This Report is a translation of the original; "Chosa-Houkokusho" issued in March 2013 written in Japanese, for convenience purpose only, and the original in Japanese shall prevail.

Nippon Shokubai Co., Ltd.　Himeji Plant

Explosion and Fire at Acrylic Acid Production Facility

Investigation Report

March 2013

Accident Investigation Committee

Nippon Shokubai Co., Ltd.

Contents

1. Preface

1.1. Introduction

At about 14:35 on September 29, 2012, an explosion occurred at the Nippon Shokubai Co., Ltd. Himeji Plant located in Himeji, Hyogo Prefecture, Japan. The explosion and subsequent fire in an acrylic acid intermediate tank killed one person and injured 36.

As a result, on October 5, 2012, an Accident Investigation Committee consisting of four external and three internal members was established with the objectives of determining the causes of the accident and developing countermeasures to prevent the recurrence of accident.

The committee has thus far convened seven times. The committee has inspected the accident site, verified records, various experimental data, analytical results, testimony etc. provided by Nippon Shokubai's Himeji Plant and discussed the causes of the accident as well as countermeasures. The investigation has confirmed the causes of the accident that led to the explosion and fire and hence proposed countermeasures to prevent the recurrence of accident. With these, the committee has prepared this final report.

1.2. Accident Investigation Committee

1.2.1. Mission and Members of the Committee

From a fair standpoint, the committee aimed to find out facts and causes which led into the accident and proposed countermeasures to prevent the recurrence of accident. The Accident Investigation Committee consists of four external experts and three company employees who are responsible for safety and production. The members of the committee are:

Chairman:	Masamitsu Tamura, Emeritus Professor, The University of Tokyo
Members:	Yasukazu Arai, Former Managing Director, The High Pressure Gas Safety Institute of Japan
	Mitsuo Koshi, Research Professor, Institute of Engineering Innovation, School of Engineering, The University of Tokyo
	Masayoshi Nakamura, Professor, The Graduate School of Technology Management, Tokyo University of Agriculture and Technology
	Yosuke Ogata, Representative Member of the Board, Senior Managing Executive Officer, Nippon Shokubai Co., Ltd.
	Masao Kitano, Director, Safe Production Technology Division, Nippon Shokubai Co., Ltd.
	Hiroya Kobayashi, Director, Responsible Care Division, Nippon Shokubai Co., Ltd.

1.2.2. Progress of the Committee Meetings

1st Meeting October 23, 2012 (Tuesday) at the Himeji Plant, Nippon Shokubai Co., Ltd.

i. Finalized the organization of the Accident Investigation Committee
ii. Confirmed the overview of accident and inspected the accident site
iii. Deliberated on the investigation approach for the causes of accident

2nd Meeting November 15, 2012 (Thursday) at the Tokyo Office, Nippon Shokubai Co., Ltd.

i. Confirmed the accident timeline and V-3138 operation history.
ii. Sorted out the damages caused by explosion and fire
iii. Deliberated on the causes of accident

3rd Meeting December 4, 2012 (Tuesday) at the Tokyo Office, Nippon Shokubai Co., Ltd.

i. Deliberated on the causes of accident (cont.)
ii. Estimated the accident scenario and the direct causes
iii. Deliberated on direction of countermeasures for the direct causes

4th Meeting December 25, 2012 (Tuesday) at the Himeji Plant, Nippon Shokubai Co., Ltd.

i. Finalized the accident scenario and the direct causes
ii. Deliberated on countermeasures for the direct causes
iii. Deliberated on the investigation approach for the background causes

The committee has issued the "Accident Investigation Committee Interim Report" on January 18, 2013 (Friday) at the Osaka Office, Nippon Shokubai Co., Ltd.

i. Explosion and Fire at the Himeji Plant

5th Meeting January 25, 2013 (Friday) at the Himeji Plant, Nippon Shokubai Co., Ltd.

i. Summarized the accident scenario and the direct causes
ii. Deliberated on the background causes
iii. Deliberated on the directions for recurrence prevention countermeasures

6th Meeting February 14, 2013 (Thursday) at the Tokyo Office, Nippon Shokubai Co., Ltd.

i. Deliberated on the background causes
ii. Deliberated on the recurrence prevention measures
iii. Confirmed the 'Table of Contents' of the final report

7th Meeting February 22, 2013 (Friday) at the Tokyo Office, Nippon Shokubai Co., Ltd.

i. Finalized the background causes
ii. Finalized the recurrence prevention measures

2. Overview of the Accident

At about 14:35 on September 29, 2012, an explosion and fire occurred in an intermediate tank (equipment item number: V-3138; nominal capacity: 70 m^3) that temporarily stored bottom liquid from the glacial acrylic acid rectifying column at the Nippon Shokubai's Himeji Plant. The fire then spread to the nearby equipment and buildings such as acrylic acid tanks, toluene tank and fire engines.

2.1. Location and Equipment Involved

(1) Location

Himeji Plant, Nippon Shokubai Co., Ltd.

992-1 Aza Nishioki, Okihama, Aboshi-ku, Himeji, Hyogo, Japan

(2) Equipment involved

An intermediate tank (V-3138) in the acrylic acid production facility

2.2. Date and Time of Accident

September 29, 2012 (Saturday) at about 14:35

2.3. Weather Conditions

Weather: Cloudy	Temperature: 24~25°C	Pressure: about 1010 hPa,
Humidity: about 60%	Wind direction: WSW	Wind speed: 2~3 m/sec

2.4. Damages

2.4.1. Casualties

Fatalities:	1 (firefighter)
Severely injured:	5 (2 firefighters and 3 employees)
Moderately injured:	13 (8 firefighters, 1 police officer and 4 employees)
Lightly injured:	18 (14 firefighters, 1 police officer and 3 employees) Total: 37 persons

2.4.2. Property Damage

The tank, V-3138 was destroyed and its surrounding equipment, racks, piping, cables, etc. were also damaged.

2.4.3. Environmental Impact

As the outlet drain was closed, no hazardous materials were leaked out from the plant site.

2.5. Situation after the Accident

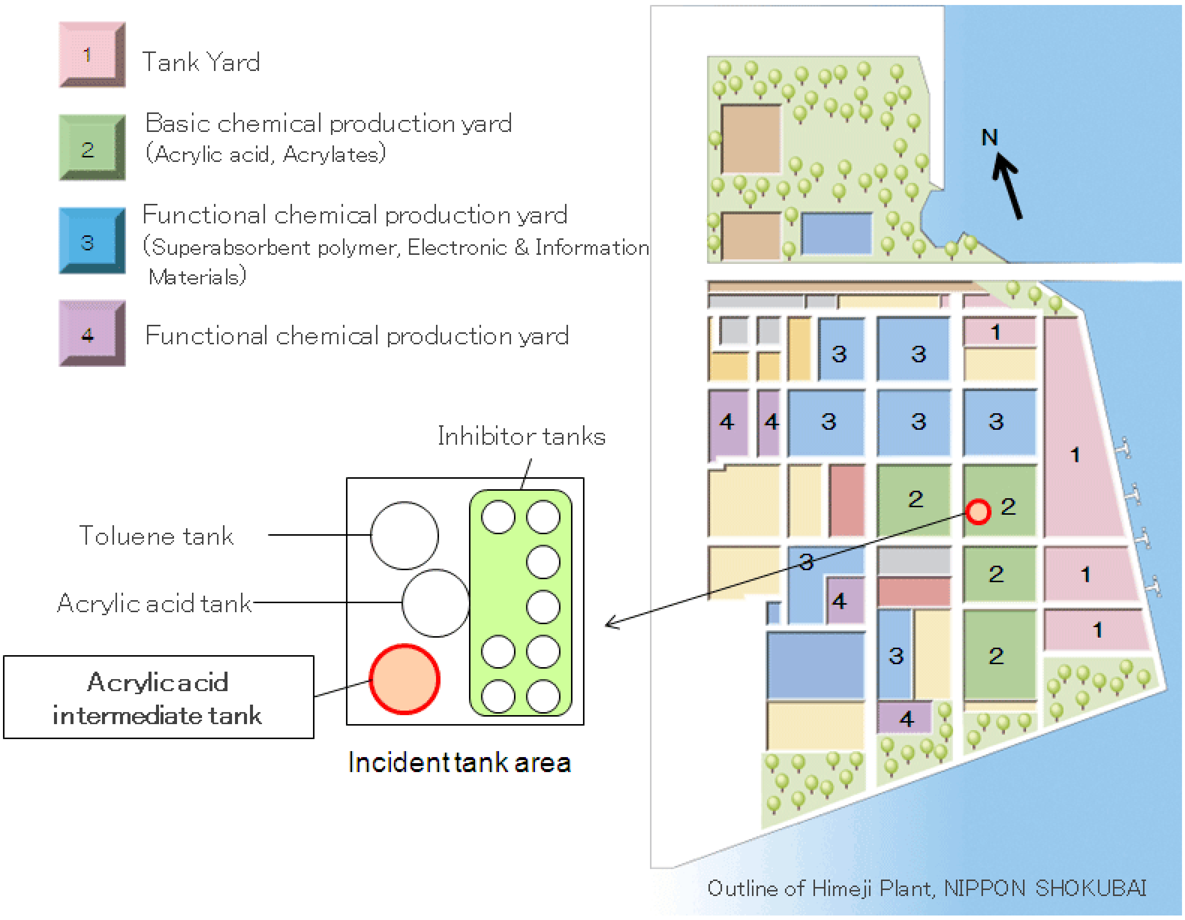
The authority temporarily issued a 'Stop Work Order' and hence all the facilities involved hazardous materials were stopped. Since then, some of the facilities have resumed to operation after the authority's approval.

3. Overview of the Himeji Plant and Equipment Involved

3.1. Overview of the Himeji Plant

The site of the accident, Nippon Shokubai's Himeji Plant, is a manufacturing plant with a site area of about 900,000 m², situated in the southwest corner of the city of Himeji, Hyogo Prefecture. The Himeji Plant produces basic chemicals (e.g. acrylic acid and acrylic esters), functional chemicals (e.g. super absorbent polymers, electronic and information materials), catalysts and other products.

The acrylic acid intermediate tank (V-3138), where the explosion and fire occurred, is located in an acrylic acid production facility in the basic chemicals production yard shown in Figure 3-1.



(Figure 3-1) Overview of the Himeji Plant, Nippon Shokubai

3.2. Overview of Acrylic Acid Production Process

3.2.1. Properties of Acrylic Acid

Acrylic acid is an organic compound with the chemical formula CH_2=CHCOOH. It is a colorless, transparent, flammable liquid having an irritating odor. Under the Japan’s Fire Service Act, acrylic acid is classified as a Category IV, Class II Petroleum flammable liquid.

The main physical and chemical properties of the acrylic acid are as follows:

Density	: 1.05 g/cm^3 (20℃)
Melting Point	: 13.5 ℃
Boiling Point	: 141 ℃
Viscosity	: 1.25 mPa・s
Ignition Point	: 428 ℃
Flash Point	: 51.4 ℃
Explosion Range	: 2～17 vol%
Specific Heat	: 2093 J/kg・℃
Heat of Dimerization	: 145.3 kJ/kg
Heat of Polymerization	: 1076 kJ/kg
Conductivity	: >10-7 S/m
Reactivity	: Due to its unstable double bond, acrylic acid is readily converted into a dimer (DAA) via dimerization reaction as shown in Figure 3-2 and to polymerize through polymerization reaction shown in Figure 3-3. In order to inhibit the polymerization, it is usually kept in an atmosphere containing at least 5vol% of oxygen and added with inhibitors.

$$2CH_2 = CH{-}COOH \longrightarrow CH_2 = CH{-}\overset{\overset{\displaystyle O}{/\!/}}{C}{-}O{-}CH_2{-}CH_2{-}COOH$$

(Figure 3-2) Chemical equation of diacrylic acid (DAA) formation

$$nCH_2 = CH{-}COOH \longrightarrow \overline{\left(CH_2 - \underset{}{\overset{\overset{\displaystyle COOH}{|}}{CH}} \right)_n}$$

(Figure 3-3) Chemical equation of acrylic acid polymerization

3.2.2. Acrylic Acid Production Process

The acrylic acid production process has two production processes: crude acrylic acid production process and glacial acrylic acid production process.

(1) Crude acrylic acid production process

The crude acrylic acid production process consists of oxidation process and purification process. In the oxidation process, propylene is converted to acrylic acid vapor via vapor phase oxidation reaction. The acrylic acid vapor is subsequently absorbed with water and formed the acrylic acid aqueous solution. In the purification process, crude acrylic acid is obtained by separating water and other impurities from the acrylic acid aqueous solution.

(2) Glacial acrylic acid production process

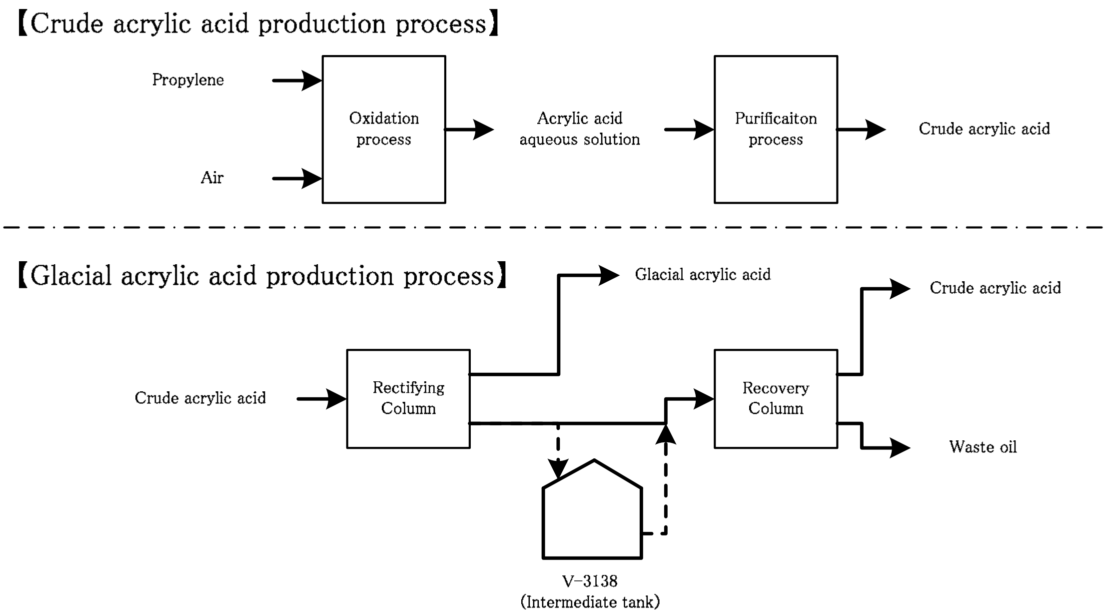
The glacial acrylic acid production facility consists of a rectifying column and a recovery column.

The crude acrylic acid is fed into the rectifying column where the impurities contained are removed and obtained as the glacial acrylic acid.

The rectifying column bottom discharge liquid which contains the removed impurities, is fed into the recovery column. In the recovery column, the impurities are discharged as waste oil and the recovered acrylic acid is used as crude acrylic acid.

Inhibitors contained in the crude acrylic acid and inhibitors fed into the rectifying column are concentrated in the rectifying column bottom liquid. This bottom liquid does not polymerize easily because it contains more inhibitors than glacial acrylic acid.

Intermediate tank V-3138 was installed in the crude acrylic acid production facility and was used for temporary storing the rectifying column bottom liquid.



(Figure 3-4) Schematic of the acrylic acid production facility

(3) Configuration of processes

The acrylic acid manufacturing plant has crude acrylic acid production facility and glacial acrylic acid production facility as shown in Figure 3-5.

