Catastrophic Explosion of a Multilayered Urea Reactor

In 2005, a urea reactor exploded in Pingyin Chemical Plant, Shandong province, China. There were two different viewpoints on the initial causes of this failure—vapor explosion and chemical explosion. In this paper, the failure of the urea reactor was analyzed and compared with other urea reactor explosion cases in history. The reasons for stress corrosion cracking (SCC) of layers, which induced large leakage, were analyzed. The results of the research showed that this urea reactor suffered vapor explosion, and the chemical explosion in the top inner gas phase space of the urea reactor was ruled out. Both the fabricator and operator should be responsible for SCC in layers and weld which caused the fracture of the urea reactor.

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Introduction

On Mar. 21, 2005, a urea reactor exploded into three main sections during the normal production run in Shandong province, China. The urea reactor suffered a chemical explosion or fracture due to SCC followed by a vapor explosion.

The urea reactor is one of the critical equipment for urea production in a urea plant, which contains water, ammonia, urea and ammonium carbamate and operates at high temperatures. Vapor explosion is an obvious candidate when the large local fracture occurred.

The basic concept of vapor explosion is that the temperature of liquids contained in a vessel was well above the boiling point.

When the internal pressure suddenly drops rapidly due to the leakage of the contents and the equilibrium of previous phase is disturbed, the superheated liquids will be transferred into vapor with a high velocity, while a violent explosion will then occur [1]. Usually, the vessel and the surrounding structure are destroyed catastrophically.
A review of the damaged urea reactor

Structures

The urea reactor is approximately 26.2 m high and 1.4 m in inner diameter and has a capacity of 37.5 cubic meters. The wall thickness of the reactor is 110 mm. It is a multilayered vessel with a 316L (urea grade) liner, a carbon steel (Q235-A, a China steel branch) annulus and 11 low alloy steel (The 1st layer is 16MnR and others are 15MnVR) outer layers. The reactor is constructed with ten sections of multilayered cylinders and two hemispherical heads (see Figure1). Each adjacent two sections or section and head are circumferentially welded together. The structure of layers and weld are shown in Figure 2. The top cylinder near the top head is designated as C1 and the lowest cylinder near the bottom head is designated as C10. The eight intermediate cylinders are designated as C2 to C9 from top to bottom. Longitudinal welds of the separate layers are staggered on the circumference.

There are four leak detection holes with leak detection tubes and six weep holes in each cylindrical section. Two of the four leak detection tubes are inlets and others are outlets of the steam, which used for leak detection (see Figure 3 and Figure 4). The leak detection tube is connected with the layer by conical thread, as is shown in Figure 5. Between the liner and the innermost carbon steel layer is an open space with the leak detection steam. The steam pressure is about 1 MPa. The steam flows into the outer surface of the liner through the steam inlet pipe in the upper section of each cylinder. Then the steam flows out from the outlet pipe in the bottom section of the same cylinder. The operator checks the pH with pH indicator paper every hour. Once the liner starts leaking, the contents will come out and dissolve in the steam. The operator could judge whether the liner of the urea reactor is in-

Figure 1. Schematic structure of the damaged urea reactor
The design pressure and temperature of the reactor are 21.57 MPa and 195°C respectively. The operating pressure of the reactor is 19.6 MPa. The operating temperature is 188°C at the top of the reactor and 178°C at the bottom. The reactor was manufactured in Dec. 1999 and put in service in March 2000. After just 5 years in service, it exploded.

Failure information

The reactor was broken into three parts. The bottom part containing C10, bottom head and skirt support were still sitting on the reactor as shown in Figure 6. The macro fracture surface appearance of the bottom section is shown in Figure 7. The intermediate section, containing a cylindrical multilayered shell, was fractured longitudinally from the position where the thermowell was installed and torn along the circumferential welds above and below. All
layers of this section were unfolded into plates and rolled back. The liner was exposed to the air and the outermost layer reversed into the innermost one (see Figure 8). The macro longitudinal fracture surface appearance of the middle section is shown in Figure 9. The middle section was ejected to the working house. The distance to its original site is 14 m. The top section was the largest one of them, containing eight cylinders and a top head. It flew off far away from its original site and was buried about three-quarter length of itself, as is shown in Figure 10. The circumferential macro fracture surface appearance of the top section is shown in Figure 11. The distance between the landing sites to the installation location was 86 m. The locations of the three sections after explosion are shown in Figure 12.

Figure 6. Bottom section, which still stood on the support.

Figure 7. Fracture appearance of bottom section. The total fracture surface looks flat, and most of layers were torn with shear fracture surfaces.

