Investigation Report

An explosion accident during tank repair at a chemical plant

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1 Introduction

At a chemical plant, during work to attach a stiffening plate to a concentrated sulfuric acid tank, the tank suddenly exploded while the contact surface of the tank was being sanded. As a result, three persons were seriously injured and one was slightly injured, all of whom are workers of a subcontractor. The explosion damaged the concentrated sulfuric acid tank, the blast broke the exterior wall of the adjacent ammonium sulfate storage building, and the top board of the tank, which was blown off, gave damage to the electric room.

2 [Omission]

3 Outline of the accident

3. 1 [Omission]

Figure 1: [Omission]

3. 2 Outline of the workplace

(1) - (2) [Omission]

(3) Category of business: Chemical industry

(4) Outline of the workplace

The workplace primarily produces basic chemicals, including tar distillation products, ammonium sulfate, and sulfuric acid, from coal tar and coke oven gas called C gas obtained in the manufacturing process of coke for iron making and other materials. Figure 2 shows the material flow sheet for the entire workplace. Figure 3 shows the flow diagram of the sulfuric acid facility in the C gas purification process. Figure 4 shows the layout of C gas purification facilities. Figure 5 shows the concentrated sulfuric acid tank (044 tank) that caused the accident. Note that this concentrated sulfuric acid tank was converted from the desulfur tower.

3. 3 Circumstances before the accident

(1) Four days before the accident, signs of oozing were detected at two places by visual observation (Figure 6). Oozing seemed to be occurring at a height of five meters just around the liquid level. To prevent concentrated sulfuric acid from leaking, concentrated sulfuric acid in the tank was discharged and its liquid level was lowered.

(2) At 8:40 on the day of the accident, arrangements for work were made and fire prevention measures were taken.

(3) At 9:20 on the same day, work started.

(4) At 9:45 on the same day, gas-detecting operation was performed at the external parts of

oozing, and it was confirmed that there was no leakage of inflammable gas or carbon monoxide.

(5) At 9:50 on the same day, sanding started, and at 9:54 the explosion occurred.

