Report on the overview of the high pressure gas accident

Reference No.	Name of the accident:		
2012-106	Explosion and fire at a resorcinol plant		
Date and time of occurrence: 2:15 am on April 22, 2012	**Place of the accident:** Waki-cho, Kuga-gun, Yamaguchi Prefecture, Japan		
Plant name: Resorcinol plant	**Equipment name:** Oxidation reactor	**Main structural material:** JIS SUS304L / JIS SM490B clad	**Summary of dimensions(mm):** Inner diameter 5,150 TL 12,000
Contents: Dihydroxy peroxide (DHP)	**Capacity to produce High-pressure gas:** 25,600m^3(Normal)/day	**Normal operating pressure:** 1.96MPa	**Normal operating temperature:** -5℃

Damage situation: (Photo 1)

A problem arose with the steam generating plant and all plants the steam was supplied to were being put through emergency shutdowns one by one when the dihydroxy peroxide (DHP) inside the oxidation reactor in the resorcinol plant (Fig. 1) decomposed. The temperature and pressure inside the oxidation reactor rose rapidly and the oxidation reactor burst (Figs. 2, 3), causing an explosion and fire. There was a second explosion at the same reactor. One employee who was working near the oxidation reactor at the time of the first explosion was killed, and 25 people including local residents were injured. Additionally, 999 buildings and homes in the surrounding areas were damaged. (Fig. 4, 5) (Based on final report from the company)

Overview of the accident:

<Timeline after the accident>

1. At 2:15 am on April 22, an explosion and fire occurred at the resorcinol plant.
2. At 2:20 am, the fire department was notified, three local headquarters were established (Command HQ, Response HQ and Administrative HQ), and firefighting activities were started.
3. At 8:05 am, a second explosion occurred at the resorcinol plant.
4. At 5:15 pm, the Iwakuni District Fire Union Fire Department declared that the fire was under control.
5. At 2:31 pm on April 23, the Iwakuni District Fire Union Fire Department declared that the fire was extinguished.

<Situation of the explosion>

1. At the resorcinol plant, raw material m-diisopropylbenzene (m-DIPB) is oxidized in the oxidation reactor with oxygen in the air to create the resorcinol intermediate, dihydroxy peroxide (DHP). (Material-1)
2. Nitrogen was introduced into the oxidation reactor to maintain replacement from air and liquid agitation, and the cooling water was switched from circulating cooling water to emergency cooling water.
3. The internal temperature of the oxidation reactor slowly began to drop, but later, the operator decided that the cooling speed was too slow.
4. So he released the interlock triggered by the emergency shutdown, and changed the cooling method to circulation cooling water which is normally used once the reaction is complete. This stopped the flow of nitrogen that was being used to keep the liquid agitated. At this point, the operator did not notice that the liquid agitation had stopped.
5. Cooling coils are installed in the bottom half of the oxidation reactor so the bottom half was being cooled, but since the nitrogen was stopped and so liquid agitation was also stopped, the DHP in the upper part of the reactor without the cooling coils began to decompose and generate heat.
6. The operations and situations leading up to the explosion are explained in Fig. 6 , but it was confirmed that when the temperature increases in adiabatic conditions, self-heating of DHP becomes significant, which causes a rapid rise in both pressure and temperature.
7. Through reaction analysis, it is assumed that the process in which the decomposition of DHP starts when radicals are generated, the heating reaction process involving peroxy radicals, and the generation

of gases due to these two processes generated pressure that exceeds the burst pressure and resulted the rupture. (Material-2)

8. It is understood that, after the rupture of the oxidation reactor, the DHP and the decomposed gases mainly consisting of methane were dispersed, diffused, ignited and caused the explosion and fire.
9. The ignition source was not identified but it is likely to be one or more of the following: the collision/friction between metals caused by the rupture of the oxidation reactor, the discharge of static electricity charged when the liquid burst out of the oxidation reactor, the electric sparks caused by short circuits of electrical cables and electric apparatus after the rupture, or the temperature elevation of the DHP exceeding the ignition temperatures.