Figure 8. Damaged middle section. All layers in this section were unfolded into plates, and rolled back, that was the liner was exposed to air, and the outmost layer changed into the innermost one.
Failure analysis

There were two different two thoughts on the potential causes of urea reactor explosion and they were chemical explosion and vapor explosion. The following would discuss the possibilities of chemical and vapor explosion in the urea reactor.
Possibility of chemical explosion

There was a small gas phase layer at the top inner space of the urea reactor (see Figure 13), where some explosive gas might have accumulated. The feed material into the reactor through three channels could have carried explosive gas. Firstly, the hydrogen gas, nitrogen gas and methane were carried into the reactor when feeding carbon dioxide. Secondly, some of the feed ammonia was also in gas state under the given pressure and temperature in the urea reactor. Finally, in order to reinforce the corrosion resistance ability of the stainless steel liner, some oxygen, usually supplied as air, was fed into the reactor together with carbon dioxide. During the normal production hours, the pressure and temperature of the contents in the reactor fluctuated in a very small range. In the gas phase layer, the partial pressure of ammonia gas and carbon dioxide was much higher than that of hydrogen, methane and oxygen. Under this condition, the partial pressure of explosive mixed gases was greatly out of the explosion limit range of ammonia-nitrogen-oxygen and hydrogen-nitrogen-oxygen.

During a shutdown, the inner pressure of the reactor drops continuously as the shutdown time is prolonged. Thus, the previous gases dissolved in the liquid would be desorbed and the partial pressure of explosive gas would increase. Moreover, condensation of some ammonia vapor in the gas phase layer might occur in winter; especially in the north of China. It might result in the mixed gases of hydrogen-nitrogen-oxygen reaching the explosion limit. The gas under this condition will explode when the urea reactor is restarted and the urea outlet valve is opened. The source of ignition for this explosion is the electrostatic charge spark, which generates from friction of high-speed gas flow and valve during the valve opening operation. This type of explosions is uncommon because the spark was not easily formed. However, there have been several chemical explosion cases of urea reactors in China.

- On Jun.28, 1983, a chemical explosion took place in gas phase space during restarting process after short shutdown in Shanxi chemical fertilizer plant. Urea outlet pipe in the gas space part was ruptured, separated into 37 fragments. The reactor body didn’t swell and rupture.

- On May 8, 1985, a chemical explosion occurred in outlet pipe during restarting process after short shutdown in Lunan chemical fertilizer plant. The gas in subsequent First Decomposer was detonated simultaneously and the trays were destroyed severely. The reactor body didn’t swell and rupture.

- On Oct.27, 1992, a chemical explosion took place in gas phase space during restarting process after short shutdown in Haolianghe chemical fertilizer plant. The Urea outlet pipe in the vapor space part was ruptured; the
flange in the end of outlet pipe leaked and a fireball was ejected. The urea reactor body shell was not destroyed.

- On Nov.27, 1992, a chemical explosion happened in gas phase space 22 hours after shutdown in Haolianghe chemical fertilizer plant. The cut-off valve filler was ejected. The urea reactor body shell was not destroyed.

The similar characteristics of chemical explosion accidents of urea reactors can be summarized as follows: the explosion occurred in the restarting operation after a short downtime, the failure component was near the explosion location, at the top part of the urea reactor.

Obviously, the Pingyin’s urea reactor was completely different from the cases described above. The trays under the top tray were destroyed completely, however, the top tray survived (see Figure 14). The outlet pipe and thermocouple pipe was not damaged (see Figure 15). According to the results of the explosion experiments conducted by Zheng J.Y. [2], the biggest deformation and fracture of pressure vessels were found at the explosion center under internal explosion loading condition. The reactor’s cylindrical shells near the bottom part were destroyed. The only explanation was that chemical explosion in the gas phase space couldn’t be a cause. Other explosions might have occurred in the accident.

![Figure 14. Tops tray and the destroyed trays below](image1)

Figure 14. Tops tray and the destroyed trays below

![Figure 15. The outlet pipe and thermocouple pipe, which were not damaged in the explosion.](image2)

Figure 15. The outlet pipe and thermocouple pipe, which were not damaged in the explosion.

Possibility of vapor explosion

The possibility of chemical explosion in a urea reactor has been discussed in the section above. Unfortunately, the failure form of Pingyin’s urea reactor didn’t have any similar feature with the former cases. So, we conclude a mechanical fracture of the reactor might have occurred in Pingyin’s urea reactor destruction. Thus, the possibility of a mechanical fracture followed by a vapor explosion will be discussed. If a vapor explosion occurs due to mechanical damage of the vessel, two sufficient conditions must be created. One, the contents in the vessel would be superheated when the pressure drops to ambient pressure. Another is that large leakage takes place instantaneously.
The contents in the urea reactor

A complete recycle process of aqueous solution was applied for this urea reactor. The ammonia and carbon dioxide were fed into the reactor through the inlet pipes on the bottom head. There was also another inlet pipe for the recycled solution of ammonium carbamate. The ammonia and carbon dioxide reacted and synthesized into ammonium carbamate. The liquefied urea was produced by the dehydration of ammonium carbamate and flowed out of the reactor through an outlet pipe on the top head.