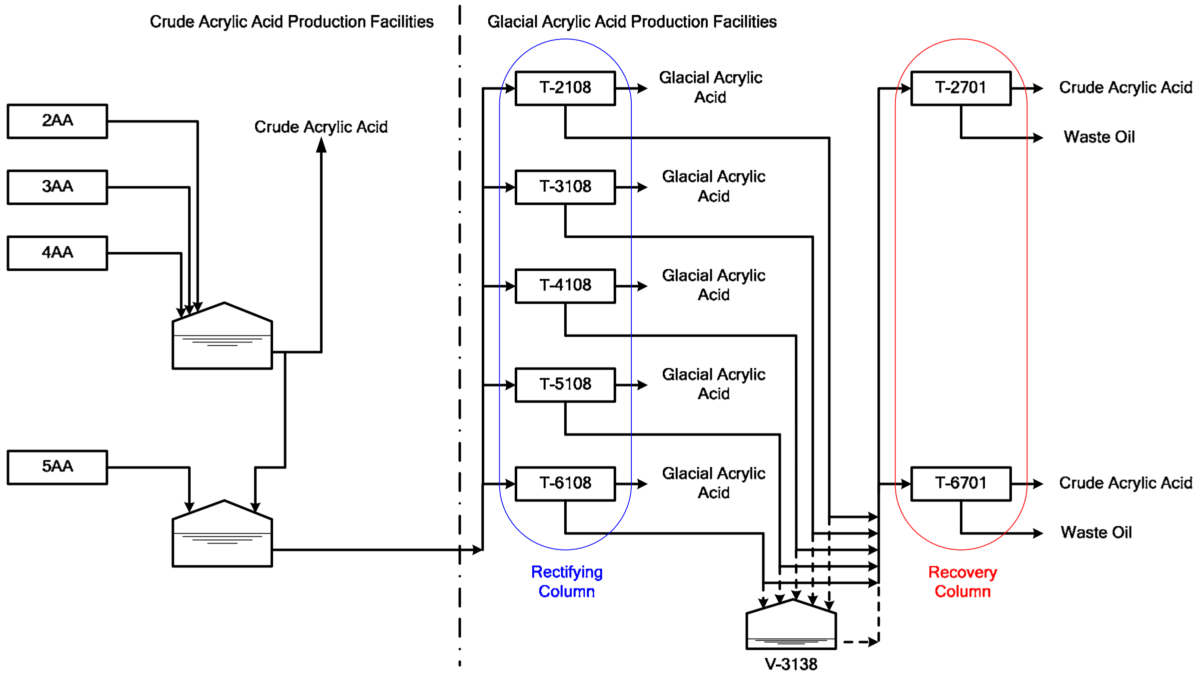
The crude acrylic acid production facility has four production lines (2AA to 5AA). Each production line was constructed (completed) in the years stated in the following:

2AA: Y1973, 3AA: Y1985, 4AA: Y1990, 5AA: Y1995

The glacial acrylic acid production facility has five series of rectifying column (T-2108~T-6108) and two series of recovery column (T-2701 & T-6701). The construction (completed) years of each series was stated in the following:

<Rectifying column>	T-2108: Y1985	T-3108: Y1985	T-4108: Y1990
	T-5108: Y1994	T-6108: Y1998	
<Recovery column>	T-2701: Y1985	T-6701: Y1998	

V-3138 is the only intermediate tank that is used to temporarily store rectifying column bottom liquid. V-3138 was constructed (completed) in 1985.



(Figure 3-5) Configuration of acrylic acid production processes

3.3. Overview of Equipment Involved

The equipment involved was the acrylic acid intermediate tank V-3138, which had a nominal capacity of 70 m^3. It was an insulated (75mm thick) cone roof type storage tank. The tank was installed in November 1985. It is used as an intermediate tank for temporarily storing the withdrawal liquid from the rectifying column when, for example, the rectifying column stopped.

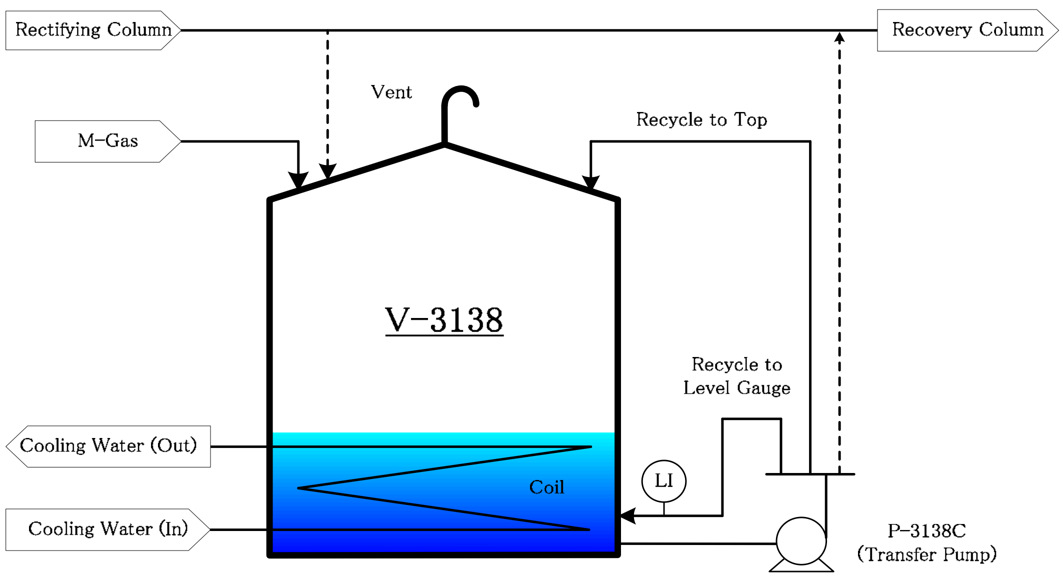
During normal operation, the bottom liquid is fed directly into the recovery column without passing through V-3138 and therefore the intermediate tank is kept stagnant.

There was a cooling water coil inside V-3138 that serves to prevent the freezing of acrylic acid and cooling the liquid that was fed into V-3138. The amount of liquid necessary to fully cover the top of the coil is 25 m^3.

Although acrylic acid is a flammable liquid, its vapor does not burn when it has an oxygen concentration of 8% by volume or less. Therefore, a mixed gas (referred to as “M-Gas”) consisting of 7% oxygen and 93% nitrogen by volume is fed into the tank for sealing purpose.

Liquid stored in V-3138 is circulated through pump P-3138C back into the same tank at two locations: liquid level gauge nozzle set near the lower side of V-3138’s wall (referred to as “Recycle to Level Gauge”) and nozzle set at V-3138’s top (referred to as “Recycle to Top”).

Initially when the V-3138 was installed in 1985, there was only the Recycle to Top line for pump circulation. In order to prevent the precipitates accumulation and results in incorrect reading at the level gauge, the Recycle to Level Gauge line was installed in 2009.



(Figure 3-6) Schematic of tank V-3138

4. Development of the Accident

4.1. Events leading to the Explosion and Fire

4.1.1. Events Timeline

The timelines for the explosion and fire accident is shown below:

September 18 to 20, 2012	
	Total power shutdown in the Himeji Plant for electrical and instrumentation maintenance work (referred to as “Total Power Shutdown Work”)
September 20, 2012	
Approx. 21:00	Intermediate tank V-3138 was re-commissioned after Total Power Shutdown Work (Cooling water charged into the coil, commissioned M-Gas seal, started P-3138C)
September 21, 2012	
Approx. 11:00 to approx. 14:00	Built up liquid level in recovery column (T-6701) from V-3138 and started T-6701 operation. Subsequently, started rectifying column (T-6108) operation and fed its bottom liquid directly into T-6701 (After building up liquid level in T-6701, V-3138 liquid volume reduced from about 14 m^3 to about 10 m^3)
September 24, 2012	
Approx. 10:00	Started rectifying column (T-5108) operation
Approx. 14:10	Started discharging T-5108 bottom liquid (fed to T-6701 via V-3138)
September 25, 2012	
Approx. 9:30	Built up the V-3138 liquid level (stopped feeding T-6701 from V-3138)
September 28, 2012	
Approx. 14:00	Liquid volume in V-3138 reached 60 m^3 and then stopped feeding V-3138. (T-5108 bottom liquid switched to feed T-6701 directly).
September 29, 2012	
Approx. 13:17	V-3138 liquid level high alarm triggered
Approx. 13:20	Discovered white smoke emitting from V-3138’s vent
Approx. 13:25	Operators started spraying water onto V-3138
Approx. 13:40	Shift Leader made the plant-wide announcement and alerted self disaster

	prevention team.
	Reading of V-3138 liquid level gauge exceeded out-of-range limit (84.8 m^3)
Approx. 13:48 to 13:49	Disaster prevention section notified public fire department through the hotline.
Approx. 14:00	Self disaster prevention team started spraying water onto V-3138
Approx. 14:02	Public fire department arrived on site and cordoned off the accident site.
Until approx. 14:35	V-3138's contents leaked out from cracks
Approx. 14:35	Reading of V-3138 liquid level gauge dropped drastically
	V-3138 liquid level low alarm triggered
	V-3138 exploded and ruptured
	Contents of V-3138 ignited and resulted in fire
22:36	Fire contained

September 30, 2012

15:30	Fire extinguished

4.1.2. Sequence of Events

The committee has divided the sequence of events leading up to the accident into four stages and investigated the accident details and causes.

(1) Before started the storing operation in V-3138

(From September 21 to about 9:30 on September 25, 2012)

After the Total Power Shutdown Work was completed, cooling water was commissioned to pass through V-3138's coil and similarly the M-Gas sealing was also commissioned. Circulation from pump P-3138C via Recycle to Level Gauge was commissioned too.

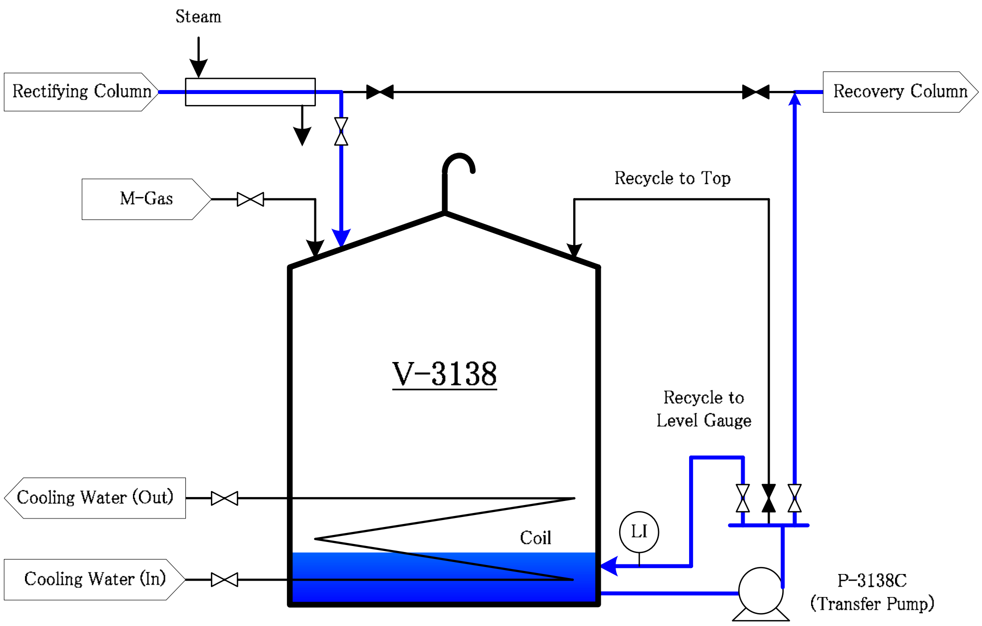
There was no abnormality observed in the operations of the crude acrylic acid production facility. The correct amount of inhibitors was also fed into the crude acrylic acid obtained from the purification process in accordance with the operation standards.

Operations of the rectifying column (T-6108) and the recovery column (T-6701) in the glacial acrylic acid production facility were started on September 21. The bottom liquid of T-6108 was fed directly into T-6701.

On September 24, another rectifying column (T-5108) was started. The bottom liquid of T-5108 was fed to the T-6701 via V-3138. During this operation, the liquid volume in V-3138 was maintained constantly at about 10m^3.

The transfer piping of T-5108 bottom liquid was steam jacketed to prevent plugging due to precipitation. The temperature of the bottom liquid as it entered V-3138 was estimated at about 100°C, based on steam temperature and the length of the jacketed piping.

Inhibitors were fed into T-5108 in accordance with the operation standards.



(Figure 4-1) Status of tank V-3138 before liquid storing

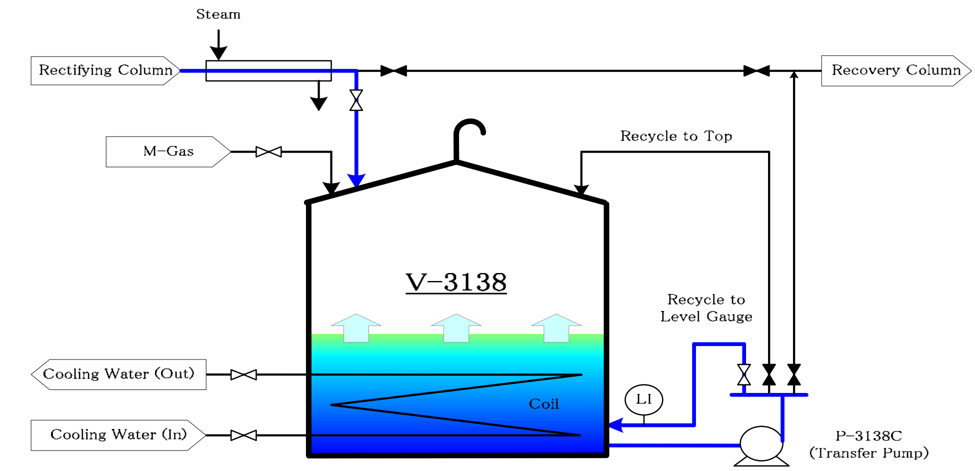
(2) During storing operation in V-3138

(From about 9:30 on September 25 to about 14:00 on September 28, 2012)

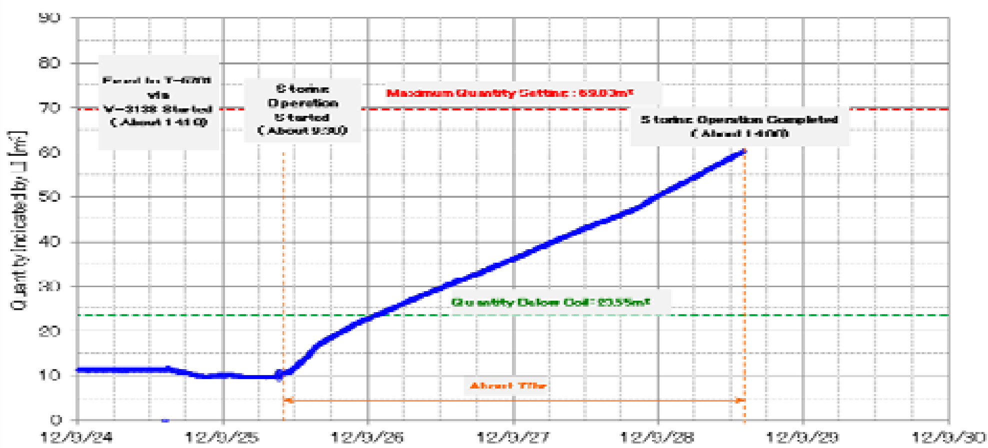
At about 9:30 on September 25, the feed of bottom liquid from V-3138 to T-6701 was stopped and commenced to build up the liquid volume in V-3138. This was to prepare a capacity load up test in the recovery column which was scheduled at a later date.

There was no particular change in the crude acrylic acid fed to T-5108 or in the inhibitors. The operation was running normally according to the operation standards.

The volume of liquid in V-3138 reached the planned 60m^3 at about 14:00 on September 28, approximately 77 hours after the commencement of storage. During this period, the circulation of Recycle to Top was not commissioned. Figure 4-3 shows the V-3138 liquid level trend during storing operation. The coil cooled the liquid in the bottom of V-3138 but was unable to cool the liquid above the top of the coil effectively. This had created an uneven temperature distribution in the vertical direction of V-3138 liquid. It is presumed that this relatively high temperature section has led to the reaction of forming acrylic acid dimer (diacrylic acid, referred to as "DAA"). With the heat of this reaction, V-3138 liquid temperature has increased steadily. However, V-3138 was not equipped with any thermometer and it was not possible to detect the temperature has increased.



(Figure 4-2) Status of tank V-3138 during liquid storing



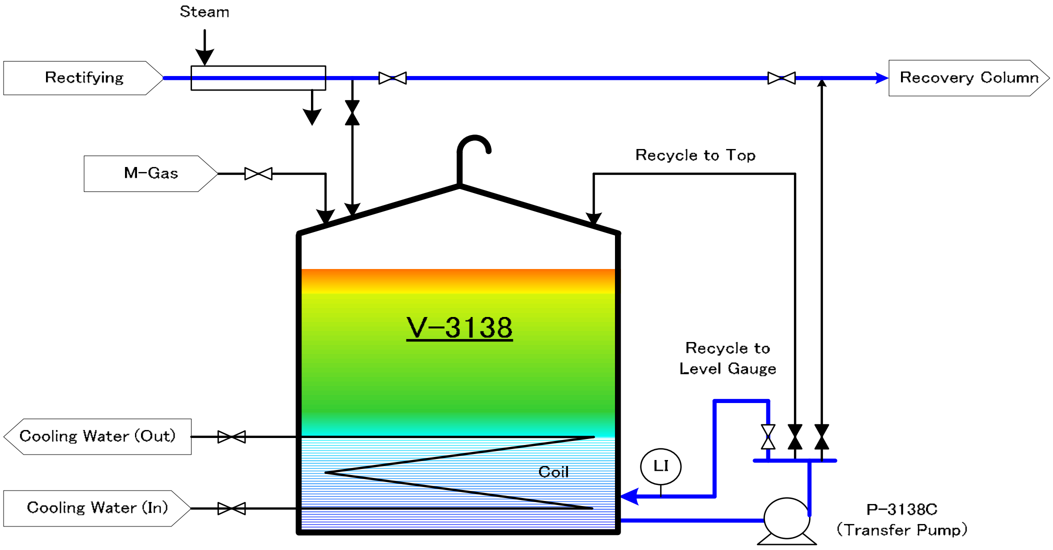
(Figure 4-3) Trend of V-3138 liquid level gauge (until liquid storing completed)

(3) After storing operation in V-3138

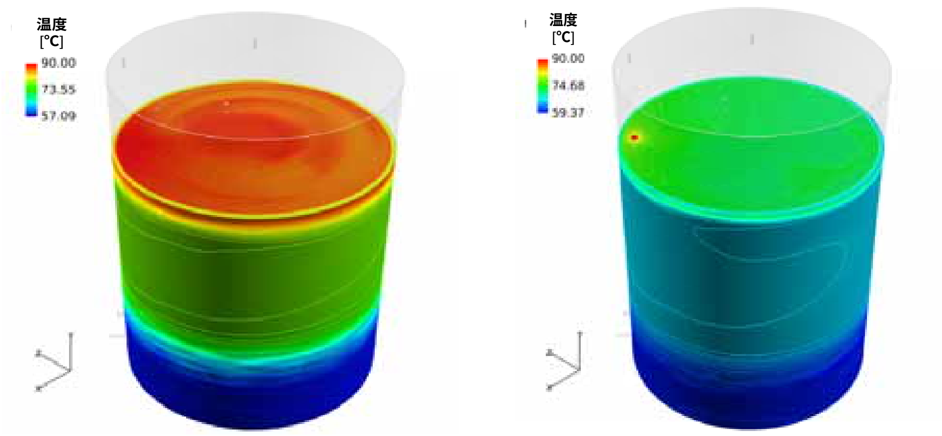
(From about 14:00 to about 14:10 on September 28, 2012)

At about 14:00 on September 28, the liquid volume in V-3138 reached 60m^3. Thereafter, T-5108 bottom liquid was switched back to feed T-6701 directly without passing through V-3138.