Causes of the accident:

1. There was insufficient capability for cooling the oxidation reactor in the event of an emergency shutdown.
2. Conditions for releasing the interlock were not clearly defined.
3. The thermometer for the interlock was set only in the lower part of the oxidation reactor and not in the upper part.
4. It was not easy to notice abnormalities during emergency shutdown just by looking at the DCS screen (Did not show nitrogen flow rate, temperature distribution in the oxidation reactor, and relationship between positions of the thermometers and the indicated temperatures) and the alarms were not appropriate (Not triggered when gas for agitation is stopped).
5. Concerning the interlock, education materials were inadequate (the fact that nitrogen is stopped when the interlock is released was not described on them, the operator did not understand the importance of agitation) and training was not sufficient.
6. The procedure in the event of an emergency shutdown of the oxidation reactor was not sufficiently defined, and risk assessments of the equipment in cases when the nitrogen supply is stopped were not conducted.

Measures to prevent recurrence:

1. Ensure the necessary capability for cooling the oxidation reactor in the event of an emergency shutdown.
2. Clarify the conditions in which the interlock may be released.
3. Install thermometers at multiple points in the oxidation reactor.
4. Create DCS screen and review alarms to ensure operators can easily notice abnormalities during emergency shutdown.
5. Prepare educational materials and conduct training regarding interlocks.
6. Review the operation procedure in the event of an emergency shutdown of the oxidation reactor and review equipment risks.

Learned lessons:

1. Insufficient risk assessment.
2. Insufficient passing down of skills (Communicate information regarding safety from the design staff to the operators, make efforts to continue passing down skills).
3. Disregarding regulations and rules (Insufficient compliance and review).
4. Decline in onsite safety management capability (Overconfident that safety has been secured).
5. Lack of ownership regarding safety/hazards (Lack of alertness and sense of crisis).

Remarks:

1. They established a "Fundamental Safety Review Committee" chaired by the company president and are currently promoting "efforts for fundamental safety" company-wide. They held a progress report meeting in October 2013, and they are continuing their efforts in safety.
2. They held a total of 8 meetings of the Accident Investigation Committee with the participation of experts.

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Related figures and material