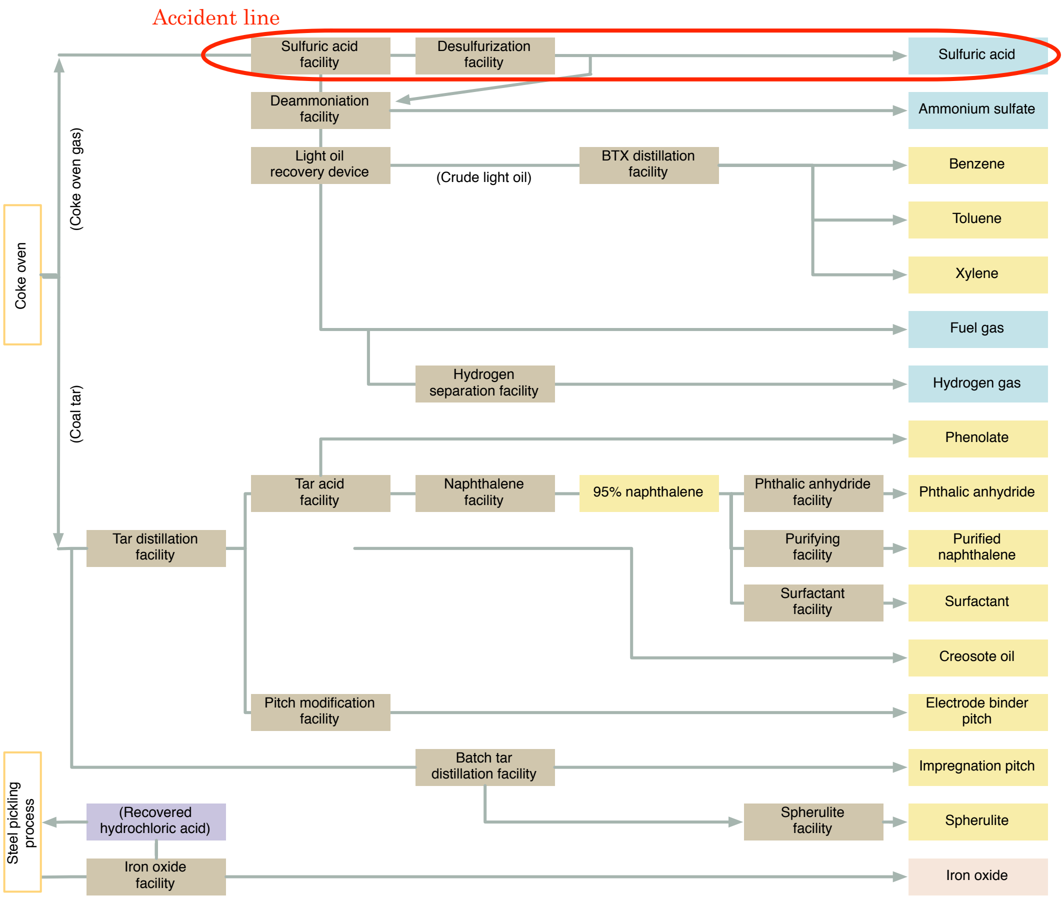

Figure 2: Material flow sheet for the entire workplace

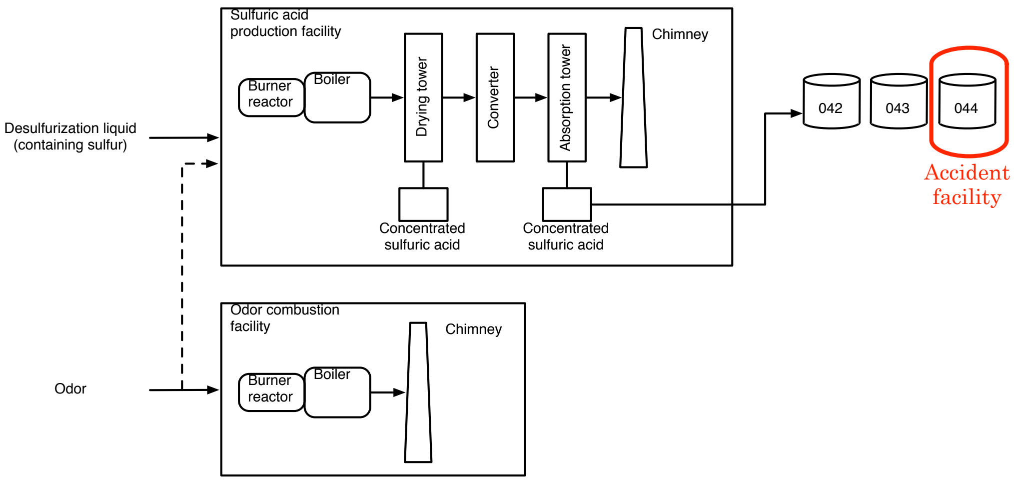

Figure 3: Flow diagram of the sulfuric acid facility in C gas purification (during normal operation)

Figure 4: [Omission]

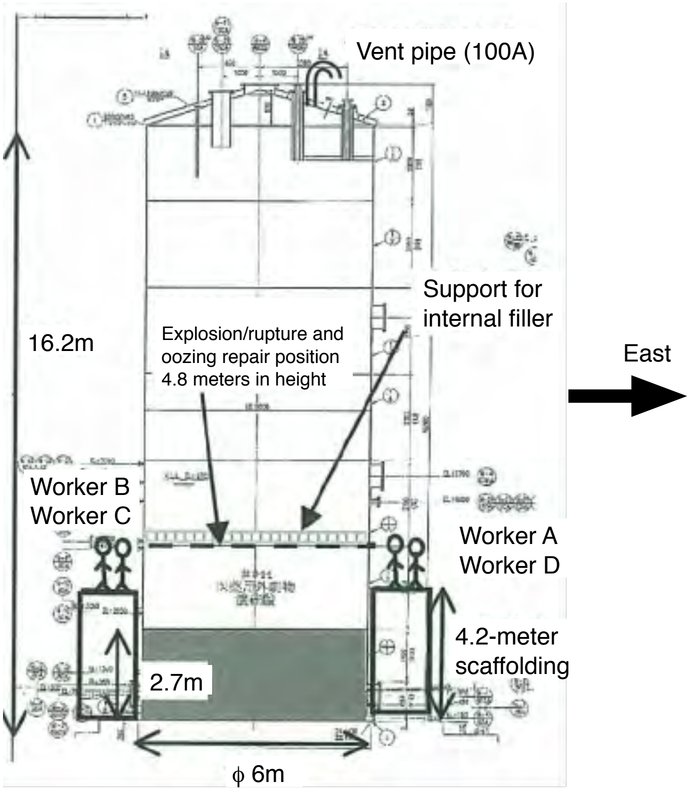

Figure 5: Schematic drawing of 044 Tank (Wokers' location at the accident)