Even then, the circulation of Recycle to Top was still not commissioned. Consequently, the liquid above the top of the coil was not cooled and remained at a relatively high temperature. In order to simulate the temperature distribution in the V-3138 liquid, a 3-D model of V-3138 was developed. The ANSYS Fluent Ver.13 was used to conduct the fluid analysis without taking the heat of reaction into consideration. The analysis showed that if Recycle to Top was not commissioned, the liquid just below surface remained at a relatively high temperature, average about 87°C immediately after reaching a volume of 60m^3. The analysis results are shown in Figure 4-5.



(Figure 4-4) Status of tank V-3138 after liquid storing



Actual condition model

(Without Recycle to Top)

Reference

(With Recycle to Top)

(Figure 4-5) Results of fluid analysis when V-3138 liquid has reached 60m^3

(4) From liquid holding in intermediate tank (V-3138) to explosion and fire

(From about 14:10 on September 28 to about 14:35 on September 29, 2012)

It is presumed that the reaction of DAA formation accelerated in the liquid stored in V-3138 and the liquid temperature continued to increase from the heat of DAA formation. In a laboratory experiment conducted under adiabatic condition, the reaction was confirmed to proceed until the composition has reached to approximately 40wt% of acrylic acid (AA), 60wt% of DAA and others. If the reaction is allowed to proceed under adiabatic conditions up till these compositions, the amount of reaction heat is able to increase the temperature of the V-3138 entire liquid volume by about 40°C.

It is also presumed that this continued rise in temperature has started the polymerization of acrylic acid and the temperature of V-3138 liquid rose even more rapidly by the heat of polymerization.

At about 13:20 on September 29, an operator discovered white smoke (acrylic acid vapor) coming out from V-3138 vent. It is estimated that the high temperature section of V-3138 liquid was about 160°C at that time. This temperature was estimated by confirming water vapor is visible as white smoke in the laboratory test and then by using Aspen Plus to confirm the vapor pressure with the composition of the V-3138 liquid.

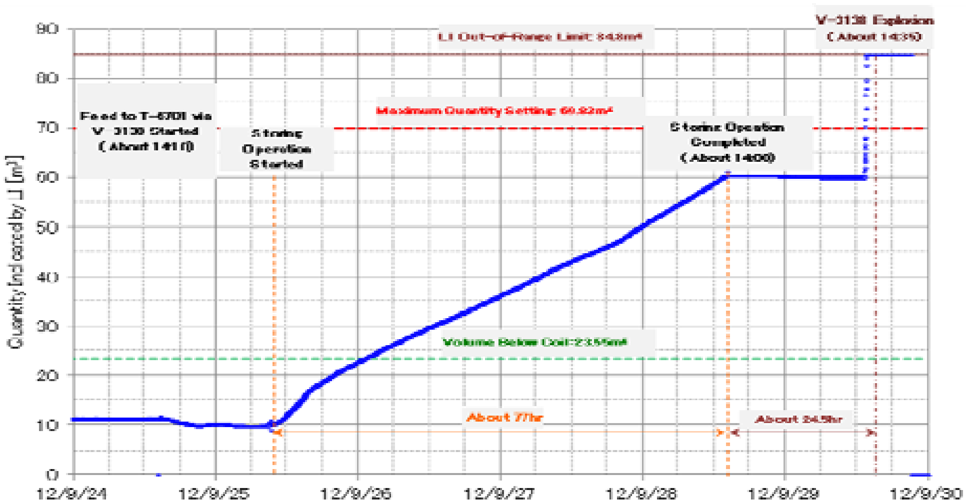
The V-3138 liquid level gauge reading (pressure differential type) has shown increasing trend. It started to rise at about 13:20, reached the maximum liquid volume setting at about 13:30 and exceeded the gauge's out-of-range limit (84.8m^3) at about 13:40. This trend has shown the V-3138 internal pressure has increased. The increasing pressure is presumed to have occurred because the vent's discharge capacity has exceeded by the increased amount of evaporated vapor resulted from accelerated polymerization. Figure 4-6 shows the V-3138 liquid level trend.

The V-3138 pressure continued to rise thereafter and cracks appeared at the shell plate. It is estimated the pressure had built up to 0.24~0.29MPaG based on tank structural analysis at the time the cracks appeared. Independently, based on the adiabatic polymerization experiment data, the V-3138 internal pressure was also estimated to reach about 0.27MPaG. The estimated trend of increased pressure is shown in Figure 4-7 and the model used for estimation is explained in Appendix 2. Also, the V-3138 liquid was estimated to be about 230~240°C in the high temperature zone. The reaction data of the adiabatic reaction test is explained in Appendix 1 and the structural analysis results will be discussed in Section 4.2.1.

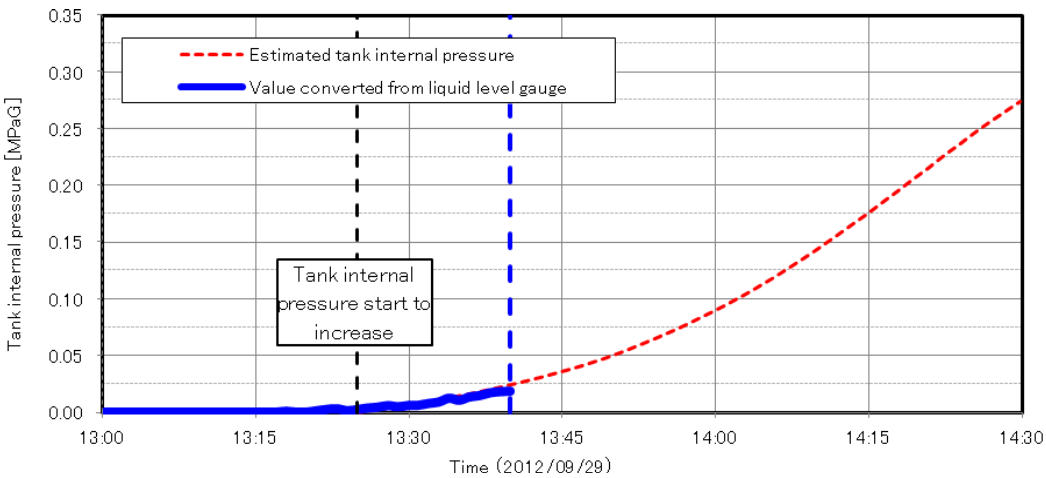
The V-3138 contents started to leak from the cracks and caused the V-3138 pressure dropped drastically.

At about 14:35 on September 29, the V-3138 liquid started to boil violently due to the drastic drop in pressure, while the liquid temperature still remained at high temperature. These resulted in Boiling Liquid Expanding Vapor Explosion (BLEVE) inside V-3138 and subsequently ruptured the V-3138. The scattered contents ignited and caused the fire. Based on the distance of scattered debris, it is estimated that the tank internal pressure at the time of explosion was about 0.45~0.64MPaG. The possible ignition sources were sparks generated from the impact of metals or from broken electrical wires during the explosion.

The explosion has also damaged the nearby tanks. Thus, the leaked acrylic acid and toluene from these tanks caused the fire to spread further. Table 4-1 summarized the major events from V-3138 liquid reached its boiling point till the explosion and fire occurred.



(Figure 4-6) Trend of V-3138 liquid level gauge (until the explosion)



(Figure 4-7) V-3138 liquid level gauge readings (converted to pressure) and pressure rise

(Table 4-1) Estimated sequence of events for V-3138 fire and explosion

All internal pressure and temperature values are estimated

Sequence of events	Time	V-3138 Internal Pressure [MPaG]	V-3138 Internal Temperature [℃]
V-3138 internal pressure started to rise	~13:20	Atmospheric	(160~170)
Exceeded the liquid level gauge out-of-range limit	~13:40	(0.025)	(175)
Self disaster prevention team started water spraying from fire engine (3,100 L/min)	~14:00	-	-
V-3138 anchor bolts broken	-	(0.1)	-
Cracks initiated at outlet nozzle of cooling water coil (nozzle position: 270°)	Till ~14:35	(0.24~0.29)	(234)
Cracks propagated and contents leaked out (at 270°, vertical directions)	Till ~14:35	(0.24~0.29)	(234)
Cracks reached vapor phase parts and tank pressure dropped drastically	~14:35	(Atmospheric)	(234)
Boiling Liquid ExpandingVapor Explosion	~14:35	(0.45~0.64)	(234)
Fire (acrylic acid: ~66 m³, toluene: ~28 m³)	~14:35	-	-
Fire contained	~22:36	-	-

4.2. Damages Resulted from the Explosion and Fire

4.2.1. Explosion Impact and its Damages

(1) Equipment damage

<Condition of V-3138 tank and its surrounding equipment>

The Figure 4-8 shows the ruptured V-3138 resulted from explosion and the damage condition of its surrounding equipment.

(1) Damaged Tank (view from southwest)

(2) Zoom-in of Damaged Tank (view from southwest)

(3) Damaged Tank (top view from east)

(4) Piperack at west of damaged tank (view from southeast)

(5) Piperack at west of damaged tank (view from south)

(6) Pumps surrounding at west of damaged tank (view from south)

(Figure 4-8) Damages around V-3138

<Damage condition of V-3138>

The damaged conditions of the V-3138 main members are described below. Figure 4-9 also shows the reconstruction figure of these members with other scattered fragments.

i. Roof Plate

The roof plate broke and separated near the roof-to-shell joint. The roof plate has split into two and being thrown to a distance of about 50m.

ii. Shell Plate

The shell plate tore vertically in a near straight line at 270° position, deformed into casement-type opening and left almost like a flat plate within the dike at the accident site.

iii. Bottom Plate

The bottom plate partly broke near the shell-to-bottom joint and remained inside the dike

Having observed the fracture surfaces of V-3138 members, most of them are slanted to the through-thickness direction and have features of being formed through shear fracture caused by glide plane decohesion. However, the fracture surface around the outlet nozzle of cooling water coil consisted of two types of fracture surfaces: ductile fracture formed through tensile deformation and shear fracture. This part was judged as a main initiation point of the cracks. The observation results of the fracture surfaces are explained in Appendix 3.

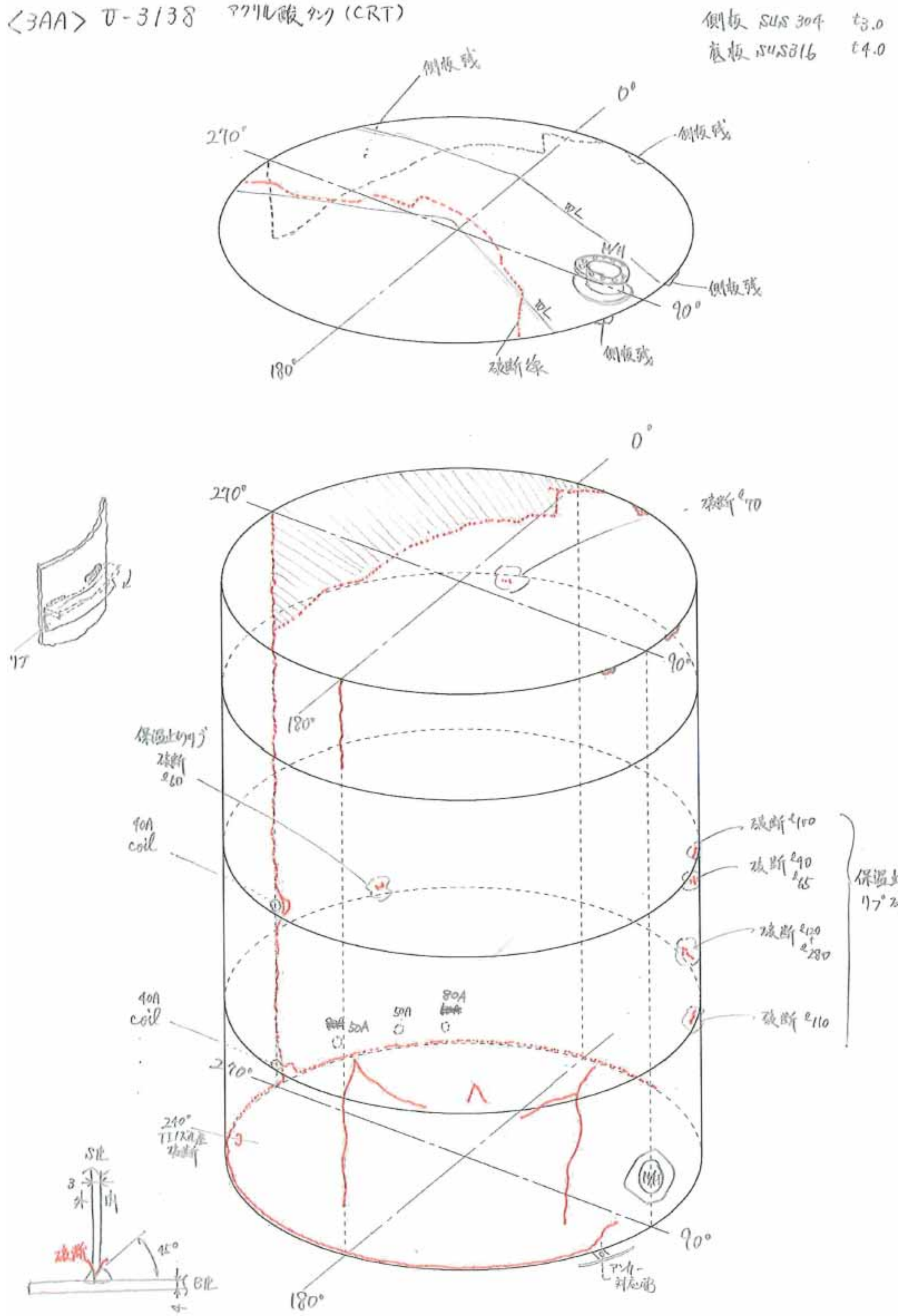
The cracks formed in this part propagated and split the tank shell plate vertically in both directions at 270° position. The upwards crack broke into the roof plate and ran through it near the 135° position. The roof and bottom plates generally cracked in the circumferential direction near their joints with the shell plate. Figure 4-10 shows the estimated crack propagation paths of the roof and shell plate in development view.

