Explosion and Fire of Hydroxylamine

【June 10th, 2000　Ojima Town, Gunma, Japan】

Hiroshi Koseki.　(National Research Institute of Fire and Disaster)
Mitsuo Kobayashi (Graduate School of New Frontier Sciences, University of Tokyo)
Masamitsu Tamura (Graduate School of New Frontier Sciences, University of Tokyo)

In Oji ma Town, locat ed in the southwest area of Gunma Pref. near the b oundary with Saitama Pref. a large expl osion of hydroxylamine occurred a t the Niss hin Chemical Industry Co. Ltd Gunma factory , wh ich is next to the national road No.17 and No.354. The explosion power of hydroxylamine is almost equivalent to the famous explosive TNT.

After 18:00 on Saturday June 10th, 2000, the explosion occurred suddenly at the re-distillation column resulting in a fire. A pillar of flames like a flash spouted out from the factory at the moment of the explosion. The damage involved the housing area that adjoined the factory . Four persons were killed and 58 persons w ere injured in the accident. 54 persons of injured persons wer e residents living near the factory . The re-distillation column disintegrated without leaving any t race, and t he factory was severely damaged. Damage outside of the factory included the complete collapse of two buildings, severe damage to five buildings and partially damage to 285 buildings.

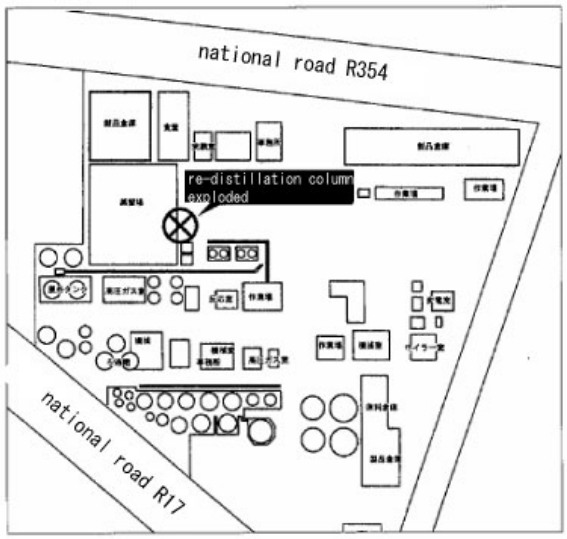

Fig. 1 Overview of the factory

The plant where the accident occurred was manufacturing a 50% aqueous solution of hydroxylamine, which contained nearly zero level impurities such as a ferrous ion. The

high purity hydroxyla mine has recently b een used as s emiconductor removers and metal surface tr eatment agents. The fe ed stock of 50% hyd roxylamine that was contaminated with about 40 to 50 ppb ferrous ion was f ed into the bott om circulation line in the c olumn whe re the 50% h ydroxylamine was evap orated, in or der to obtai n products with under 1 ppb ferrous ion. The concentration of the bot tom ci rculation liquid reached 80 to 85% as a result of concentration of the 50% feed stock. A part of the solution was drawn off from the circulation line in order to prevent the concentration of a ferrous ion from the dangerous zone.

This accident seemed to be ca used by an explosion of the 80 to 85% high-concentration hydroxylamine aqueous solution at the bottom of the column and in the botto m circulation l ine, and th e exp losion exp anded to the near by equip ment. High-concentration hydroxylamine has a dangerous tendency to decompose explosively at high te mperatures, and it may explode even at ambient temperature if th e ferrous ion concentration incr eases. It was not possible to p erfectly elucidate t he cause of the explosion, because the area around the re-distillation column was completely destroyed, and all the operators w ere killed. Since the emergency draw-off line branched from the bottom circulation line and a valve was mount ed at the li ne, the pa rt of the draw-off line from the branch point to the valve became dead-end piping. There is a possibility that the ferrous ion concentrat ion in the de ad-end piping had be come high and it is regarded as one of the cause of the accident.

At least eleven examp les have bee n reported as accid ents caused by hyd roxylamine in the past twenty years. Although the company was sufficiently aware of the danger, and appeared to have ta ken appropriate co untermeasures against the d anger, still t he accident occurred. After the a ccident, the company stopped m anufacturing of the 50% aqueous solution of hydroxylamine.