Figure 6: Oozing observed before the accident

3.4 Extent of the damage

(1) [Omission]

(2) Material damage

Damage to the concentrated sulfuric acid tank, damage to the exterior wall of the adjacent ammonium sulfate storage building caused by the blast, damage to the electric room brought by the top board of the tank that was blown off, and other damage.

4 Investigation into the cause of the accident

4.1 Substance that caused the explosion

C gas, composed mainly of hydrogen and carbon monoxide, is highly inflammable by its nature. However, since this workplace is a facility that processes sulfur content extracted from gas and has the burner reactor in the previous stage, C gas is unlikely to flow into the tank.

The 044 tank that exploded was made of SUS304 and SS41 (previous name per JIS: SS400) and has not undergone a process of surface protection inside, including lining, since the time it was used as a desulfur tower. Therefore, a reaction with sulfuric acid can generate hydrogen. In the case of concentrated sulfuric acid, however, the amount of water contained is too small to facilitate the generation of ionized hydrogen, and generally the dissolution rate of iron is sufficiently low in concentrated sulfuric acid. For this reason, SS400 and other similar materials are widely used for concentrated sulfuric acid tanks. Nevertheless, if concentrated sulfuric acid is diluted with water for some reason, the generation of hydrogen can be facilitated.

As a possible cause of dilution with water, the leakage of rainwater is considered. There is little record on the inspection of the inside of the tank, with the only record being about opening a manhole when the facility was converted. And since the top board part (Figure 7) was blown off by the explosion and reached the adjacent electric room (Figure 4, upper right), it is not possible to examine if any leakage had occurred just before the explosion. If, meanwhile, rainwater comes into the tank through the top, mixing is only by diffusion because the specific gravity of concentrated sulfuric acid is heavier than that of diluted sulfuric acid and thus convection is not generated. In this case, the layer of diluted sulfuric acid is formed in the uppermost part of the concentrated sulfuric acid in the tank and can lead to a disaster like this accident if the diluted sulfuric acid erodes the tank.

In addition, as concentrated sulfuric acid is hygroscopic in itself, even if there was no rainwater leakage, sulfuric acid concentration may decrease at a portion near the liquid level if left under high humidity. The inside of the 044 tank comes in contact with the outside air via the vent 100A pipe that was bent into a J-shape, reversed, and attached to the top board (Figure 7). So the sulfuric acid inside the tank could have been diluted if the tank was left under the outside air with humidity high enough to develop a dense fog for a long time. However, the 100A pipe is thin with respect to the tank capacity, which accordingly limits the amount of moisture that comes in and out, suggesting that outside air humidity is unlikely to have decreased the concentration.

Although the possibility of the above two causes cannot be eliminated, the investigation revealed a higher probability of dilution as described in 4.3. Therefore, it can be considered that the primary cause was dilution (as described in 4.3) and the explosion was caused by the mixture of hydrogen and the air.

Figure 7: The 044 tank top board (blown off and separated from the tank, the original position was upside down)

4.2 Ignition source

The absence of inflammable gas was confirmed according to work instructions by using a 4-point gas detector (inflammable gas, carbon monoxide, hydrogen sulfide, and oxygen) at the scaffolding on the east side just before the explosion. However, as detecting operation was performed only at the outside of the container, the concentration of the inside is considered to have been undetectable. Figure 8 shows a ruptured section of the 044 tank. The ruptured part showed apparent thinning that ranged from several centimeters to several dozen centimeters heightwise. This part is considered to have appeared as oozing four days before the accident, opened wide at the time of marking-off or sanding, and leaked the gas mixture out of the tank. It is highly likely that this leaked gas or internal gas was ignited by sparks generated by the sander. Note that after oozing was found, the 044 tank was used mostly for discharge and its liquid volume was continuously decreased to prevent the leakage of sulfuric acid (Figure 9); therefore, the back side of the oozing area was a gas phase.