<Damage conditions of surrounding equipment>

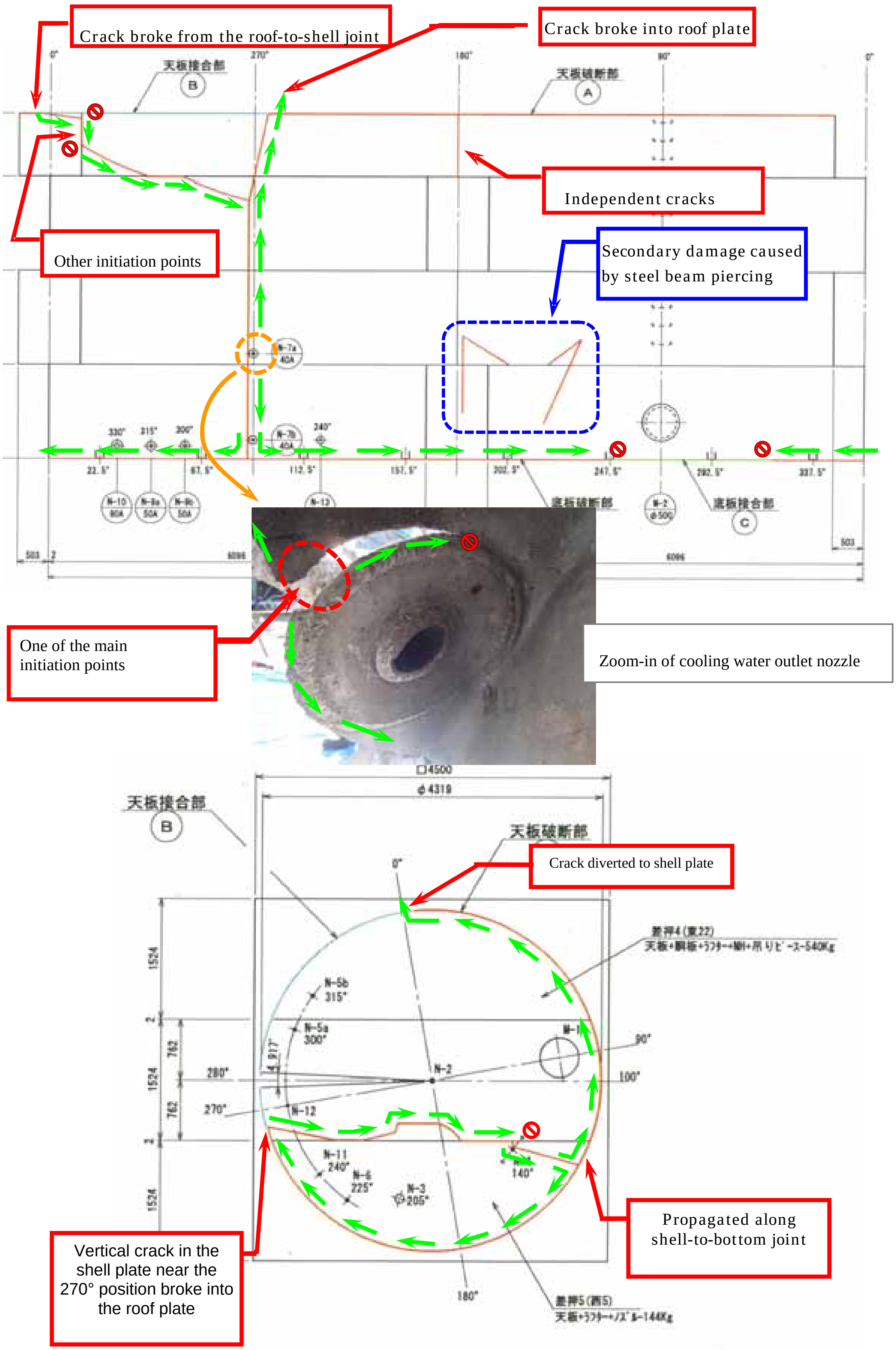
The damage conditions of the surrounding equipment are shown in Figure 4-8. Six tanks which were located within the same dike as V-3138 were severely damaged together with several pumps installed near the west side of the dike. The six tanks were V-3116 (100m^3: acrylic acid tank), V-3124 (50m^3: toluene tank), V-3145B, V-3147B, V-3147C, and V-3148C (5m^3 each: inhibitor tanks). Furthermore, building (electric room) at the south side of the dike, nearby piperacks, piping, cables and fire engines were severely damaged also.

<Scattered conditions>

About 80 pieces of broken fragments from V-3138 and surrounding equipment scattered within 100m radius. The tank contents were also scattered within 70m radius, particularly in the west direction of shell plate's opening (270° position).



(Figure 4-9) Reconstruction diagram (sketch) of V-3138 fragments



(Figure 4-10) V-3138 crack initiation and estimated propagation paths (top/ shell plates development view)

(2) Internal pressure at the time V-3138 ruptured by explosion

The internal pressure at the time tank ruptured by explosion was estimated by: i. the tank structural analysis and ii. the distance of scattered fragments.

i. Estimation results of tank internal pressure by structural analysis

The V-3138 structural analysis used the finite element method to determine the tank internal pressure. The Figure 4-11 shows the 3-D model developed for structural analysis. The model divided the tank into 100,000 elements for analysis. Main members of the modeled tank are shown in Figure 4-12.

Based on the structural analysis, the anchors were estimated to break at about 0.1MPaG and the pressure which initiated the cracks at the tank was estimated to be 0.24~0.29MPaG. The generic nonlinear structural analysis code, LS-DYNA was used for the analysis code.

The analysis of two predicted failure points was described as follows:

a) Anchor points

It is thought that as the tank internal pressure increased, the tank was uplifted but the tendency was restrained by the anchors which created a large resistant force locally. This analysis was conducted by using the 3-D model.

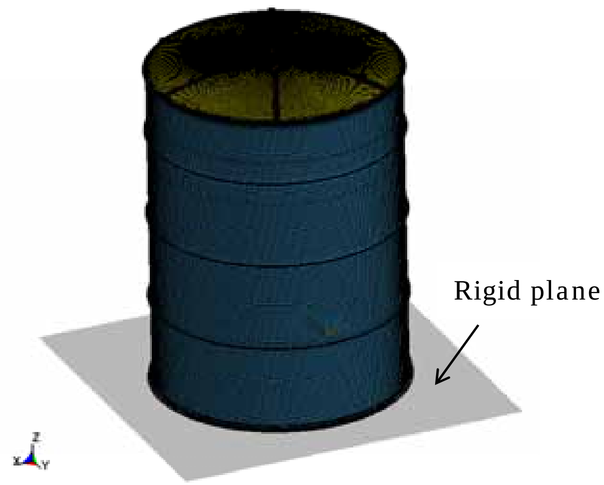
Figure 4-13 shows the equivalent plastic strain on the tank surface caused by the tank internal pressure. Figure 4-14 shows the vertical reaction force acting on the anchors as a result of the tank internal pressure. The lower limit for the tank pressure to create the anchor breaking load of 1005kN was 0.073MPaG. The tank pressure at which the vertical reaction force exceeds the breaking load was estimated to be about 0.1MPaG. However, the strain on the shell plate at that time was about 2~3% which was not a level rupture would occur at the shell plate.

b) Cooling water coil outlet nozzle

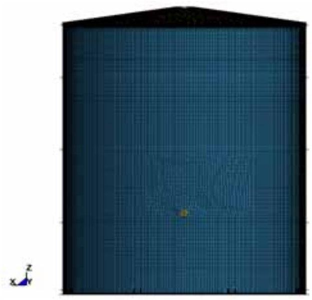
The thickness of the ruptured V-3138 shell plate measured at about 2.8mm which was the same thickness as at the time of manufacture. Because of this, it was presumed that plate thickness reduction, which begins when the elastic limit of the material is exceeded, had not occurred. The pressure at which plate thickness reduction would become noticeable was estimated at about 0.25~0.30MPaG through structural analysis using the 3-D model. Figure 4-15 shows the results of plate thickness reduction against the tank internal pressure.

Presuming the cracks initiated before reaching this pressure, the structural analysis was conducted focusing on the tank’s weak points. These included the nozzles of cooling water coil, roof-to-shell joints, shell-to-bottom joint and the edges of the tank. The results have confirmed a larger strain appeared locally at the outlet nozzle of cooling water coil than its surrounding. Figures 4-16 and 4-17 show the analysis results.

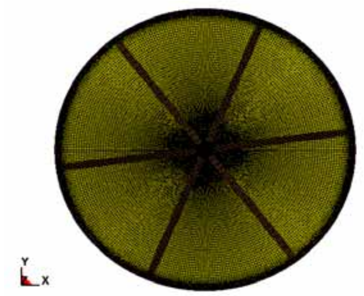
In order to improve the analytical accuracy around this area, a local shell model was used to zoom-in the nozzle vicinity for estimating the pressure at which the plastic deformation increase indefinitely would occur. The pressure was estimated to be about 0.24~0.29MPaG. Figure 4-18 shows the results. The reason why the cracks appeared in this area is presumed due to a structural discontinuity at which a flange with a diameter of about 150mm and a plate thickness of about 8mm was attached to the shell plate. It is presumed that excessive stress and strain were developed near the structural discontinuity.



（1） Bird's Eye View

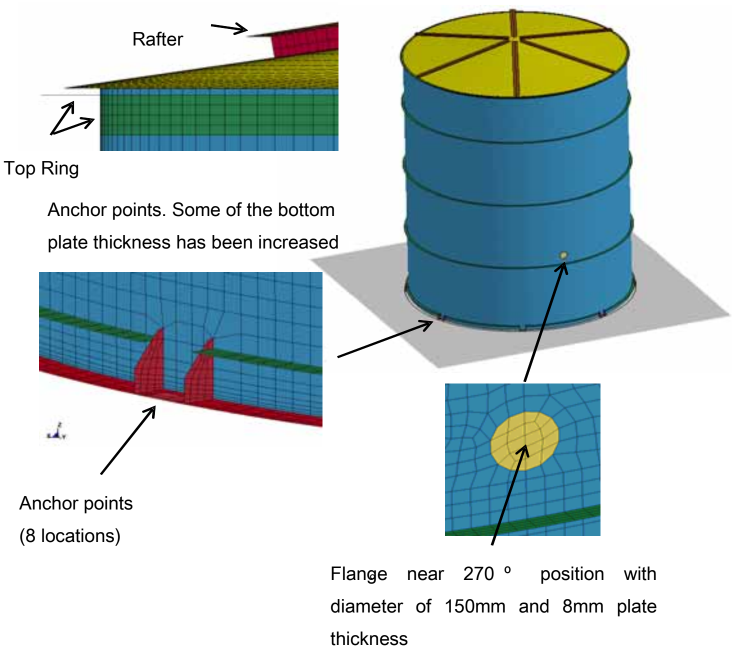


（2）Shell Plate（Front: 270° position）

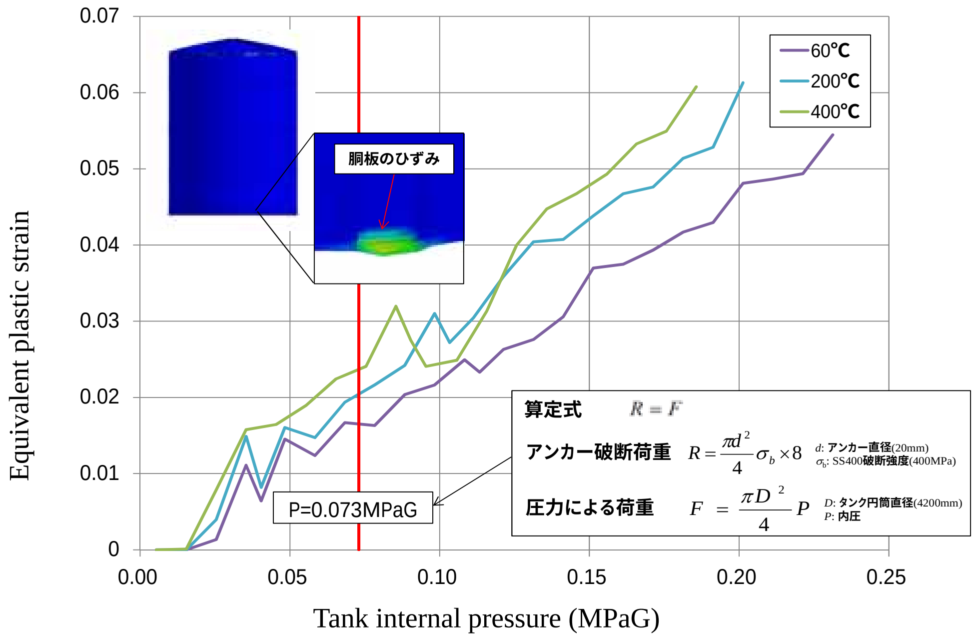


（2） Roof

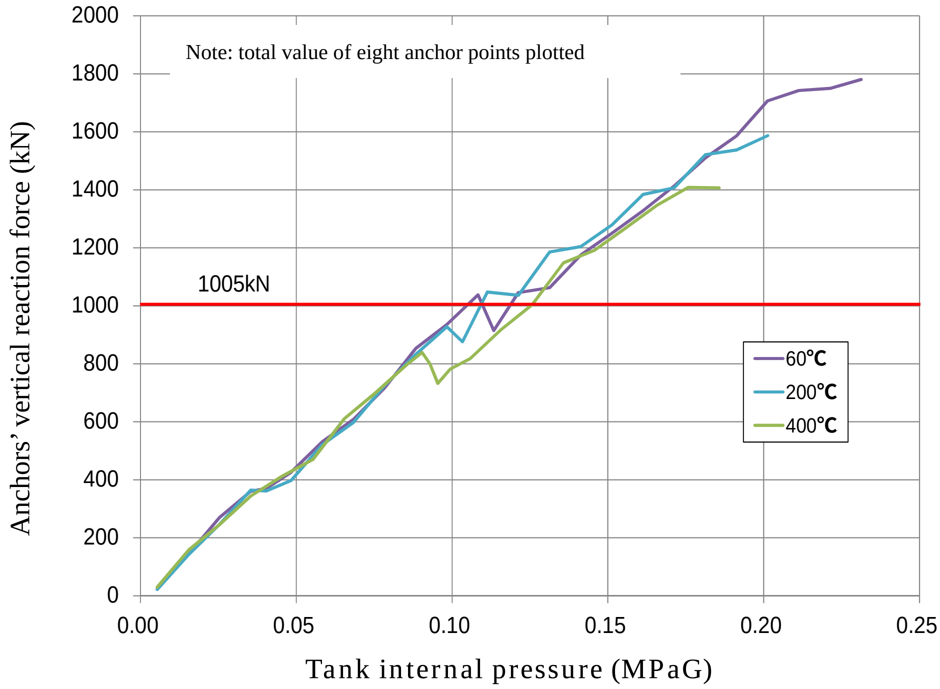
(Figure 4-11) 3-D model used in structural analysis



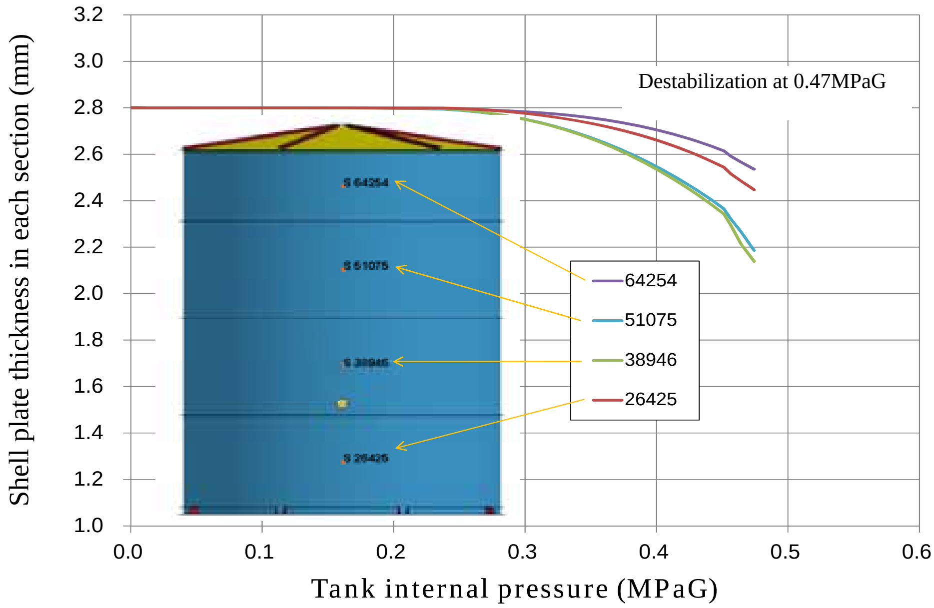
(Figure 4-12) 3-D model of tank constituent components



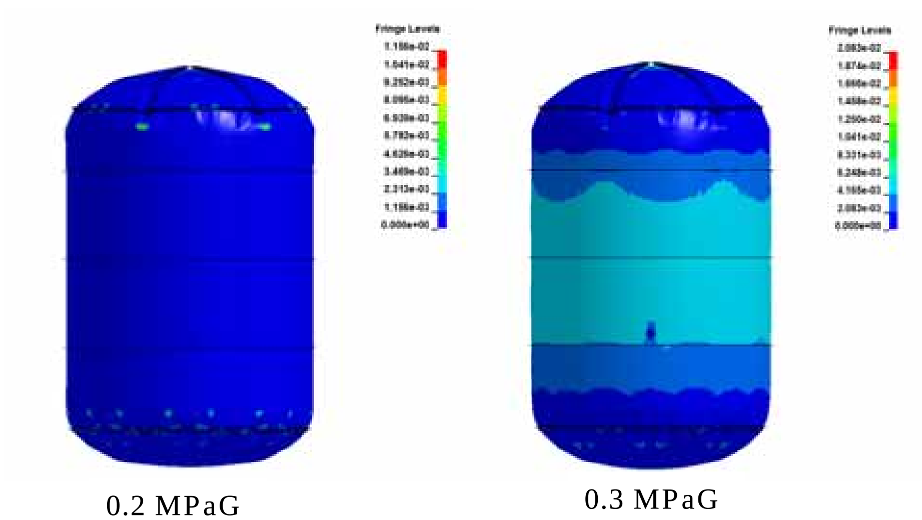
(Figure 4-13) Equivalent plastic strain on the tank surface caused by the tank internal pressure