The cause was not complet ely clarifie d, as described abo ve. Furtherm ore, hydroxylamine was not designated as a d angerous material und er the fire p rotection law at the time of the a ccident. However, after the accident, both the hydroxylamine aqueous solution and salt were d esignated as self-reactive materials in the No .5 group of the fire protection law's classification of dangerous materials. However, regardless of the designation in the law, it is necessary for manufacturing plants and processi ng facilities that treat hi gh-concentration hy droxylamine t o prepare a dequate safety countermeasures, considering both its explosion power and handling volume.

1. Event

The company that caused the accident had been manufacturing and selling

hydroxylamine used for medicine and pesticides. In addition, from 1982 they also manufactured and sold a 50% aqueous solution with a very low level of contaminant nearly equal to zero under the trade name of "Free hydroxylamine", which was used for semiconductor removers and metal surface treatment. "Free hydroxylamine" was manufactured from a 50% aqueous solution by decreasing the ferrous ion concentration from 40 to 60ppb in the 50% solution to be low 1 ppb using re-distillation column. The 50% hydroxylamine aqueous solution was obtained by concentrating a low concentration of hydroxylamine made by two kinds of manufacturing processes.

The method of re-distillation was as follows. A large amount of 80-85% hydroxylamine aqueous solution was circulated at the bottom of the column. A feed stock 50% hydroxylamine was fed to the circulating liquid, and the whole circulating liquid was heated and partially evaporated, and then charged to the column. The column was operated at a vacuum of 20 to 30torr, and the temperature was controlled so that the vapor concentration should be the same with the 50% feed stock. As the vapor pressure of a ferrous ion is almost zero, ferrous ions remained at the bottoms without being entrained, and were accumulated in the bottom circulation. The vapor at the top of the column was totally condensed, and after adjusting concentration, it was shipped as "Free hydroxylamine". The flow of the Re-distillation column is shown in Fig. 2.

A part of the bottom circulation was continuously drawn off so that the ferrous ion concentration would not exceed the danger threshold. About 4% of the feedstock was drawn off in order to keep the concentration at 3ppm or less. An emergency line branched from the bottom circulation line for emergency evacuation of the circulating liquid at the column bottom into the underground vessel for cooling and diluting, when a temperature rise was detected. There was about 70 to 80 mm of a dead-end piping between the stop valve and the branch point. The valve had never been opened after the initial start-up.

On the day of the accident, the oil of the vacuum pump of the column became dirty, and after stopping the operation of the column and exchanging the oil, operation was restarted at around 17:30. The start-up began by starting of the bottom circulation, next the feedstock supply, and then the vacuum pump. Finally the steam supply to the vaporizer started. After about 39-40 minutes from the re-start, the explosion occurred suddenly at 18:08.

