, and at 8:40 the refrigerator of the hydrochloric acid removal column was shut off, and then the reflux tank of the hydrochloric acid removal column in which the liquid level rose higher than the normal condition was disconnected from the hydrochloric acid removal column.

8. At 11:39, since the value of the liquid level indicator of the reflux tank of the hydrochloric acid removal column was nearly 100%, transferring part of its volume to the liquid hydrochloric acid buffer tank was started. After that, both the temperature and the pressure in the reflux tank of the hydrochloric acid removal column and the liquid hydrochloric acid buffer tank gradually increased. The initial speeds of those increases were so slow that the operator could not notice the anomaly.
9. At around 15:00, upon recognizing the increase of the pressure in the liquid hydrochloric acid buffer tank, work to decrease the pressure was carried out.
10. At around 15:15, abnormal noise and eruptions of white smoke were observed from the upper portion of the liquid hydrochloric acid buffer tank during the work to decrease the pressure.
11. At around 15:23, the pressure of the reflux tank of the hydrochloric acid removal column increased to over 2.0MPaG.
12. At 15:24, the reflux tank of the hydrochloric acid removal column burst and exploded, and a wide area of the vinyl chloride monomer production plant unit 2 burst into flames.

Causes of the accident:

1. Operation to reduce the load of the hydrochloric acid removal column

- It became necessary to reduce the load of the hydrochloric acid removal column because of a significant decrease in the feed volume to that column due to the shutdown of the interlocking of the Oxy A series and the emergency shutdowns of the cracking furnaces A series and B series.
- It was required to adjust the amount of steam of the heater and the reflux volume by monitoring the temperatures at the column top and at the column bottom when there was a rapid fluctuation in operating load at the hydrochloric acid removal column. However, it was only stated in the emergency measures manual at the time of an emergency stop of the Oxy A series “to adjust the amount of steam of the heater and the reflux volume of the hydrochloric acid removal column”, and no specific value was indicated.
- As the temperature of the middle stage (18th stage) returned to 80˚C because of the increase of the amount of steam of the heater, the operator misunderstood that the hydrochloric acid removal column had recovered to the stable state, and he moved to work on other equipment. As a result, the operation continued without the amount of steam of the heater and the reflux volume being changed to values matching the reduced load, which led to an increase in the temperature at the column top and allowed for the mixture of VCM in the reflux tank of the hydrochloric acid removal column in which HCl only exists in the normal condition.
- In the operation management of the hydrochloric acid removal column, since it was not enough to be aware that an abnormally high temperature at the column top would lead to the stoppage of the oxy chlorinating reaction, so the facility was not configured to detect the anomaly positively. In addition, there was no detailed description in the emergency measures manual based on the assumption of the need to reduce the load of the hydrochloric acid removal column and there was also a lack of training to deal with such situation.

2. Explosion of the reflux tank of the hydrochloric acid removal column

- It was found that the explosion was caused by the fact that 1, 1-ethylene dichloride (1, 1-EDC) is easily generated by a reaction between HCl and VCM in the presence of Lewis acid catalysis such as iron chloride (III) ($FeCl_3$).
- HCl and VCM were found mixed within the reflux tank of the hydrochloric acid removal column and the liquid hydrochloric acid buffer tank, and $FeCl_3$ was generated by the reaction of iron rust in a vapor phase portion on the inner wall with HCl. Then the reaction to generate 1,1-EDC progressed with FeCl3 as the catalyst. Subsequently, the abnormally high temperature at the column top of the hydrochloric acid removal column was noted based on the trend data on the Distributed Control System, reminding the operators of the possibility of the mixture of VCM in the reflux tank of the hydrochloric acid removal column. Since the generation of 1,1-EDC could not be assumed, normal instructions to stop the operation in accordance with the manual of the hydrochloric acid removal column were given.
- This reaction is accompanied by an increase in temperature due to an exothermic reaction and the reaction speed gets exponentially faster with the rise in temperature. Then, it is presumed that the pressure within the reflux tank of the hydrochloric acid removal column increased rapidly allowing combustible fluid to leak from the liquid hydrochloric acid buffer tank, and the reflux tank of the hydrochloric acid removal column burst resulting the explosion of leaking VCM and 1,1-EDC induced by an unidentified ignition source.