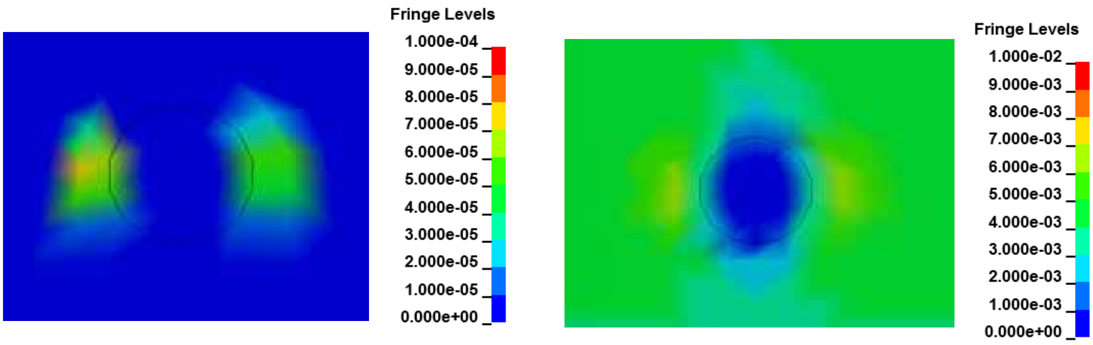
(Figure 4-14) Vertical reaction force acting on the anchors as a result of the tank internal pressure



(Figure 4-15) Plate thickness reduction against the tank internal pressure by 3-D model (at 200°C)



(Figure 4-16) Strain analysis by 3-D model (at 200°C)

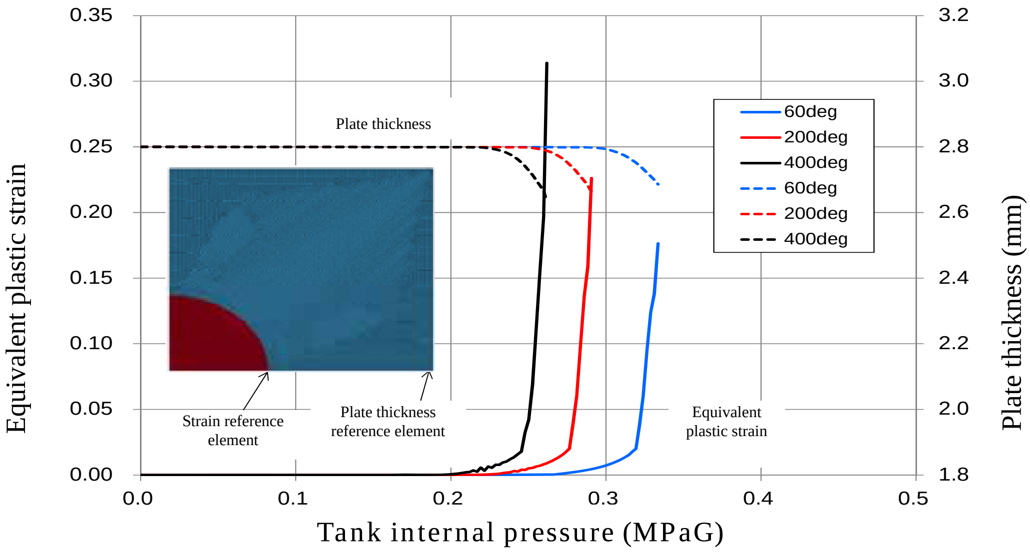


Zoom-in view of cooling water coil outlet nozzle at 0.2MPaG

Zoom-in view of cooling water coil outlet nozzle at 0.3MPaG

(Figure 4-17) Strain analysis by 3-D model (at 200°C)

Zoom-in view of cooling water coil outlet nozzle



(Figure 4-18) Analysis results of cooling water outlet nozzle vicinity

ii. Estimation results of tank internal pressure at ruptured by distance of V-3138 scattered fragments

From the scattered distance of V-3138 roof plates, deck and vent pipe, fragments' minimum initial velocity is determined and converted into Mach number. As a result the tank internal pressure at ruptured was estimated to be 0.45~0.64MpaG.

(Table 4-2) Estimated tank internal pressure at ruptured by distance of V-3138 scattered fragments

Fragments	Scattered Distance	Weight	Exposed Area	Minimum Initial Velocity	Tank Internal Pressure
Roof plate – 1	52m	144kg	$2m^2$	28.4m/s	0.49MPaG
Roof plate – 2	49m	540kg	$11.1m^2$	27.4m/s	0.45MPaG
Deck	94m	171kg	$2.3m^2$	35.7m/x	0.64MPaG
Vent pipe	91m	14kg	$0.02m^2$	31.5m/s	0.57MPaG

Also the Table 4-3 has listed down some of the V-3138 surrounding structures which were not affected by the fire. In general, the structures impact by a load such as a blast wave, which has a very short action time, should be examined by dynamic response analysis. However, it is supposed that the load received duration was sufficiently long in relation to the natural frequency inherent to these structures. Therefore, the blast pressure was estimated based on a static model.

(Table 4-3) Estimated blast pressure based on the damage sustained by V-3138 surrounding structures

Structures	Distance from Tank Center	Damage Conditions	Specification	Blast Pressure [MPaG]
Dike (south side)	3.3m	Collapse	$630mm^{H} \times 150mm^{t}$	More than 0.067
Dike (west side)	3.3m	No damage	$480mm^{H} \times 150mm^{t}$	Less than 0.115
H-steel piperacks	5.2m	Severe bent	$125mm^{W} \times 4820mm^{H} \times 7mm^{t}$	0.032~0.066
Lamp post	13.9m	Bent	$125A \times 940mm^{H} \times +$ $80A \times 2950mm^{t}$	0.014~0.018
Window glasses	74m	Broken	$430mm^{W} \times 860mm^{H} \times 3mm^{t}$	0.001~0.002

The explosive power was evaluated based on the blast pressure acted on the surrounding structures and distance from the tank center. As a result, the mass of TNT equivalent was estimated at about 1~3kg.

Reference [4.2.1-1]
C.J.H. van den Bosch, R.A.P.M. Weterings, Methods for the calculation of physical effects - due to releases of hazardous materials (liquids and gases) - 'Yellow Book'

(3) Types of explosion

Considering the following three types of explosion as the energy that brought the above mentioned explosive power, the Boiling Liquid Expanding Vapor Explosion was thought to be the closest probable type.

i. Vapor Cloud Explosion (Acrylic Acid Vapor)

This is a phenomenon in which a vapor cloud of flammable gas ignites and explodes. It is accompanied by an extremely large explosive power.

Oxygen is necessary to form this type of explosion and it is unlikely the vapor cloud has ignited inside the tank, since V-3138 was sealed with M-Gas. But given the flying directions of the fragments and scattered contents, it is presumed that a huge pressure was generated in V-3138. These were not coincided with the facts found after the explosion.

According to the estimated mass of TNT equivalent as the explosive power, the amount of acrylic acid vapor that contributed to the explosion was calculated to be about 2~8kg. On the other hand, the estimated amount of acrylic acid vapor released from V-3138's vent to the surrounding up till explosion was about 5,500kg (refer to Appendix 2). In view of explosive power, it was hard to conclude that this type of explosion has occurred.

ii. Explosion (rupture) caused by V-3138 increased pressure due to runaway reaction (polymerization)

This was an explosion (rupture) associated with a rise in V-3138 internal pressure and it coincided with the conditions of scattered fragments and contents.

The V-3138 internal pressure at the point of explosion was estimated to be about 0.27MPaG from the data obtained in the adiabatic reaction test. Also the pressure that initiated the cracks was estimated by the tank structural analysis as being 0.24~0.29MPaG. The estimated V-3138 internal pressures according to these two methods were nearly matched. However the tank pressure estimated from the distance of scattered tank fragments at the time of V-3138 exploded was about 0.45~0.64MPaG. This was nearly twice the estimated pressure that initiated the cracks and these differences cannot be explained convincingly.

According to the process data, the recorded reading of V-3138 liquid level gauge has exceeded the out-of-range limit at about 13:40 and dropped drastically before the explosion. This dropped has triggered an abnormal low liquid level alarm at 58.6m^3. These phenomena showed that tank internal pressure had ever dropped just before the explosion occurred and this cannot be explained convincingly if the explosion is caused by a runaway reaction.

iii. Boiling Liquid Expanding Vapor Explosion (BLEVE)

This is a phenomenon which phase equilibrium has destroyed by the rupture of a tank containing a pressurized liquid above its boiling point. The dropped in liquid level gauge reading (tank internal pressure) have coincided well to this phenomenon.

It has been reported in the literature that BLEVE will have an overpressure of about twice the initial pressure. By comparing the estimated initial pressure which initiated the cracks (0.24~0.29MPaG) and the estimated pressure at the time of explosion (0.45~0.64MPaG), the pressure at the point of explosion was about twice the initial pressure.

The phenomenon of BLEVE occurred inside the tank has coincided with the scattered conditions of V-3138 fragments and contents.

4.2.2. Fire Effect and Damages

The fire locations followed by the explosion have been confirmed based on the firefighting activities and they are listed as below. Figure 4-19 shows the areas which caught fire.

i. Pool fire within the dike where V-3138 was installed
ii. Fire on the building (electric room) located south of V-3138
iii. Fire spread to surrounding cables and fire engines
iv. Fire spread due to the scattered contents that flew to the east direction

Table 4-4 shows the liquid volume before and after accident of each tank located within the same dike as V-3138. Besides the V-3138, there are three tanks, i.e. V-3116, V-3124, and V-3148C, whose contents varied before and after the accident. It is estimated that these tanks were damaged by the explosion and the contents leaked out within the dike. These contents continued to fuel the pool fire (acrylic acid: approx. 67m^3, and toluene: approx. 28m^3).

(Table 4-4) The tanks installed within the dike and its liquid volume before and after accident.

Tank No.	Main Contents	Nominal Capacity [m^3]	Liquid Volume [m^3]		Equipment Condition After Accident
			Before	After	
V-3138	Acrylic acid	70	60	-	Ruptured
V-3116	Acrylic acid	100	67	2	Damaged (leaked)
V-3124	Toluene	50	30	1.5	Damaged (leaked)
V-3145A	Toluene	15	9.4	9.4	
V-3145B	Toluene	5.2	0.4	0.4	Damaged
V-3146A	Acrylic acid	15	8	8	
V-3146B	Acrylic acid	15	13	13	
V-3147A	Acrylic acid	10	7	7	
V-3147B	Acrylic acid	5.2	3	3	Damaged
V-3147C	Acrylic acid	5.2	4.2	4.2	Damaged
V-3148C	Acrylic acid	5.2	1.5	0.08	Damaged (leaked)

In addition, the highly possible causes of casualties are assumed due to the following factors:

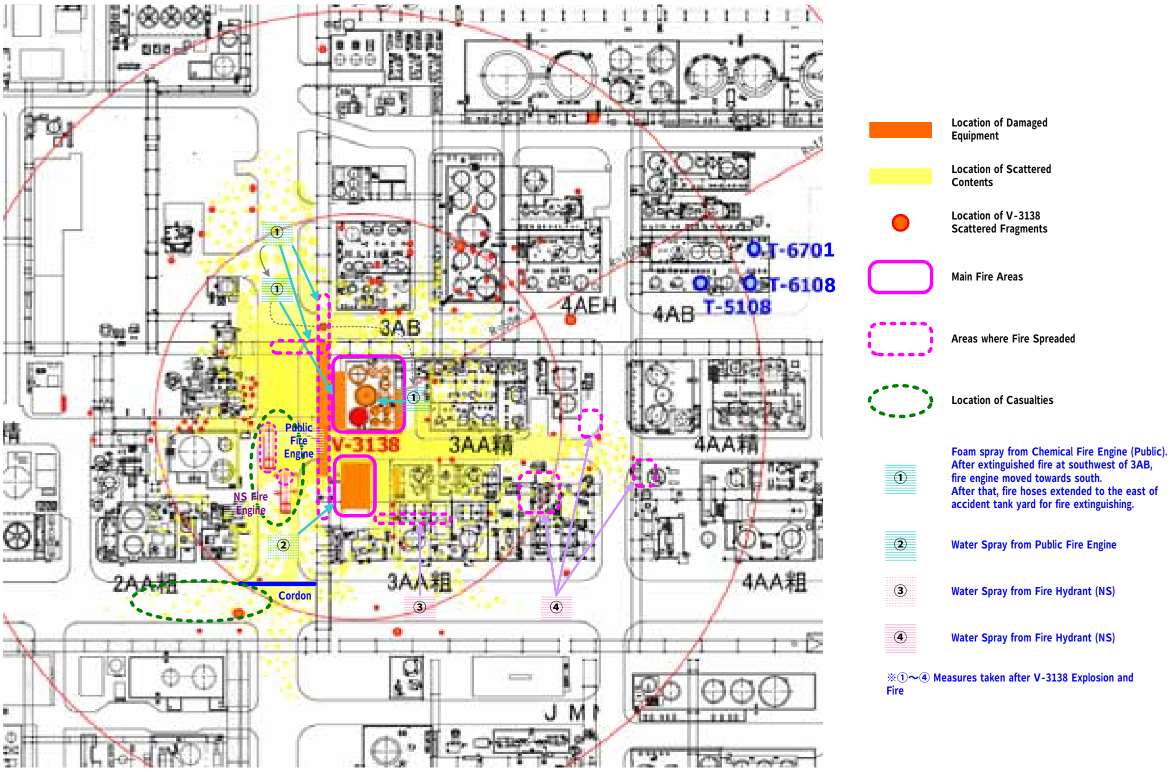
i. Splashed by V-3138 high temperature contents which were released during the explosion.
ii. Burned by radiant heat generated from the pool fire at dike where V-3138 was installed.
iii. Burned by radiant heat generated from the possible fireball occurred after the BLEVE.

It is assumed that fire was possibly ignited by the following objects:

i. Sparks generated from the impact of metals at time of explosion
ii. Sparks generated from the broken electric cables

Fire Areas Around the Tank

※ This information is prepared based on the status confirmed after the accident and Nippon Shokubai (NS) employees interviews.



(Figure 4-19) Fire areas around the tank

5. Determining the Causes of the Accident

5.1. Contributing Factors of the Explosion and Fire

5.1.1. Direct Causes of the Accident

Based on the investigations and analysis, the committee has identified the direct causes of the accident as following:

i. Even though high temperature T-5108 bottom liquid was building up in V-3138, the fact that the circulation of Recycle to Top was not commissioned has caused acrylic acid to remain stagnant for a significant long period of time at high temperature in the upper portion of the tank.

ii. DAA formation accelerated in the tank liquid with high temperature zones and the heat of dimerization has caused the liquid temperature to increase. This has also caused the acrylic acid start to polymerize and increased the liquid temperature further.

iii. Due to lack of thermometers and inadequate temperature monitoring, it was not possible to detect the abnormal condition until polymerization had proceeded.

These have resulted in V-3138 exploded, followed by fire and caused enormous casualties and property damage.

5.1.2. Contributing Factors of the Accident

(1) Fault-Tree diagram (FT diagram) of accident contributing factors

In light of the direct causes of the accident, an FT diagram was used to systematically analyze events in order to clarify contributing factors that could have caused the accident and their connections. The results are shown in Figure 5-1. The following eight items are determined as contributing factors that caused the accident:

a) Excessive heating in tank feed liquid

The T-5108 bottom liquid temperature was about 65°C but it has increased to about 100°C by the steam jacketed transfer piping before charging into V-3138.

b) Recycle to Top valve was closed

When tank liquid was to be maintained for several days above 25m^3, Recycle to Top was required to be commissioned. However this valve was not operated and remained closed.

c) Inadequate tank control temperature setting

d) Inadequate tank temperature detection

There was no setting for tank control temperature and there was no thermometer installed.