Figure 8: Ruptured part showing apparent thinning

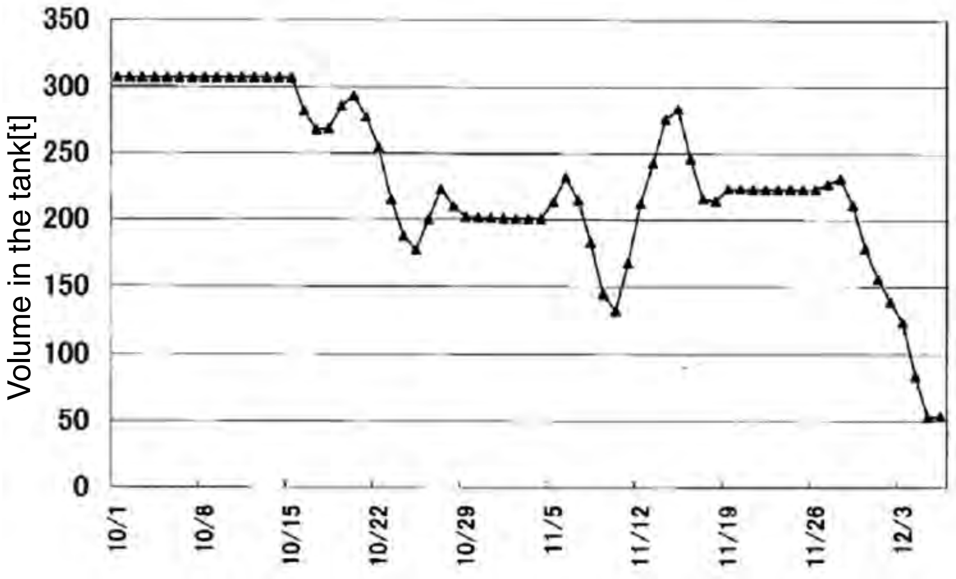

Figure 9: Sulfuric acid volume in the 044 tank

4.3 Cause of sulfuric acid dilution

The facility that caused the accident is mainly used to obtain high-purity sulfuric acid by burning desulfurization liquid coming from the desulfurization facility but sometimes also used to remove odors of exhaust gas and other substances as shown in Figure 3. There is another odor treatment facility, but the investigation found that this odor treatment facility had been undergoing the annual inspection since one week before the accident, and thus the facility that caused the accident was used as an alternative to the odor treatment facility. During that period, the facility only treated odor, which accordingly did not make sulfuric acid obtained at the drying tower sufficiently concentrated. As a result, sulfuric acid that was more dilute than usual was transferred to the 044 tank on November 26. This is the primary cause of the accident.

Examining sulfuric acid that was left in the drying tower confirmed that its concentration was approximately 20%. This concentration is low enough to erode iron. In addition, the facility was converted from the desulfur tower and had a shelf to put catalysts and other substances inside, the aspect which is different from regular tanks. Therefore, the surface of the wall has many welded parts that can be easily eroded, and the shelf itself also has many parts that can be easily eroded.

4.4 Mechanism of the occurrence of the accident

This accident is a gas explosion accident caused by the explosion of a mixture of hydrogen and the air. Hydrogen was generated by reaction between sulfuric acid and the tank, which was caused by the unintended dilution of sulfuric acid, and the ignition source was sparks generated by friction/impact at the time of sanding.