The contents in the urea reactor are subjected to high temperature and pressure. The mixture in a urea reactor will keep vapor-liquid phase at equilibrium under normal operating conditions. Engulfing the external fire, or mechanical damage due to impact, or the sudden propagation of the initial small defects, especially sub-stable cracks due to weld or corrosion, SCC in the reactor wall during its service time, may lead to a catastrophic vapor explosion accident. In this situation, when the inner pressure of the urea reactor drops to a certain low value, the liquid will be superheated suddenly. It will trigger phase transformation of the superheated liquid into vapor. The volume of the liquid increasing rapidly when it vaporizes will generate a strong pressure wave.

Initial fracture of C9

The leakage from a vapor explosion is an instantaneous process of loss of contents. It is different from when the reactor contents penetrate through the pinhole in the liner. Why was C9 of this urea reactor damaged so seriously? Where was the initiation point of this explosion? The answer will be given in the follow sections.

As is shown in Table 1 and Table 2, the composition and the mechanical properties of steels used in the construction of the reactor meet the required mechanical properties of the standards in China.

From our investigation of the longitudinal fracture surface appearance of the damaged C9, it seems that the layers had been damaged before the explosion. They were many old fracture surfaces under and around the thermocouple pipe. As shown in Figure 9, the longitudinal fracture surface of C9 passes through the thermowell. The fracture surface is brittle in every layer under and around the thermowell except the liner. A great deal of longitudinal and opening cracks under the thermowell can be seen near the main fracture plane. The fracture surface above the thermowell is an inclined ductile fracture. There were no small cracks that could be found in every layer near the main fracture plane above the thermowell. The different fracture appearances suggest they were destroyed by different ways.

The SEM photograph of the fracture surface under the thermowell of the 2nd layer is shown in Figure 13. The fracture surface is characterized by intergranular pattern on a micro level. There are lots of corrosion grooves and pits on grains surface, as well as the secondary intergranular cracks. The cracks in the 1st and the 6th layer propagated along grain boundaries consisting of ferrite and pearlite are shown in Figure 14 and Figure 15. The liner fracture can be characterized as shear dimple pattern; the expansion force in the explosion might generate it.
Figure 13. The intergranular fracture of the 2nd layer of C9.

Generally speaking, the fracture surface resulting from explosion will be characterized by transgranular pattern. From crack appearances we can confirm that cracks in layers were not formed in the explosion. They had the typical characters of SCC. There were also many cracks in the other cylinder layers, and their appearances were also similar to the characters of SCC.

Table 1 Chemical composition of steels (%)

<table>
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<tr>
<th>Materials</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>V</th>
<th>N</th>
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<tr>
<td>316L</td>
<td>0.023</td>
<td>17.30</td>
<td>13.19</td>
<td>2.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q235-A</td>
<td>0.19</td>
<td>0.023</td>
<td>0.0035</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16MnR</td>
<td>0.17</td>
<td>0.018</td>
<td>0.0050</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manor</td>
<td>0.14</td>
<td>0.023</td>
<td>0.088</td>
<td>0.0044</td>
<td></td>
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</tbody>
</table>

Table 2 Mechanical properties of steels

<table>
<thead>
<tr>
<th>Materials</th>
<th>Elastic modulus / MPa</th>
<th>Poisson’s ratio</th>
<th>Yield strength / MPa</th>
<th>Tensile strength / MPa</th>
<th>Density / Kg/m³</th>
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<tr>
<td>316L</td>
<td>2.00×10⁵</td>
<td>0.280</td>
<td>170</td>
<td>485</td>
<td>7980</td>
</tr>
<tr>
<td>Q235A</td>
<td>2.12×10⁵</td>
<td>0.288</td>
<td>235</td>
<td>375</td>
<td>7800</td>
</tr>
<tr>
<td>16MnR</td>
<td>2.07×10⁵</td>
<td>0.286</td>
<td>345</td>
<td>510</td>
<td>7800</td>
</tr>
<tr>
<td>15MnVR</td>
<td>2.08×10⁵</td>
<td>0.275</td>
<td>390</td>
<td>550</td>
<td>7800</td>
</tr>
</tbody>
</table>

SCC in the weld and C8

If SCC was prevalent in C9, SCC must have existed in other zones away from the exploded section because they had similar structures and running conditions. Based on this, we had made specimens from the upper section of C8 and the weld zone between C7 and C8. The fracture surface appearance of the annulus is a typical intergranular fracture, so are the 1st and 2nd layers of C8, as is shown in Figure 17, 18 and 19 respectively. The macro appearance of the cross-section of weld is shown in Figure 20; it also has the typical appearance of SCC.