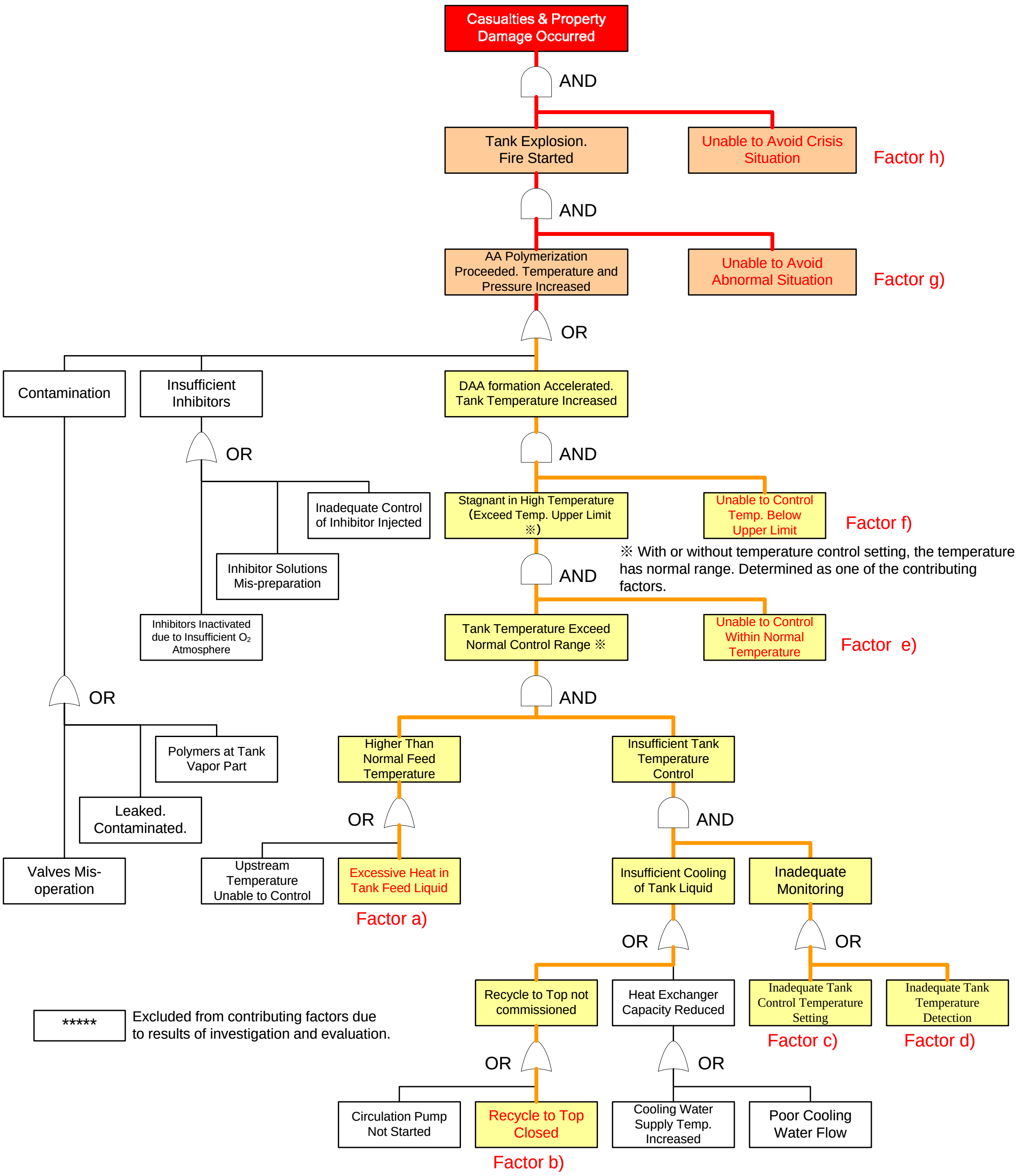
e) Unable to control the temperature within normal range

f) Unable to control below temperature upper limit

g) Unable to avoid abnormal situations

h) Unable to avoid crisis situations

No criteria were developed to judge the symptom and abnormality of tank temperature. Also the response procedures to handle abnormal situations were not established.



(Figure 5-1) Fault Tree Diagram (FT Diagram) of Contributing Factors

(2) Contributing factors of the accident and its management elements

In view of matters related to contributing factors of the accident, developing a safer system and background of the surrounding circumstances etc., the management elements of each contributing factor was investigated respectively. Table 5-1 shows the management elements related to each contributing factors of the accident.

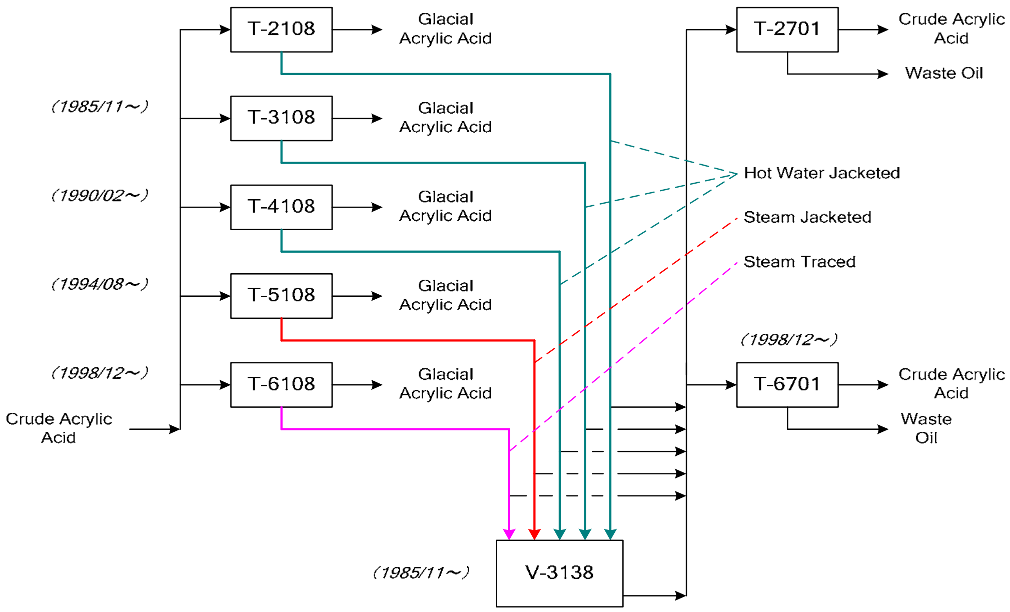
(Table 5-1) Management Elements of Respective Contributing Factors of the Accident

No.	Contributing factors	Management Elements
(1)	a) Excessive heating in tank feed liquid	Design review, validation and design philosophies handover
	b) Recycle to Top valve was closed	
(2)	-1) V-3138 Control Procedure	Operation manuals development and dissemination
(3)	-2) T-6701 load up test	Risk assessment and safe work management for non-routine work
(4)	c) Inadequate tank control temperature setting d) Inadequate tank temperature detection	Operating conditions setting and management
(5)	e) Unable to control the temperature within normal range f) Unable to cool down the temperature below the upper limit g) Unable to avoid abnormal situations	Criteria for abnormal situations and its respective response procedures
(6)	h) Unable to avoid crisis situations	Crisis management and disaster prevention activities

5.1.3. Background of Accident Contributing Factors

Investigate the management elements of contributing factors background

(1) Contributing factor a) Excessive heating in tank feed liquid



(Figure 5-2) History of glacial acrylic acid plants

i. Equipment history

In the past, hot water jacket was used for distillation columns and piping to prevent polymerization and precipitation. As the polymerization prevention technology advanced, equipment using hot water jacket has been reduced and hot water supply equipment also decreased.

When T-5108 was constructed, hot water jacket was not necessary for the T-5108 as a result of technological improvement. On the other hand, the heating facility was still necessary for T-5108 bottom liquid transfer piping to prevent freezing and precipitation. However, since there was no hot water equipment, steam jacket was chosen. Steam tracing was used for the T-6108 bottom liquid transfer piping which was constructed at a later stage (See Figure 5-2).

ii. Design and construction stages

T-5108 was constructed as part of the 5AA construction project and commissioned in August 1994. The project was carried out by a mixed team of members from three departments: Production, Technology and Engineering.

It was widely known that T-108 columns' bottom liquid presented concerns of sludge precipitation at low temperature and polymerization at high temperature. But, it had little recognition on trouble may caused by insufficient cooling in V-3138 liquid, since the T-108 columns' bottom liquid contained a lot of inhibitors. A steam pressure regulating valve and a temperature control steam trap were installed at the steam jacketed piping considered the T-5108 bottom liquid may polymerize due to the excessive heat from steam jacket. However, the cooling capacity of the V-3138 coil was not verified and the risk of causing inadequate cooling in the upper portion of the tank liquid was not considered.

During that time, there was no design review system in place to verify, assess and review the design of new equipment and hence the new installation has no appropriate evaluation from various perspectives.

iii. Test run stage

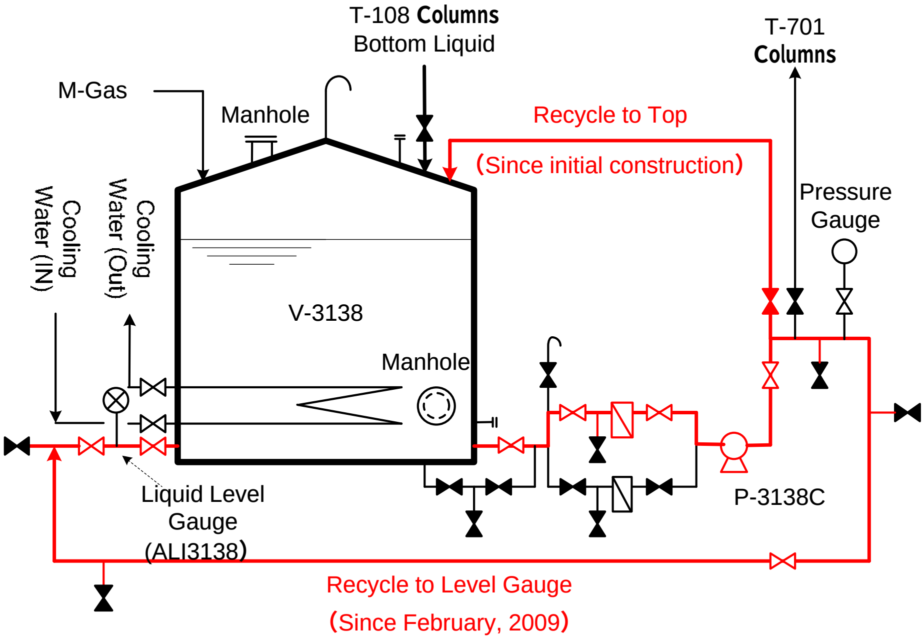
The pressure setting of steam regulating valve at the steam jacketed piping that transfers T-5108 bottom liquid was set at 0.02MPaG based on setting stipulated in the operation manuals. The temperature setting for the temperature control steam trap was set at 90°C based on the test run results. But there was no monitoring device provided to monitor liquid temperature at the steam jacketed piping outlet. It was assumed that at this point, the liquid has already been excessively heated to a temperature higher than the T-5108 bottom temperature.

iv. After commercial operation

The T-5108 bottom liquid temperature at the steam jacketed piping outlet was not widely recognized in the Production department. It was assumed to be about the same as the T-5108 bottom temperature. This lack of accurate information (design concept, technical evaluation, adopted rational, etc.) in the Production department was thought to be due to improper handover from the project team to the Production department.

Moreover, the temperature control steam trap has frequently experienced drain accumulation in the jacket due to rust blockage at the drain outlet part. Ultimately it was decided to remove the temperature control steam trap and allowed the steam to flow through the jacket continuously. As the result, the T-5108 bottom liquid was heated to about 100°C. Also in December 2009, the steam regulating valve was changed and the pressure setting was adjusted to 0.005MPaG. Therefore, it was assumed that the temperature control steam trap was removed sometimes after this point. There was no record on when the temperature control steam trap was removed or any investigation or procedure relating to this removal.

(2) Contributing factor b) -1) Recycle to Top valve was closed (V-3138 Control Procedure)



(Figure 5-3) V-3138 status before the accident

i. Chronology: Year 1985 to 2009

V-3138 was an intermediate tank between the T-108 columns and the T-701 columns. It had a nominal capacity of 70m^3 and was installed in 1985. At the time, it took two days to stop T-2701 operation for maintenance and V-3138 was designed with a capacity that could store the bottom liquid from the T-108 columns (T-2108/3108) during this two days period. Also, only Recycle to Top circulation is provided in the tank. During normal operation of T-108 and T-701 columns, it was not necessary to store large volume of liquid in V-3138. Therefore, the liquid volume was usually kept low not to exceed the top of cooling coil.

T-108 columns bottom liquid was supplied either via V-3138 or directly to the T-701 columns. But since Year 2000, it was supplied via V-3138 in order to stabilize the supply flow rate to the T-701 columns. If V-3138 liquid temperature decreases, it would cause sludge precipitation and accumulated inside the tank. This has caused problems such as wrong readings in liquid level gauge and plugged the P-3138C strainer. It took a lot of works and efforts to handle these problems. In February 2009, an additional circulation line, Recycle to Level Gauge, was installed as a countermeasure to fix the wrong readings in the liquid level gauge.

ii. Chronology: Year 2009 to 2010

Even after the Recycle to Level Gauge was installed, there were still a lot of works to be done such as cleaning and washing the pump strainer and its surrounding piping. After opening up and cleaning the tank in August 2009, the procedures on how to use the tank was changed temporarily starting from September 2009 in order to confirm the effectiveness of the new procedure. The temporary procedure relating to tank usage was communicated and documented in the Operation Knowledge Base system (a database which provides a centralized store of operational related information). The content is presented as follows:

-1) Only withdrawing column bottom liquid to V-3138 when T-108 column is stopped.

-2) After feeding liquid into V-3138, supply the tank liquid to the T-701 column for processing and reduce the tank liquid volume until $5m^3$, the minimum required liquid volume which need to keep inside the tank.

-3) After processing the tank liquid, blow clean the surrounding piping and commission only the Recycle to Level Gauge for tank circulation.

-4) Close the cooling water valve to the coil.

About five months later, at the end of January 2010, the above procedures were revised as the "V-3138 Control Procedure". Notification of this change was raised in the Operation Knowledge Base and the content was listed in the following:

-1) When the T-108 columns are in operation, supply the T-108 columns bottom liquid directly to the T-701 columns.
Only withdrawing column bottom liquid to V-3138 when T-108 column is stopped.

-2) After feeding liquid into V-3138, supply the tank liquid to the T-701 columns for processing. Reduce the tank liquid volume until $5m^3$, the minimum required liquid volume that covers the lower portion of the cooling coil.

-3) After processing the tank liquid, blow clean the surrounding piping and commission only the Recycle to Level Gauge for tank circulation.

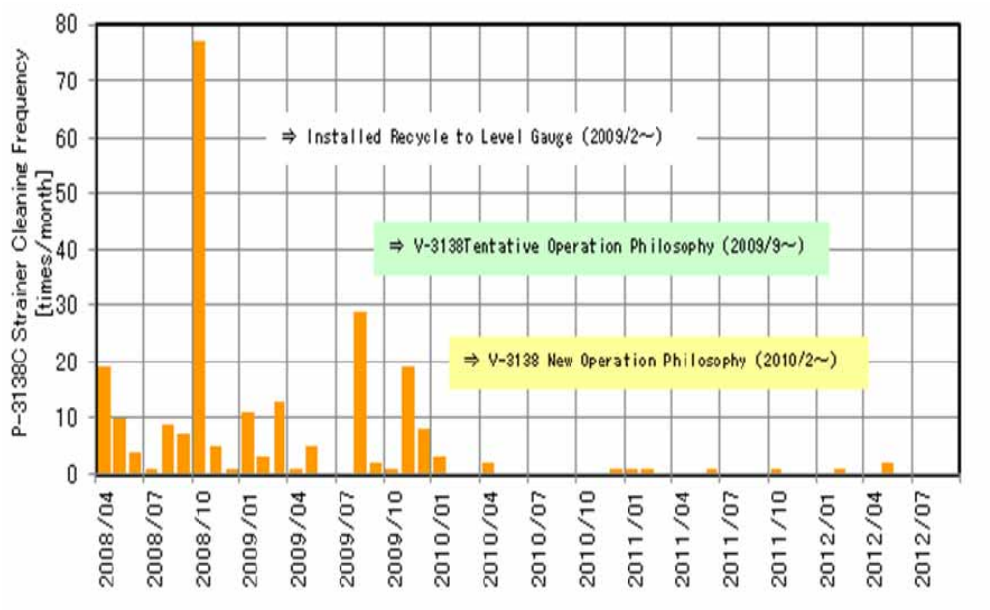
-4) In the situation where the liquid in the tank is unable to process and need to keep inside the tank for several days, commission the Recycle to Top if the liquid volume has more than $25m^3$ (liquid volume up to the top of the cooling coil).

-5) The cooling water valve to the coil should be opened normally.

This "V-3138 Control Procedure" was a permanent matter, however it has not reflected in any documentation (ex. operation manuals etc.) or management system other than notification in Operation Knowledge Base. However, in order to assist the site operators, signage was posted above the Recycle to Top valve on site stating: "Normally Closed, Open Recycle if above $25m^3$."

iii. Chronology: Year 2010 to 2012

After changing to V-3138 Control Procedure, the frequency of cleaning the pump strainer has dropped sharply. This has significantly reduced the workload of operators. Moreover, the tank internal has not been washed since the last cleaning in August 2009. Figure 5-4 shows the frequency of pump strainer cleaning.



(Figure 5-4) Frequency of P-3138C strainer cleaning

Originally, the cleaning and washing works around V-3138 is due to the precipitate accumulation inside the tank. By changing the procedures of operating the tank, the effectiveness of this improvement has verified by the reduced frequency in strainer cleaning, etc. However, any change in the amount of deposition inside the tank and the need for Recycle to Level Gauge was not re-examined.

Thereafter, the chances of storing the liquid above $25m^3$ in V-3138 or opportunities to operate the Recycle to Top valve were hardly experienced by operators. Hence the operators have become unaware of the necessity to commission the Recycle to Top.

Furthermore, there were multiple rectifying columns connected to V-3138. Switching the feed of T-108 columns bottom liquid to V-3138 or to the T-701 columns was carried out by operating the header valve in different locations. These locations were about 15m away from the P-3138C discharge header as indicated in Figure 5-3. For this reason, it might be difficult for operators to notice the sign pertaining to Recycle to Top valve.

(3) Contributing factor b) -2) Recycle to Top valve was closed (T-6701 load up test)

i. Background relating to safe work management and operating instructions

In the Production department, “Permit-To-Work System” (PTW) is applied for any works which required special attentions and safety measures. Also PTW is applied to “Standard for Non-Regular Works” which are not specified in the Standard Operating Procedure. Approval is necessary to carry out such works and safe work procedures are prepared in advance for each different type of works. These safety measures and its contents are required to make known to all members before any work is allowed to start.