The explosion of the mixture of hydrogen and the air can occur with hydrogen of 4 vol.% to 75 vol.%, and detonation, a type of explosion in which the flame propagation velocity exceeds the velocity of sound, can occur with hydrogen of around 30 vol.%. If there is an obstruction in the direction of flame propagation, turbulence is caused in the front part of the flame flow. Then, the flame becomes wrinkled in the turbulence, increasing the substantial flame area and the reaction velocity, and accelerating the propagation velocity. Repeating this acceleration to exceed the velocity of sound is the mechanism leading to detonation. In this accident too, the flame is considered to have accelerated as the shelf to put catalysts for desulfurization corresponds to the obstruction. If the accident leads to detonation, the energy of the explosion, which can escape from an aperture area if it exists, cannot escape due to the flame velocity that exceeds the velocity of sound and concentrates in the flame front, generating an extremely high pressure of more than 1 MPa. During this process, many parts of the tank would be ruptured. In this accident, the whole tank maintains its shape, suggesting the accident did not lead to detonation. It can be considered that the top board part was ruptured and separated by the pressure that increased in a certain part due to the reflection of the pressure wave generated by flame propagation, and by the stress that was concentrated due to the board's shape.

One explosion in a sealed container can generate the absolute pressure of about 400 kPa; the tank is destroyed unless it was specially designed to withstand high pressure. In this accident, pronounced thinning was observed at the part where the layer of dilute sulfuric acid is considered to have formed, indicating reduced strength. Actually, the rupture occurred at that particular part.

5 Recurrence prevention measures

5.1 Improvement of work instructions

In this accident, there are work instructions for tank repairs, records regarding the results of the inflammable inspection and the inspection of surrounding conditions, and the instruction sheet for fire prevention measures that has been filled out. The instruction sheet for fire prevention measures has items of "Removal of internal inflammables" and "Detection of internal inflammable gas," but they were not filled out maybe because they did not apply to the work in question. This indicates no operation was performed to detect internal hydrogen gas, which led to the accident. Operations for detection need to be mandatory not optional. In addition, specific detection methods need to be considered not only for the tank that caused the accident but for facility repairs in general, and work instructions need to be improved accordingly.

5.2 Thorough impact assessment at the time of process change

A remote cause of this accident is the regular inspection of the odor treatment facility. This accident was caused because the impact of the difference in the concentration of sulfuric acid generated in the two processes (sulfuric acid production and odor treatment) was not recognized sufficiently when the impact of the regular inspection of the odor treatment facility was examined. The principle that the reaction of a chemical substance varies according to the concentration must be assumed.

Generally, when a change was made to a process, the change history needs to be recorded, and the impact of the change needs to be estimated every time and made known to workers not only in the previous and following processes but also adjacent facilities. Particularly in chemical plants, where multiple changes may occur simultaneously, if the estimated impact of the change is not shared by all related workers, even a known reaction may not be foreseen and can lead to an accident.

The regular inspection of the odor treatment facility is conducted once a year, meaning the inspection was not the first one even after the introduction of the 044 tank. Hydrogen gas that may have been generated at the previous regular inspection is considered to have leaked out, but there may be similar conditions with respect to thinning of the tank. It is therefore desirable to identify the current conditions by conducting an inspection or other means.

5.3 Monitoring of the concentration of liquid-phase sulfuric acid

The concentration of sulfuric acid, which was the direct cause of this accident, needs to be monitored in some way. The concentration of the liquid level portion in particular must be monitored since the possibility of rainwater and humidity diluting the liquid level portion cannot be denied. Although partly due to the impact of the explosion, the vent pipe shown in Figure 7 was corroded and also the height of the tank was more than 16 meters high, it is practically difficult to continue monitoring the rainwater. Because it took only two days to detect oozing after the tank was supplied six days before the accident, at least one inspection need to be conducted daily. This time interval varies depending on the tank shape without question, so continuous monitoring is recommended. Since it is necessary to detect a drop in sulfuric acid concentration before hydrogen gas is generated at substantial amounts, it is necessary to use a method that allows the detection of changes at relatively high concentrations.

Examining the concentration of discharged sulfuric acid can be an alternative to the monitoring of the concentration of the liquid level portion, if the uniformity in the tank can be secured by stirring or other means. However, in the case where the tank has been converted as in this accident, stirring is extremely difficult and the monitoring of the liquid level is more realistic.

5.4 Monitoring of the concentration of gas-phase hydrogen

Considering that the eventual explosion was caused by the mixture of hydrogen and the air, detecting hydrogen gas around the vent pipe will make it possible to take measures before an explosive mixture forms. Since hydrogen gas is light, it can be satisfactorily detected by installing a monitoring device at the vent pipe area, for example. The detection of internal inflammable gas during repair work can be achieved automatically with this monitoring device.