3. Failure of the emergency relief valve

・ The failure that eventually set the stage for the interlocking action of the Oxy A series was caused by the contact failure of the coil in the torque motor within the positioner due to temperature fluctuations. Incidentally, it was not assumed that this valve failure would cause problems of primary importance in which the oxy chlorination process was shut down emergently and there was no detailed description in the emergency measures manual about how to deal with the situation nor was there adequate training provided for predicting the danger or dealing with the anomaly in advance.

Measures to prevent recurrence:

1. Equip the hydrochloric acid removal column with an interlock system, which shut down not only both of the cracking process and the oxy chlorination process but also the steam to the heater of the hydrochloric acid removal column, in case a plurality of thermometers at the column top record abnormally high temperatures. In addition, it must be clearly stated in the operation manual that, when starting shut down process of the hydrochloric acid removal column due to an anomaly in the column top temperature, a full reflux operation should be performed, and then it shall be stopped after checking the column top temperature becoming -24°C as in the normal condition.
2. To the Distributed Control System, add alarms for notifying that the pressure of the reflux tank of the hydrochloric acid removal column is different from the vapor pressure of the HCl alone due to the mixture of VCM into the reflux tank of the hydrochloric acid removal column, and also add indications of changes in temperatures and pressures per a unit of time.
3. Eliminate residues of iron rust on the inner wall when the reflux tank of the hydrochloric acid removal column and the liquid hydrochloric acid buffer tank have been opened for periodic maintenance, and make sure of their complete elimination by comparing with the finish photos attached to the work specifications.
4. Newly install a rupture disk for emergency depressurization in the reaction process with respect to the oxy system in order to reduce the risk of the shutdown. In addition, the emergency relief valve must not be used for emergencies by considering that the valve is a remotely controlled valve used for the depressurization of the series in periodic maintenance only. Add to the emergency measures manual the measures to be taken when the rupture disk is activated, and provide educational training for danger prediction and for how to deal with anomalies with the manual.

Learned lessons:

1. It is necessary to make clear the objectives and functions of the installation of safety measures such as the emergency relief valve, the rupture disk, etc. in chemical reaction processes, in order to secure the reliability of their actions, implement risk assessment in case of malfunction or incorrect operation and review how to deal with such a situation.
2. Since the conditions or situation after an emergency shutdown are different from the normal conditions or situation, it is necessary to operate equipment carefully because such differences might change management points from those in the normal condition. For this reason, it is important to prepare in more detail the checklist after an emergency shutdown and expand the operation support system as well as operations manual. In addition, it is significant to conduct periodic training assuming operations after an emergency shutdown and prepare for an emergency.
3. In the implementation of risk assessment of chemical reactions, it is necessary to provide more quantitative review by adding a variety of perspectives on the appropriateness of control methods, setting values and parts to be detected, and it is important to provide specific measures and training in which the result of risk assessment is reflected.
4. In plant operations it is important to provide education on fundamental rules and principles behind the significant control values for persons who are involved in those operations and maintenance, and hand down their expertise and skills.
5. It is important to make a database of information on operational experience, problems and accidents including other plants and companies, but it is more important to master expert knowledge so that anybody concerned can make good use of it.