However, in regards to operation and safe work management, there are no rules specified things such as approval route, issuance of operating instructions. Practices on operating instructions differ by each department. But basically if necessary, they will be issued with Production Manager approval regardless whether there is any manual in place. Generally the operating instructions are often issued to supplement the manuals.

ii. Risk management associated with changes

The rule of "Management of Change" (MOC) is applied for risk management associated with permanent or temporary changes in equipment and processes, etc. This rule was established in August 2004 and revamped completely in September 2009, after which this rule has been implemented through database. Each department evaluated their practices to MOC and conducted the necessary countermeasure.

According to this rule, any changes are evaluated using a MOC check sheet. The depth of review and approval route are then determined based on the check sheet's result. Changes in which this rule is not applied are also described with examples. Examples which this rule is not applicable included "changes involving same specification in facility, piping, equipment" or "changes involving operating conditions and procedures but within the safe operating scope". However, the interpretations of whether this rule is applicable may differ between individuals. If they think this rule is not applicable, the MOC check sheet will not be used.

iii. Load up test in Year 2009

The V-3138 liquid level built up in order to conduct a load up test in T-6701. This intentionally liquid built up was not a normal but non-routine work. Moreover, the load up test for T-6701 was an operation conducted under temporary conditions and was not covered in the operation manuals.

The purpose of the T-6701 load up test was to confirm the operating conditions under which the quality of distillate could be ensured. The testing conditions for T-6701 were thought to be adjusted within the range of equipment capacity, given that the rectifying column load was within the operating range of the past track records and the liquid volume to store in V-3138 was within the tank's nominal capacity. Accordingly, a testing plan indicating matters such as T-6701 test method, conditions and schedule was prepared. However, the risks pertaining to storing liquid in V-3138 were not investigated.

The testing plan was issued with the approval of Production Manager but no operating instruction was issued. However at that time, the methods of provisional use of V-3138 were verified and the Recycle to Top was commissioned after liquid built up in the tank.

iv. Load up test in Year 2012

The understanding regarding the T-6701 load up test was the same as test carried out in Year 2009. Hence the risks associated to build up V-3138 level were not investigated. Moreover, this V-3138 storing operation was expected to carry out according to the "V-3138 Control Procedure", however its contents had not been reflected in manuals and no operating instructions were issued. Therefore operators were not aware of the "V-3138 Control Procedure".

(4) Contributing factor c) Inadequate tank control temperature setting

Contributing factor d) Inadequate tank temperature detection

i. V-3138 temperature control

An acrylic acid plant is made up of various unit operations such as absorption, distillation in addition to the oxidation reaction. The temperatures in each of this main process unit need to be precisely controlled.

Regarding the temperature control in V-3138, the tank temperature has to be maintained within a range due to concerns of acrylic acid freezing, sludge precipitation at low temperature and polymerization at high temperature. Normally only small volume of liquid with high contents of inhibitors was stored in V-3138 and it could be cooled by the cooling coil inside the tank. Hence the precise control of temperature was not necessary. Moreover, compared to the main process equipment, there was relatively little awareness of the need for quantitative temperature control in V-3138. This status has been the same since the tank constructed till now.

Furthermore, inhibitors and the atmosphere condition are not able to prevent the formation of DAA, whereas the temperature has a big impact. But these risk information associated to DAA formation were not widely shared. Hence it is assumed that awareness of temperature control to prevent DAA formation was not established.

ii. Necessity of instrument installation

The need to install a thermometer and how to use it (on-site or remote monitoring) is established based on matters such as the necessity of temperature control, the temperature monitoring cycle and legal requirements. But, the plant has no standard on means of temperature monitoring that reflects these points comprehensively. Meanwhile assessment for the need of temperature control and monitoring was carried out by each plant individually. When the need for temperature control is assessed as low and intermittent detection is sufficient, thermometers will not be installed. This has created variation in the assessment and awareness of temperature control and monitoring.

iii. V-3138 thermometer: design and construction stages

As described above, there was low awareness of the need for quantitative temperature control in V-3138, and hence thermometer installation was not planned at the design stage. Later, additional nozzle and other changes were made as the project moved into detailed design and construction stages, the addition of thermometer nozzle was one of these changes. However, there were no records available that can accurately identify the intention on how to use the nozzle or the existence of a thermometer when the equipment commissioned.

iv. About the V-3138 thermometer: relation to lateral deployment following a trouble

In April 1994, polymerization trouble occurred in another acrylic acid intermediate tank. Countermeasures proposed at that time included implementing continuous temperature monitoring and installing external heat exchangers at similar tanks other than the tank where the trouble occurred. Even though V-3138 was found of not having thermometer installed during that time, it was not included in the lateral deployment scope. It is assumed the reason for this was because the equipment subject to the lateral deployment was tanks that received column bottom liquid at 80~100°C whereas the bottom temperature in the T-108 columns were only about 65~70°C. Also, T-5108 has not yet been constructed at that time.

During that time, the causes investigation and countermeasures implementation for this trouble were concluded only within the involved department. There was no system in place to involve participation of other departments likes Technology in investigation for preventing similar trouble in other areas.

(5) Contributing factor e) Unable to control the temperature within normal range
Contributing factor f) Unable to cool down the temperature below the upper limit
Contributing factor g) Unable to avoid abnormal situations

i. Overall safety measures for acrylic acid

In acrylic acid plant, if any abnormality is detected and prevent the normal operation to continue, the plant will be shutdown through interlock system. Conventionally, safety measures for acrylic acid focused on measures to prevent trouble. However, emergency criteria and response procedures were not established for the abnormal situations which cannot be controlled even if the equipment is shut down.

ii. V-3138

Since there was insufficient temperature monitoring device in V-3138, it was not possible to detect the temperature has exceeded until the equipment has been shut down or some sort of actions have been taken. Also there were no criteria and means for handling abnormal situations established and therefore, there was no equipment to handle this situation.

(6) Contributing factor h) Unable to avoid crisis situations

i. Past trouble

The Himeji Plant has not experienced a tank ruptured or explosion due to acrylic acid polymerization. However, acrylic acid polymers have been discovered during tank internal inspection and basic measures to prevent polymerization have been implemented for each tank, such as the removal of unnecessary structures.

Measures taken in the past when acrylic acid polymerized in the tanks included two instances of spraying water onto the tank and one instance of charging water and inhibitors from the manhole. Other measures which have been taken included charging cooling water into the tank jacket.

ii. Activities relating to responses to abnormal phenomena

With the aim of improving the disaster prevention capabilities of the safety team in the Himeji Manufacturing Innovation (HMI) division, various activities have been conducted together with the Responsible Care (RC) activities since Year 2007. Furthermore, other than the complex-wide disaster prevention trainings, each of the various workplaces will also implement its own planned disaster prevention exercises. One of these trainings is the fire fighting exercises which include a yearly fire fighting competition. Others also include building up a good supply of the disaster prevention equipment.

Immediate response procedures for abnormal phenomena such as hazardous materials or high pressure gas leakage and fires, etc. have been developed in the Plant's Emergency Response Plan but none of these covered for runaway reaction. (In the training materials relating to abnormal phenomena and alerting procedure (in the process for approval), there was illustration to cool the tank by spraying water as a way of responding to runaway reaction).

iii. Status of rules development

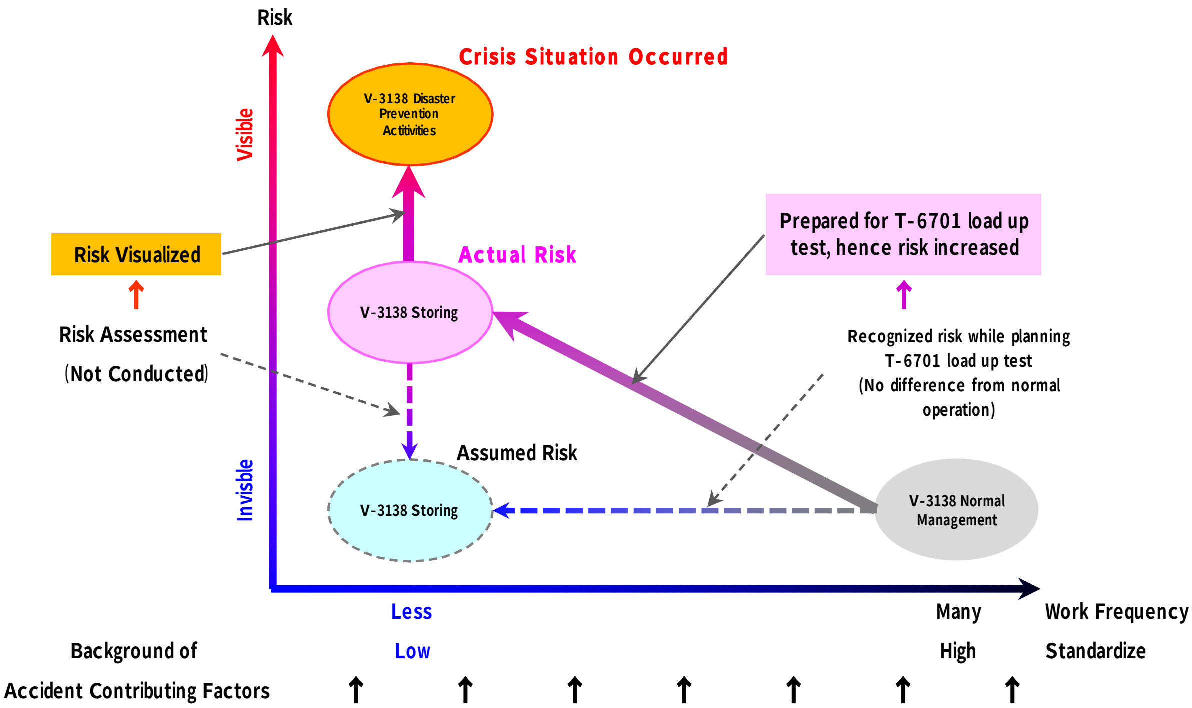
A self disaster prevention manual has been developed as part of the Himeji Plant Rules and Regulations. However, the role and responsibility on providing information to public fire department was not clearly defined in self disaster prevention team. Also, there was no manual to standardize each plant criteria for abnormality and its respective response procedure.

iv. Responses during this accident

Tank cooling was judged to be necessary based on the V-3138 conditions and hence the tank was sprayed with water. At first, operators sprayed water from six fire hydrants (each at 400 liters/min.). Later, the self disaster prevention team sprayed additional water (3,100 liters/min) from the fire engine. However V-3138 was insulated and it was assumed that water spraying did not have much cooling effect to the tank liquid.

Since acrylic acid vapor was being released from V-3138, the intention of spraying water onto the tank was to cool and to absorb the acrylic acid vapor. This action may have prevented vapor cloud explosion. However under such circumstances additional measures such as charging water and inhibitors inside the tank could not be taken. There was no means to control the abnormal situations progress other than spraying water.

Based on the above, the backgrounds of each contributing factor are summarized in the Figure 5-5. Also, each of the contributing factors, management elements of its background and consideration to prevent recurrence are summarized in Table 5-2.



(1) Insufficient design review and design philosophy handover procedures
(2) Insufficient operation manuals development and dissemination
(3) Weak systems in safe work management and risk evaluating of changes, non-routine works
(4) Inadequate management of operating conditions settings
(5) No establishment of criteria for abnormal and crisis situations and its respective response procedures
(6) Poor coordination with public fire department during disaster prevention acitivities

Safety culture and safety climate issues that derived from the above backgrounds
(Safety awareness and hazards sensibility, etc.)
(Lack of understanding of technical knowledge, expertise and hazardous information)

(Figure 5-5) Summary of background of accident contributing factors

(Table 5-2) Consideration points for recurrence prevention

<table>
<tr><td>No.</td><td>Contributing factors</td><td>Management elements</td></tr>
<tr><td></td><td colspan="2">Consideration Points for recurrence prevention</td></tr>
<tr><td>(1)</td><td>a) Excessive heating in tank feed liquid</td><td>Design review, validation and design philosophy handover</td></tr>
<tr><td></td><td colspan="2">1) Conduct risk assessment and design review during the design stage.
2) Verify the operating conditions at the test run stage
3) Educate and disseminate any changes and its technical evaluation contents to operators.
4) Conduct risk assessment for any changes in equipment and verify the changes after the modification.
5) Manage the records and revision history thoroughly.</td></tr>
<tr><td>(2)</td><td>b) Recycle to Top valve was closed
1) V-3138 Control Procedure</td><td>Operation manuals development and dissemination</td></tr>
<tr><td></td><td colspan="2">1) Include the control procedure of intermediate tanks in the operation manuals
2) Conduct risk assessment for any changes in operating procedures and verify them after the changes
3) Disseminate the operating procedures to operators and confirm the procedures are executed.
4) Enhance the works’ reliability (easy-to-understand signage for field operators, etc.)</td></tr>
<tr><td>(3)</td><td>b) Recycle to Top valve was closed
2) T-6701 load up test</td><td>Risk assessment and safe work management for non-routine work</td></tr>
<tr><td></td><td colspan="2">1) Confirm risk assessment is executed for non-routine works and changes.
2) Review the MOC system (risk evaluation scope, check sheets usage, etc.)
3) Establish system to ensure risk assessment is conducted before operation, issuance of operating instructions and its approval routes, etc.
4) Enforce precaution checks before work implementations based on operating instructions.
5) Strengthen risk management system through education and personnel development</td></tr>
<tr><td>(4)</td><td>c) Inadequate tank control temperature setting
d) Inadequate tank temperature detection</td><td>Operating conditions setting and management</td></tr>
<tr><td></td><td colspan="2">1) Standardize temperature monitoring methods.
2) Standardize temperature control methods and improve the accuracy of temperature controlling.
3) Share the hazardous information of the handled materials.
4) Manage the equipment revision history thoroughly.
5) Strengthen participation of multiple departments including technology department in any trouble investigation.</td></tr>
<tr><td>(5)</td><td>e) Unable to control the temperature within normal range
f) Unable to cool down the temperature below the upper limit
g) Unable to avoid abnormal situations</td><td>Criteria for abnormal situations and its respective response procedures</td></tr>
<tr><td></td><td colspan="2">1) Establish the criteria for abnormal situations and its respective emergency response procedures.</td></tr>
<tr><td>(6)</td><td>h) Unable to avoid crisis situations</td><td>Crisis management and disaster prevention activities</td></tr>
<tr><td></td><td colspan="2">1) Establish the criteria for crisis situations and its respective emergency response procedures.
2) Improve cooperation with public fire department (information sharing development, review communication structure, etc.)</td></tr>
</table>

5.2. Matters Related to Expanded Damage Resulted from the Explosion and Fire

Based on Section 5.1 contributing factors of the accident, matters related to expanded damage are discussed below:

(1) Property damage

i. The abnormal development that led to the tank explosion was due to the progressive polymerization of acrylic acid. One of the reasons for damage to expand was due to the fact that abnormal conditions could not be detected at early stage as a result of inadequate temperature detection.

ii. As mentioned in Section 5.1.3, another factor that caused the property damaged to expand was no other means were available to prevent the development from abnormal situations to crisis situations besides water spraying.

(2) Casualties

i. Casualties in this accident were caused by tank explosion while one team was preparing and the other team was spraying water onto the tank. They were exposed to fire radiant heat and splashed by the high temperature contents from the tank. The casualties' injuries were related to their distance from the tank and personal protection equipment worn.

ii. For conducting disaster prevention activities from an appropriate distance with the right equipment, factors such as criteria to determine abnormality, response plan, organization, etc. are important. However these factors were not fully established for crisis situations and hence the casualties have expanded.

6. Recommendations for Accident Recurrence Prevention Countermeasures

The following countermeasures are recommended to prevent the accident recurred, based on the contributing factors and background that led to the accident as summarized in the preceding section. The recurrence prevention countermeasures were derived using 6M-5E analysis based on the perspectives described in Table 6-1. The details of the analysis are described in Table 6-2.

Table 6-1. Perspectives of 6M-5E analysis

6M: Perspectives on background types of accident contributing factors	5E: Perspectives of deriving the recurrence prevention countermeasures
Man	Education
Machine	Engineering
Method	Enforcement
Material	Environment
Measurement	Example
Management	

6.1. Recurrence Prevention Countermeasures for Equipment Involved

For restoring equipment involved, in order to ensure greater safety and stable production activities, the following recurrence prevention countermeasures should be implemented.

(1) Revise the specification of the T-5108 bottom liquid transfer piping

In order to prevent overheating of tank feed liquid, the following items should be implemented:

i. Reconfirm the liquid properties and setting of the design conditions.

ii. Conduct risk assessment for the piping specification change and evaluate its propriety.

iii. Confirm the piping operating conditions and status through test run.

(2) Study the specifications of V-3138 and its associated equipment (new installation)

In order to control the V-3138 liquid temperature at the appropriate temperature and to ensure evacuation criteria and to clarify its response procedures, the following items should be implemented:

i. Reconfirm the liquid properties and temperature control settings.

ii. Provide means to control the temperature (include thermometers installation, Recycle to Top line is always commission).

iii. Establish the abnormal temperature criteria and its respective response procedures (study the emergency inhibitors injection, etc.)

iv. Conduct risk assessment for the V-3138 and its associated equipment installation and evaluate its propriety.

v. Confirm the operating conditions, status, etc. of V-3138 and its associated equipment through test run.