Photo 1 View of accident site

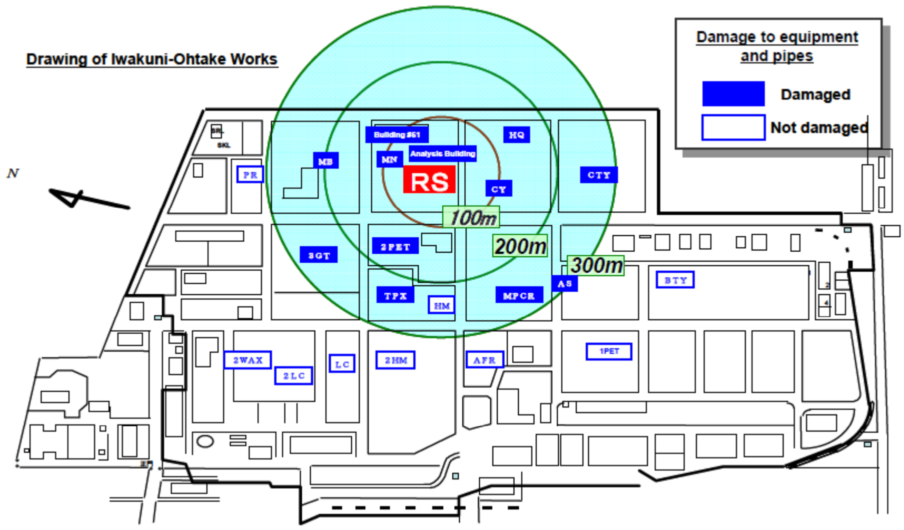


Fig.1 Position of the resorcinol plant and damage to equipment and pipes

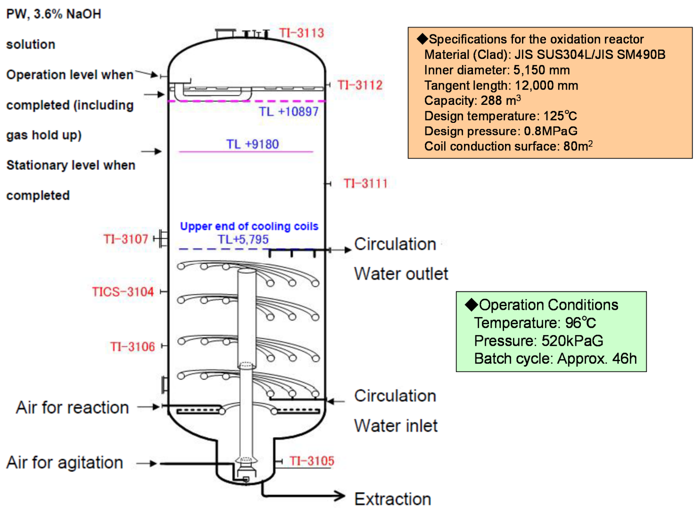


Fig.2 Specifications of the oxidation reactor

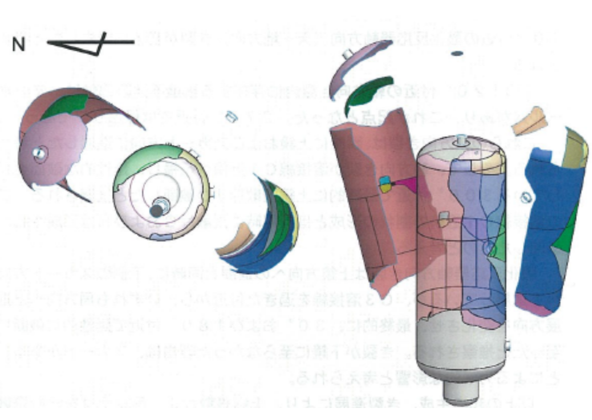


Fig. 3 Image of the scattering of the oxidation reactor

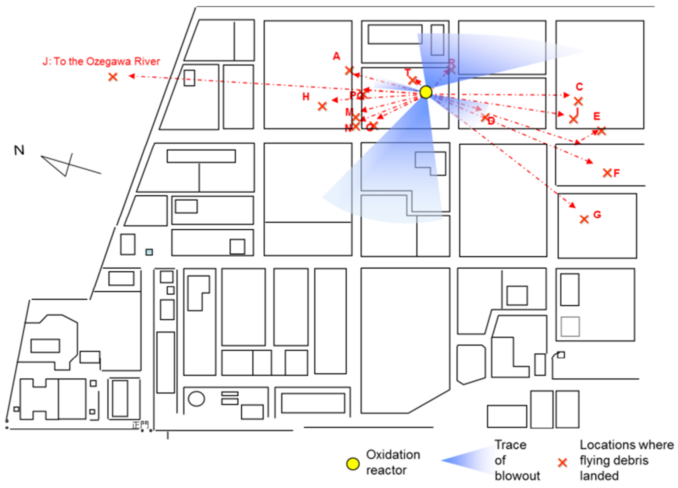


Fig. 4 Scattering of large debris from the oxidation reactor

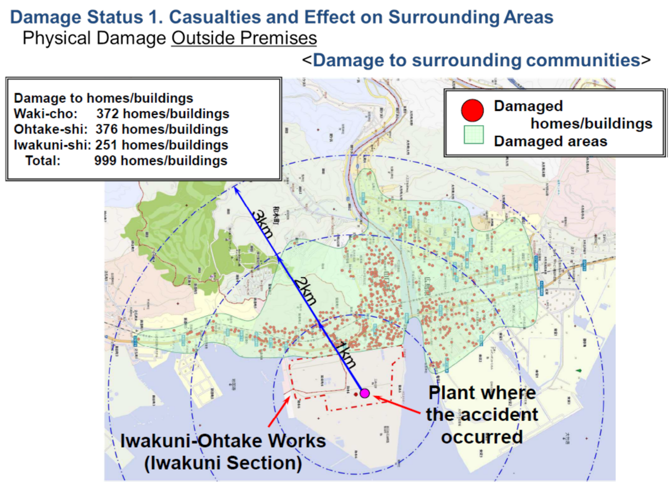
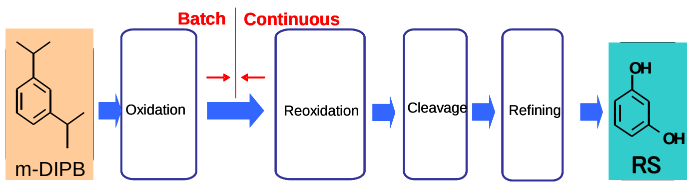
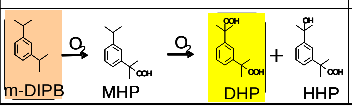
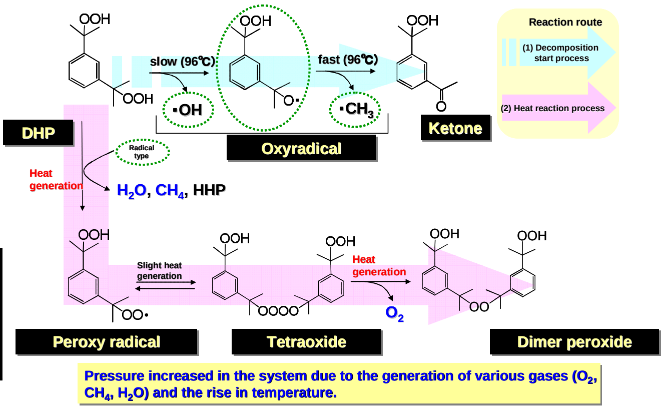