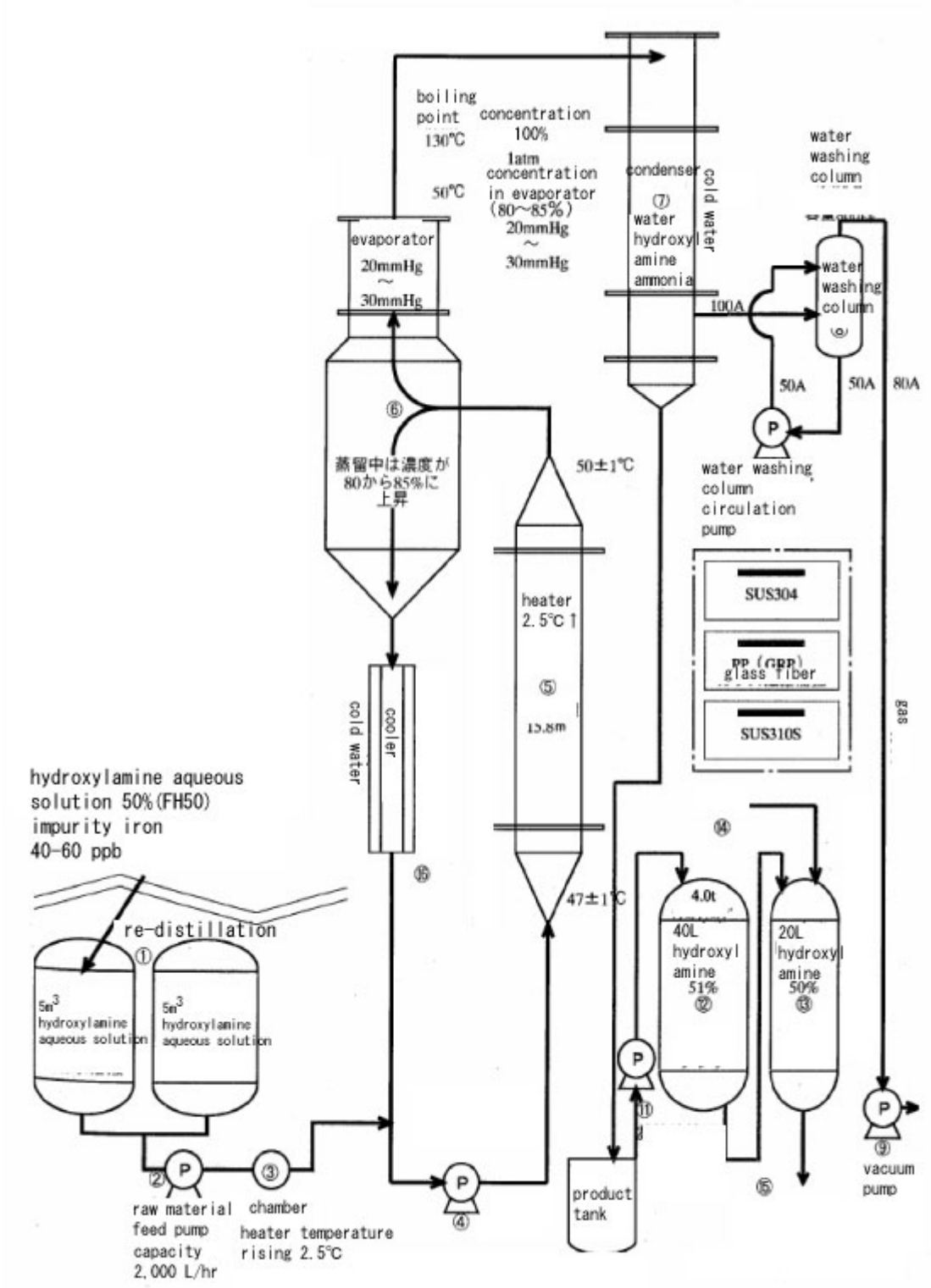

Fig.2 Flow sheet around the re-distillation column

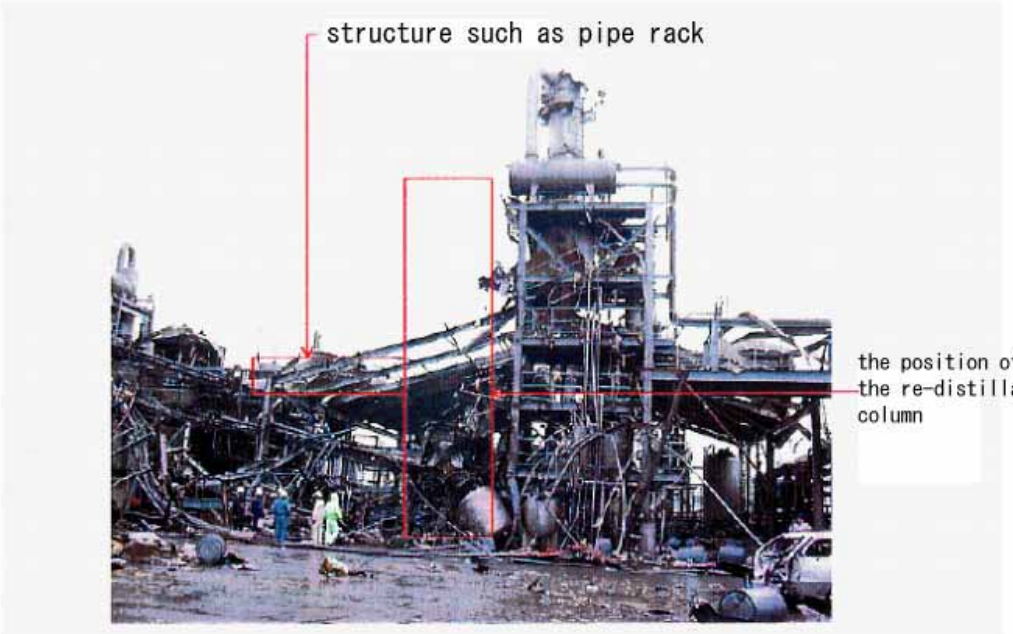

Fig. 3 Photo of the re-distillation column after the accident

2. Course

1.1. Progress on the day

At 13:30, shutdown work of the re-distillation column started, and the shutdown work finished at 14:00. The exchange of the oil of the vacuum pump, which was the cause of the stop, was carried out.