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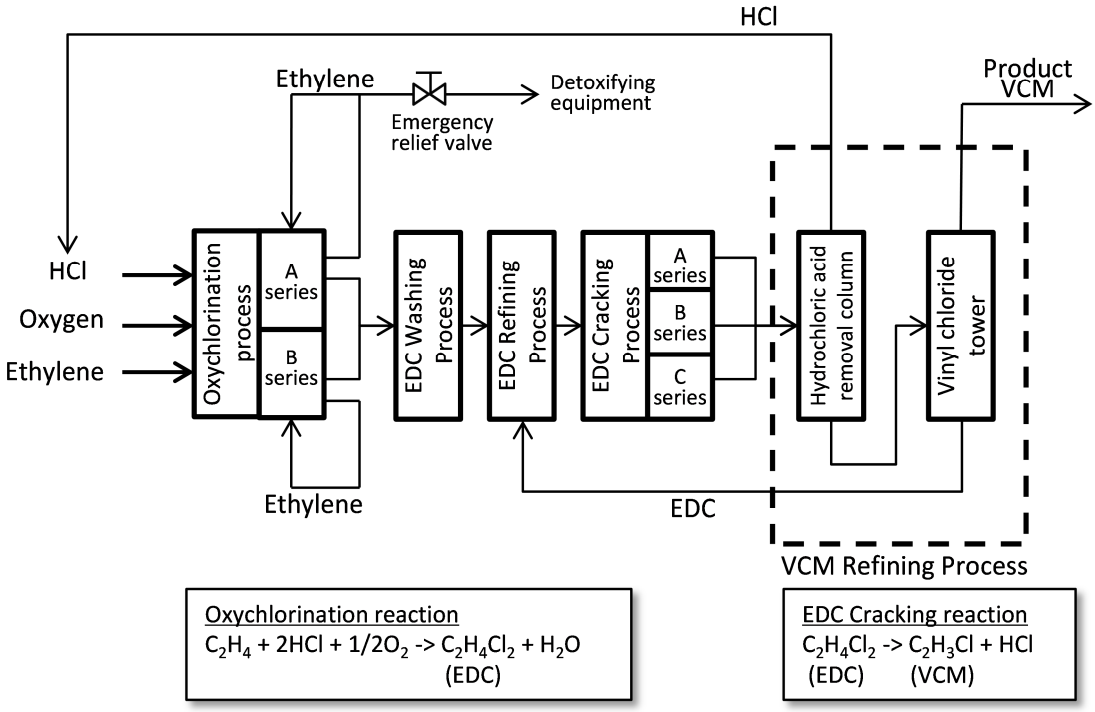

Fig. 1 Block-Flow of the Vinyl Chloride Monomer Production Plant Unit 2

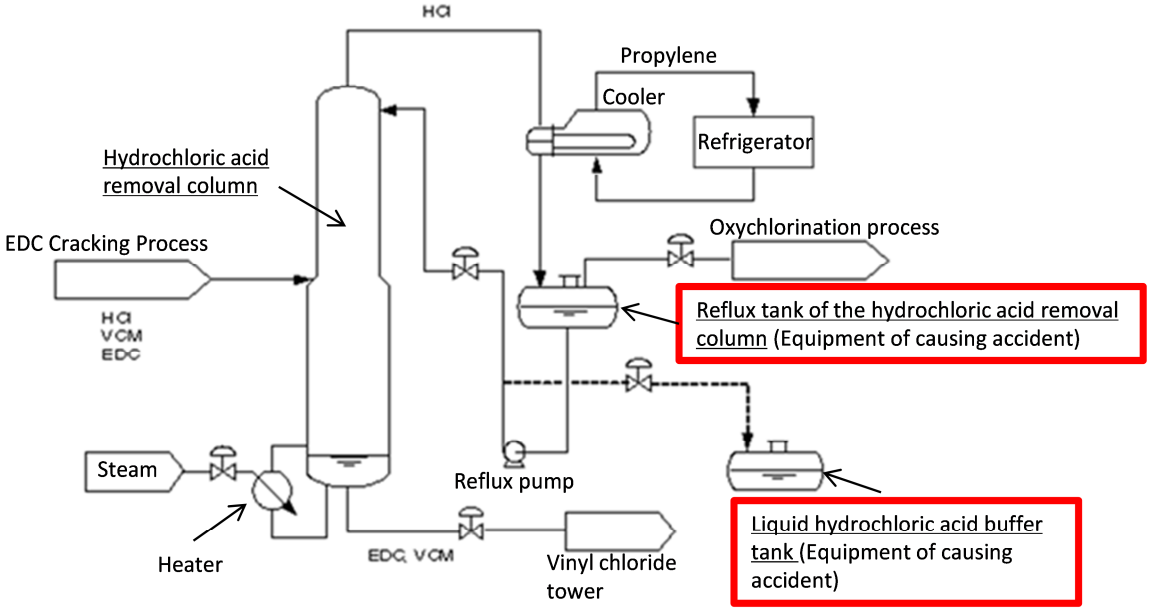

Fig. 2 VCM Refining Process – Flow Sheet around the Hydrochloric Acid Tower

Photo 1 Overall Damage View

Photo 2 Magnification of Photo 1