Fig. 5 Damage outside plant premises



Process	Conditions	Reaction formula	Explanation
Oxidation	Temperature: 96℃ Pressure: 520kPa Reaction time: Approx. 40hr Batch reaction		m-DIPB is oxidized with air to obtain DHP. HHP is also obtained as a by-product.

Material-1 Resorcinol plant block flow and reaction formula



*The three types of radicals are highly reactive, so they mostly disappear after reacting with DHP.

Material-2 DHP decomposition reaction mechanism

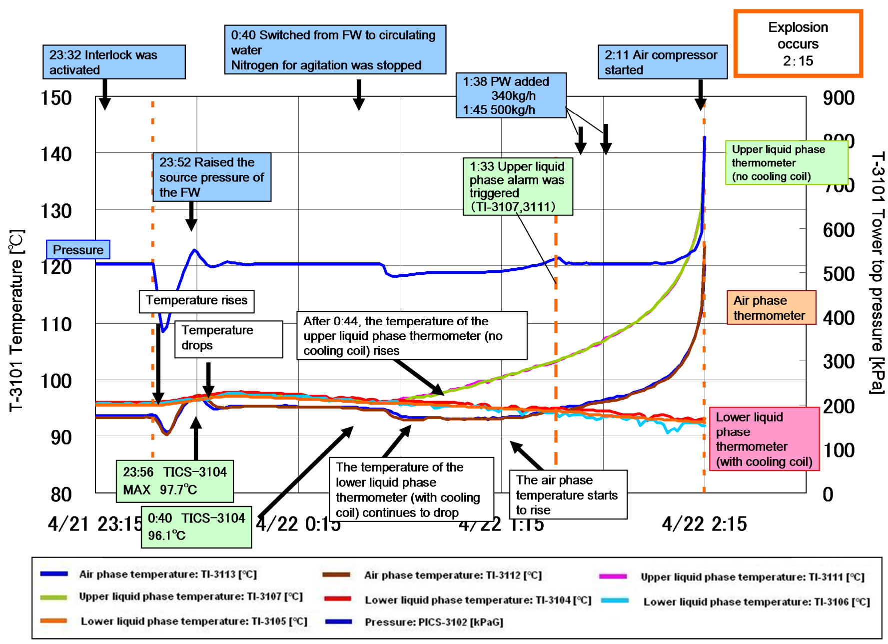


Fig. 6 Operation condition up to the explosion and fire and temperature and pressure trends