At 15:45, the preparations for re-starting operation began, and the operation restarted from 17:20 to 17:30.

An explosion occurred at 18:08, and a large sound was heard from around the cooler nearby the vacuum pump.

At 18:11, the fire fighting team turned out, and the traffic of the national road next to the plant was restrained at the same time.

At 23:10, the extinguishment of the fire was confirmed.

1.2. History of the company

The company was established in 1953, and manufacture and sale of hydroxylamine hydrochloride was started. A new factory was established in1960 at the site where the accident occurred. The hydroxylamine sulfate manufacturing facilities were constructed in 1977, and the hydroxylamine hydrochloride manufacturing facilities were established in 1980. The sale of “Free hydroxylamine” started in 1982 ,

and the manufacturing capacity of “Free hydroxylamine” increased to 8000 tones per year in 1988.

2. Cause

All four operators died, and the operation record was destroyed. Furthermore, the re-distillation column was also completely disintegrated, and so investigation into the causes of the accident was very difficult. The cause was estimated from status investigations, interviews of the related parties, characteristics of hydroxylamine, and so on. Though the cause could not be made perfectly clear, it was estimated to be as follow.

The material that exploded was 80 to 85% hydroxylamine at the bottom of the column and in the bottom circulation line, which was estimated from the fact that the detonation position was in the column, that the explosion had occurred at the circulation line or near the heater, and that the only flammable material that existed in the column was the 80-85% aqueous solution. It was confirmed that the detonation of 80 to 85% hydroxylamine aqueous solution was possible from experiments on the explosive properties and calculations.

As for the cause of the accident, following three possibilities were considered; 1) a rise in the ferrous ion concentration, 2) a rise in the temperature of the aqueous solution, and 3) a rise in the aqueous solution concentration. As a result, it was shown that the cause was the "partially rise in the concentration of a ferrous ion that had accumulated in the dead-end piping in the emergency piping ".

3. Process of cause elucidation

At first, the place where the accident occurred and material that caused the explosion were estimated. Interviews and examination of the situation after the explosion showed that the explosion had occurred at the lower section of the column or at the circulation system of the bottom liquid. Only the 80 to 85% hydroxylamine aqueous solution existed in those places, and the solution had the possibility of detonation. Therefore, the 80 to 85% concentration hydroxylamine aqueous solution was concluded to be the material causing the explosion.

Three possibilities for the cause of the accident were given, as described in the “cause” section above. First, the possibility of a temperature rise was rejected from the consideration of the temperature control system and the fact that the temperature rise alarm did not ring. The possibility of a temperature rise by the destruction of the vacuum system was also considered to be low, because only the lower section was

destroyed severely. A rise in the concentration of the circulation liquid was also rejected, because 1) the area of severe destruction was limited to the lower part, and, 2) the temperature at which decomposition starts is about 130℃, is not lowered, even if the concentration rises, and the outlet temperature of the evaporator was only about 50℃. Therefore, only a rise in the ferrous ion concentration remained. The possibility of an insufficient quantity of chelate of the inhibitor was also rejected because the sample taken on the previous day was normal and the feedstock of the day of the accident was from the same lot as that of the previous day. There is no possibility that ferrous ions could have been supplied by rapid dissolution, because stainless steel was used as the material of the column and piping. So by the process of elimination, the cause was estimated to be an increase in the ferrous ion concentration at the downward dead-end piping located in the emergency line which had been accumulated over the long-term operation.

4. Immediate action

There is no record of immediate actions conducted. It is estimated that no actions could be taken immediately because the explosion was too rapid and large.

5. Countermeasure

No concrete countermeasures were taken, because the manufacture of "Free hydroxylamine" was stopped. Furthermore, no concrete countermeasures have been shown in the report of previous accidents that have occurred overseas.

6. Knowledge

1) Even if previous accidents have occurred in foreign countries, the information is not useful, if there is no detailed report of the cause and countermeasures of the accident and/or if the receiver has insufficient ability to understand the report.
2) It is desirable that factories that handle dangerous materials are located far away from the places where a lot of people gather or where a large number of the private residences are located.
3) There are a lot of examples of accidents that have been caused by dead-end piping. Although the appearance of each accident is different, the accidents can be divided into two types. One pattern is the accident that occurs at the contact position of a flow part and no flow part, and the other is that occurs because of no flow.