Figure 14. The micro appearance of crack in the 1st layer of C9
The mechanism of SCC of layers

Generally, for SCC, three conditions must exist: tensile stresses, certain steels and sensitive substances.

Layers of the urea reactor endure tensile stress during normal operating conditions. There is a stress concentration in the zone around the thermowell due to the discontinuity of structures. The X-ray energy spectrum inspection shows that the main components of the corrosion products in the fracture surface are S, Si, Na, K and Ca. Na and K are not the elements of contents in the urea reactor, they have not resulted from the leakage of liner. The desalt water used for the generation of leak detection steam contained Cl⁻5.4mg/L, \( \text{CO}_3^{2-} \) 13.02mg/L, \( \text{NH}_4^+ \) 15.82mg/L, \( \text{K}^- \) 0.013mg/L and \( \text{Na}^+ \) 0.181mg/L. They might be brought into interlayer by the leak detection steam. In the normal condition, for the middle layers, they have no access to the substance such as Na and K except the fracture of the 1st layer or the sealing failure of the conical thread. As shown in Figure 5, when the seal of leak detection tubes failed, the steam could flow into every interlayer. Obviously, it was not a good structure for seal. There are many cases of sealing failures due to the vibration in the transport or production process of urea reactor. We have suggested to the fabricator plant to develop this structure. The fabricator should be responsible for the bad sealing structures of leak detection tube. The presence of \( \text{Na}^+ \) and \( \text{K}^+ \) may create an alkalescent solution environment, which can induce the SCC of low alloy steel. The operator should bear the responsibilities for the high \( \text{Na}^+ \) in the steam for leak detection.

Figure 15. The micro appearance of crack in the 6th layer of C9

Figure 16. The dimple fracture of the liner of C9

Figure 17 The intergranular fracture of annulus of C8
Thus, the explosion reason and process can be described as follows: many cracks, some of them even very large, existed in the carbon steel annulus and low alloy steel layers. They were generally in the same location in each layer. When the weakened layers couldn’t endure the inner pressure of the urea reactor, cracks in the annulus and layer C9 propagated rapidly and the liner was torn due to the total pressure acting on it. In this situation, leakage from the reactor occurred resulting in rapid depressurization of the reactor. This resulted in a catastrophic vapor explosion. The longitudinal rupture propagated up and down, and changed direction when it encountered the top and bottom circumferential welds of C9. The circumferential welds were ruptured and the urea reactor was broken into three main parts, as is shown in Figure 21.

As a matter of fact, urea reactors have suffered vapor explosion several times in the past. They can be divided into three catalogues. They are (a) the ammonium carbamate penetrated the reactor’s liner due to the defects in liner. Then the outer carbon steel or low alloy steel layers were corroded at a very high speed, as the case that a urea reactor exploded in Colombia, 1977[3]; (b) the initial manufacture defects in the heavy
circumferential weld. The crack propagated under the high pressure, especially when the pressure fluctuated, and a larger break formed, as the case that a urea reactor exploded in China, 1995; (c) the cracks in feed pipe of ammonia liquid, enlarged suddenly, as the case that a urea reactor exploded in Burma, 2004[4]. At this situation, the alkalescent solution environment induced the stress corrosion cracking of outer layers at the same location.

Conclusion

From the discussion above, we can come into conclusions as follows:

- Pingyin’s urea reactor suffered fracture due to SCC followed by vapor explosion that ruptured it into three pieces. For such a reactor, the high temperature contents, especially liquid ammonia and water, would transfer into vapor rapidly when the inner pressure dropped to a low level due to the leakage. Both the fabricator and operator are responsible for the SCC in layers and weld.

- The fundamental method for prevention of vapor explosion is how to reduce the possibility of leakage. Vapor explosion is an instantaneous process of energy release. Once the vapor explosion takes place, the catastrophic accident becomes inevitable due to the high speed of phase transformation. Under this condition, maintaining the integrity of the reactor may be an effective method to prevent vapor explosion. This method may include improving the detection ability of a defect in the liner or in layers with advanced non-destruction testing techniques. A leakage detection system should be developed due to impurities in steam-damaged steels.

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References