7. Influence of failure

The factory was near the intersection of two national roads. The place was a key point of the traffic, and there were many stores and private houses along the national roads. The Ishidagawa River was flowing nearby. The explosion caused damage in a 1500m radius of the factory.

As for the human damage, four persons died and 58 persons were injured including 54 persons living in the area outside the factory.

As for the physical damage, the column where the explosion occurred was completely disintegrated and many buildings in the factory site were damaged. Outside of the factory, two buildings were completely destroyed, five buildings were half destroyed and 285 buildings were damaged partially, and 47 cars were damaged.

As for the social damage, the local traffic was regulated, the power was cut for 249 households, telephone service was interrupted for 47 lines, and using city water was prohibited in the east district of the prefecture due to the death of fish in the Ishidagawa River near the place of accident.

8. On the side

There seems no domestic manufacturer any more, since it is too dangerous at present. As shown in the "Cause" section, the only one possibility, which remained as the cause of the explosion, is the emergency blowdown piping. If the cause is correct, the piping, which was mounted for preparation for very rare troubles, was the cause. It is very unfortunate. Although it has not been specified in the reports, probably the piping branched off from the lower part of the main piping. If the piping had branched off from the upper part, the remained possibility might be also rejected. There are some accidents that are caused by a mistake in the direction of the branch piping. Careful attention and adequate consideration are necessary even in the design of simple piping.

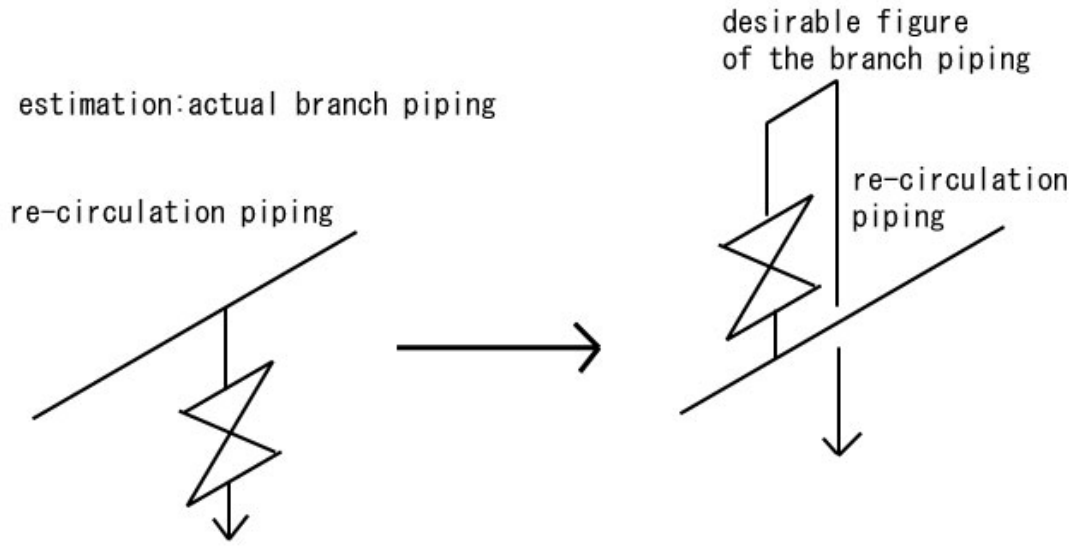

Fig.4 about the branch piping

References

- Dangerous Material Safety T echnique A ssociation, "Investigation Report on hydroxylamine explosion and fire accident occurred at th e chemical plant in Gun ma Prefecture" (2001)
- Masamitsu T amura, "Safety countermeasu re learn ed from r ecent accidents at chemical plant", Seminar on accident cases due to hazardous materials, 1-17 (2001)
- Sakae Kajima, Fire-Defense Headquarters, Ota District Fire Fighting Uni on, "Situation of explosion and fire accident occurred in Nisshin Chemical Industries and extinguishing and rescue operation with to ugh and difficult y", Sem inar o n accide nt case due to hazardous materials, 19-39 (2001)
- Terushige Ogawa et all, " Hydroxylamine explosion", Saigai no Kenkyu, 32,233-242(2001)