(3) Development of manuals, etc.

To clarify safety of the restored equipment and necessary matters for stable operation, the following items should be implemented:

i. Develop manuals and other documentations for T-5108 and V-3138

ii. Update the P&ID, etc. around T-5108 and V-3138.

iii. Prepare site signage around T-5108 and V-3138.

(4) Education and training

To operate the restored equipment safely and stably according to the manuals, the following items should be implemented:

i. Provide training of T-5108 and V-3138 operation manuals, etc. to operators.

ii. Re-educate employees to fully understand the detailed behavior of DAA formation and the hazards of acrylic acid.

6.2. Countermeasures to Prevent Recurrence of Similar Accidents and its Lateral Deployment

6.2.1. Countermeasures to Prevent Recurrence of Similar Accidents

To prevent similar accidents from occurring at other production facilities in the Himeji Plant, the following items should be implemented:

(1) Operation and safe work management

To ensure risk assessment is conducted whenever there are changes in non-routine works, procedures, methods, equipment, etc. and each work details are disseminated, the following items should be implemented:

i. Establish basic rules for safe work management

Establish basic rules for safe work management and standardize the definitions and safe work management system for each work. Also, provide training on the application of these rules, ensure safety checks are enforced and consider all the potential hazards thoroughly before starting any works.

ii. Review rules of Management of Change

Prevent risk evaluation overlook by reviewing the target which covered under MOC and check sheets exercise. Moreover, strengthen the risk management framework by providing training on MOC application through case studies, by training the safety manager, etc.

iii. Review the practice of operating instructions

Specify the rules for issuing operating instructions and its approval routes with consideration of risk evaluation, while revising safe work management and MOC systems. Also practices such as in advance risk assessment, hazards evaluation before the works implementation and confirmation after works completion should be enforced.

(2) Crisis Management

To strengthen the emergency response capabilities when the abnormal situations arise, the following items should be implemented:

i. Develop the crisis management manual

Clarify the basic policy and the framework of crisis management, and set out the activities to be carried out during normal circumstances for preparing any abnormal situations. In addition, when the abnormal situations arise, establish measures to secure human safety, minimize the damages and prevent secondary disaster. Clarify the communication routes between public fire department.

ii. Review the self disaster prevention manual

Review the individual roles and definition of self disaster prevention organization including arrangement during evening and off-days, in views of the communication structure likes information conveying to public fire department. Improvements of initial responses (includes reporting) to the abnormal situations and disaster prevention equipment should be reviewed as well.

iii. Provide education and training on these manuals

Establish a self disaster management system which enables effective collaboration with public fire department by implementation of trainings and drills.

(3) Other Countermeasures

i. Re-educate the hazards of the handled substances.

ii. Review the design standards for the tank associated equipment.

iii. Review the system of lateral deployment following a trouble.

Trouble investigation should be executed by multiple relevant parties including Technology department for ensuring that no countermeasure is overlooked during lateral deployment process.

iv. Collect and make full use of the external incident case studies and technical information

Develop engineer and improve technical capabilities through the above countermeasures and various informations collected externally.

6.2.2. Disaster Prevention Measures for Equipment Handling Acrylic Acid

To prevent the recurrence of similar disaster in the equipment handling acrylic acid, the following items should be implemented:

i. Standardize tank temperature monitoring methods (thermometer installation).

ii. Review the tank control temperature range and temperature control methods

Review the control temperatures for tanks that storing acrylic acid. Establish methods to control the tank temperature within the pre-defined temperature range and supplementary measures to control the tank temperature.

iii. Establish the criteria for judging abnormal symptom and the basic concepts of the response procedures

Establish the basic concept of temperature criteria for foreseeing abnormal situations and the response procedures when the temperature criteria exceeded.

iv. Establish the temperature criteria of each equipment based on the criteria for judging abnormal symptom

v. Establish the response procedure for each equipment considering the foreseeable abnormal events and crisis situations.

The response procedures to the abnormal events include feed isolation, delaying the abnormality progress, release, withdrawal and isolation. Depends on the characteristics of the equipment, the suitable response procedures will be applied. In order to minimize the damage caused by abnormal events, the existing response procedures should be further strengthened.

vi. Conduct risk assessment and evaluate its propriety for the above items i to v.

vii. Modify equipment handling acrylic acid based on the above items i to vi.

viii. Update the manuals and conduct the related trainings to all facilities handling acrylic acid.

6.2.3. Lateral Deployment of the Accident Prevention Countermeasures

Review the countermeasures described in Sections 6.2.1 & 6.2.2 and compare them against the current practices in other plants.

Furthermore, share the knowledge and information gained through the accident investigation to other companies and the industry. With these, contribute to the acrylic acid industry or even the entire chemicals industry through the safer production activities.

6.3. Fostering a Safety Culture of Safe Manufacturing Plant and Corporation

Nippon Shokubai has until now implemented diverse safety activities under a corporate commitment of “Safety takes precedence over production”. Under these circumstances, the company repeatedly expanded the production capacity of the Himeji Plant as its backbone plant without any major accident. Despite these, the explosion and fire which occurred in acrylic acid production facilities (the main facilities in the Himeji Plant) has resulted in significant casualties and property damage.

Our investigation has revealed various diverse factors have complicatedly combined and caused the accident in the Himeji Plant. The continuous stable production over the past years has softened the safety awareness and became less sensitive towards dangers. As a result, these factors have led into the accident in the Himeji Plant.

These factors should not be downplayed as being localized and restricted to specific organizations and facilities. Rather, they should be recognized as the representation of Nippon Shokubai current safety capabilities. The company therefore needs to fully accept this accident, each employee should contemplate and realize the corporate commitment from now on.

To accomplish these, there is a need to renew employees understanding that safety is not something others provide but rather they need to recognize and achieve safety by themselves. The company must ensure that this attitude is reflected in the future behavior of its organization and individuals. Achieving safety begins with “abiding” the safety rules and ”noticing” circumstances that could detract from safety, these will result in “changing” to a safer corporation. In any event, it is unlikely to achieve safety without the knowledge, realization, and expertise of organization and individuals. Therefore, the company needs to treat these safety issues as the company-wide challenge including personnel development, alongside implementation of the recurrence prevention countermeasures.

The lesson learned from the accident in the Himeji Plant must not be forgotten over time. In order to guarantee the effectiveness of recurrence prevention countermeasures, evaluation must be continuously carried out not only by Nippon Shokubai and the Himeji Plant but also third party. The third party evaluation will also provide newfound awareness for ensuring safety.

A corporate safety culture is fostered over time by engaging in these kinds of diverse activities. The company is therefore advised to formulate medium- and long-term plans for implementing the recurrence prevention countermeasures derived through the accident investigation, rather than simply implementing a short-term response. By ensuing these plans are implemented, it will help the entire Nippon Shokubai organization to foster a safety culture.

(Table 6-2) 6M-5E analysis for background of accident contributing factors and recurrence prevention countermeasures (1)

Contributing factor a) Excessive heating in tank feed liquid

Background of accident contributing factors	Man	Machine	Method	Material	Measurement	Management
Design and construction stages	Concerns T-108 columns' bottom liquid at low and high temperatures were widely known. But, it had little recognition on trouble may caused by insufficient cooling in V-3138 liquid since it contained a lot of inhibitors.	Hot water jacket was not necessary for the T-5108. Steam jacket was installed at bottom liquid transfer piping. Concerning the bottom liquid will be heated up due to excessive heat from steam jacket, a steam pressure regulating valve and a temperature control steam trap were installed. The cooling capacity of the V-3138 coil was not verified and the risk of causing inadequate cooling in the upper portion of the tank liquid was not considered.		T-108 columns' bottom liquid presented concerns of sludge precipitation at low temperature and polymerization at high temperature.		T-5108 was constructed as part of the 5AA construction project. The design, construction and project team consisted of members from departments: Manufacturing, Technology and Engineering. There was no design review system in place to verify, assess and review the design of new equipment and hence new installation had no appropriate evaluation from various perspectives.
Test run stage			Steam pressure regulating valve: 0.02MPaG Temperature control steam trap: 90°C	It was presumed that at this point, the liquid has already been excessively heated to a temperature higher than the T-5108 bottom temperature.	The temperature setting for the temperature control steam trap was set at 90°C based on the results of the test run results. But there was no monitoring device provided to monitor the liquid temperature at the steam jacketed piping outlet.	The pressure setting of steam regulating valve at the steam jacketed piping that transfers T-5108 bottom liquid was set at 0.02MPaG based on setting stipulated in the operation manuals.

(Table 6-2) 6M-5E analysis for background of accident contributing factors and recurrence prevention countermeasures (1)

Contributing factor a) Excessive heating in tank feed liquid

Background of accident contributing factors	Man	Machine	Method	Material	Measurement	Management
After commercial operation	The T-5108 bottom liquid temperature at the steam jacketed piping outlet was assumed to be about the same as the T-5108 bottom temperature.	The temperature control steam trap has frequently experienced drain accumulation in the jacket due to rust blockage at the drain outlet part. Ultimately, the temperature control steam trap was removed.	The pressure setting of steam pressure regulating valve was adjusted to 0.005MPaG.	As a result of removing the temperature control steam trap, the T-5108 bottom liquid was heated to about 100°C.		Improper handover of accurate information (design concept, technical evaluation, adopted rational, etc.) from the project team to the Production department. There was no record on when the temperature control steam trap was removed.
Perspectives of Countermeasures						
Education	Educate risk management in relation to MOC (Regulations and case studies)	Educate operators the piping specification change (Specification, design conditions, etc.)	Educate operators the piping specification change (Operating instructions, control standard, etc.)	Educate operators the piping specification change (Liquid properties, etc.)	Educate operators the piping specification change (Test run results)	
Engineering		Revise the specification of T-5108 bottom liquid transfer piping. (Design conditions, etc.). Risks evaluation in relation to specification change.	Update the P&ID, etc. around T-5108.	Revise the specification of T-5108 bottom liquid transfer piping. (Reconfirm liquid properties, etc.).	Confirm piping operating conditions, status, etc. through test run.	Evaluate propriety of the specification of T-5108 bottom liquid transfer piping.
Enforcement	Enforce of risk evaluation for changes and equipment design.		Update operation manuals of glacial acrylic acid production facilities.			Develop manuals and other documentations. Manage the revision history thoroughly.
Environment		Update site signage in relation to piping specification changes				
Example		Prepare MOC for actual case studies. (Equipment changes).				

(Table 6-2) 6M-5E analysis for background of accident contributing factors and recurrence prevention countermeasures (2)

Contributing factor b) -1) Recycle to the Top valve closed (V-3138 Control Procedure)

Background of accident contributing factors	Man	Machine	Method	Material	Measurement	Management
Year 1985-2009	Sludge precipitation accumulated inside the tank always caused such as wrong readings in liquid level gauge, plugged the P-3138C strainer, etc. It took a lot of works to handle these problems.	The V-3138 had nominal capacity of $70m^3$ and the liquid volume up to the top of cooling coil was $25m^3$. At the time of construction, only Recycle to Top was installed. V-3138 liquid volume was usually kept at low level when T-108 and T-701 columns were running normally.	V-3138 liquid volume was usually kept low not to exceed the top of cooling coil. T-108 columns bottom liquid was supplied either via V-3138 or directly to T-701 columns. But since Year 2000, the T-108 columns bottom liquid was supplied to T-701 columns via V-3138 only.	Sludge precipitation will accumulate inside the tank if V-3138 liquid temperature is low.		
Year 2009-2010	Even after the Recycle to Level Gauge was installed, there were still a lot of cleaning and washing works at pump strainer, the surrounding piping, etc.	In February 2009, the Recycle to Level Gauge was installed as a countermeasure to fix the wrong readings in liquid level gauge due to sludge precipitation accumulated inside the tank. At the time when V-3138 Control Procedure was revised, a signage was posted above the Recycle to Top valve on site stating: "Normally Closed, Open Recycle if above $25m^3$"	From September 2009, the procedure on how to use V-3138 was temporarily changed to withdraw column bottom liquid to V-3138 only when T-108 column is stopped. Within the next five months, the effectiveness of this procedure is confirmed. In January 2010, including changes in tank recycle (depends on liquid volume), the V-3138 Control Procedures was revised.			The temporary procedure was communicated in the Operation Knowledge Base system. The notification of the permanent V-3138 Control Procedure was only stopped at Operation Knowledge Base system. It has not reflected in operation manuals etc.

(Table 6-2) 6M-5E analysis for background of accident contributing factors and recurrence prevention countermeasures (2)

Contributing factor b) -1) Recycle to the Top valve closed (V-3138 Control Procedure)

Background of accident contributing factors	Man	Machine	Method	Material	Measurement	Management
Year 2010-2012	The pump strainer cleaning frequency has dropped sharply which has significantly reduced the workload of operators. However after these, opportunities to operate the Recycle to Top valve were hardly experienced. Operators have become unaware of the necessity to commission the Recycle to Top valve.	Switching the feed of T-108 columns bottom liquid to V-3138 or to the T-701 columns was carried out by operating the header valve in different locations which were away from the P-3138C discharge header. For this reason, it might be difficult for operators to notice the signage pertaining to Recycle to the Top valve.				The effectiveness was verified by the reduced frequency in strainer cleaning. However, any change in the amount of deposition inside the tank was not checked and the need for Recycle to the Level Gauge was not re-examined.
Perspectives of Countermeasures						
Education		Educate operators the new development in V-3138 (Specification, design conditions).	Educate operators the new development in V-3138 (Operating instructions, control standard, etc.).	Educate operators the new development in V-3138 (Reconfirm liquid properties, etc.).	Educate operators the new development in V-3138 (Test run results).	
Engineering		Study the specifications of V-3138 and its associated equipment (new installation) (Control temperature, means to control, etc.) Risk assessment for new installation.	Update the P&ID, etc. around V-3138.	Study the specifications of V-3138 and its associated equipment (new installation) (reconfirmation of liquid properties).	Confirm the operating conditions, equipment status, etc. through test run.	Evaluate specification propriety of V-3138 and its associated equipment
Enforcement	Confirm the procedures were executed.		Update operation manuals of glacial acrylic acid production facilities.			Reflect methods to control intermediate tank in operation manuals.
Environment	Enhance the works' reliability (easy-to-understand signage etc.).	Prepare site signage for new installation.				
Example		Establish methods and supplementary measures to control the tank temperature. Review the equipment based on above establishment.	Review design standards for tank associated equipment			

(Table 6-2) 6M-5E analysis for background of accident contributing factors and recurrence prevention countermeasures (3)

Contributing factor b) -2) Recycle to the Top valve was closed (T-6701 load up test)

Background of accident contributing factors	Man	Machine	Method	Material	Measurement	Management
Background relating to safe work management and operating instructions	Safety measures (PTW, safe work procedure, etc.) and its contents are required to make known to all members before any work is allowed to start. Basically, operating instructions will be issued with Production Manager approval regardless whether there is any manual in place.		In the Production Department, PTW is applied for any works which required special attentions and safety measures. Also PTW is applied to “Standard for Non-Regular Works” which are not specified in the Standard Operating Procedure. In regards to operation and safe work management, there are no rules specified things such as approval route, issuance of operating instructions.			Approval is necessary to carry out works and safe work procedures are prepared in advance for each different type of works. Practices on operating instructions differ by each department but generally they are often issued to supplement the manuals.
Risk management associated with changes	Interpretations of whether MOC is applicable may differ between individuals. If they think it is not applicable, the MOC check sheet will not be used.		The rule of MOC is applied for risk management associated with permanent or temporary changes in equipment and processes, etc. Changes which MOC is not applied are also illustrated with examples.			MOC has been implemented through database. Any changes are evaluated using a MOC check sheet. The depth of review and approval route are then determined based on the check sheet’s result.

(Table 6-2) 6M-5E analysis for background of accident contributing factors and recurrence prevention countermeasures (3)

Contributing factor b) -2) Recycle to the Top valve was closed (T-6701 load up test)

Background of accident contributing factors	Man	Machine	Method	Material	Measurement	Management
Load up test in Year 2009	The purpose of the T-6701 load up test was to confirm the operating conditions under which the quality of distillate could be ensured. The testing conditions were thought to be adjusted within the range of equipment capacity based on past track records.	The past track records of column load have the T-6701 testing conditions. The liquid volume to store in V-3138 was within the tank's nominal capacity. The risks pertaining to storing liquid in V-3138 were not investigated.	Testing plan indicating matters such as T-6701 test method, conditions and schedule was prepared. At that time, the methods of provisional use of V-3138 were verified and the Recycle to Top was commissioned after liquid built up in the tank.			The intentionally liquid built up was not a normal but non-routine work. The T-6701 load up test was an operation not covered in the operation manuals. Testing plan was issued with the approval of Production Manager but no operating instruction was issued.
Test implemented in fiscal 2012	The test was understood same as test carried out in Year 2009.	Same as Year 2009, the risks associated to build up V-3138 level were not investigated.	The testing plan was prepared in the same manner as Year 2009.			Same as Year 2009, no operating instruction was issued. Operators were not aware of the "V-3138 Control Procedure".
Perspectives of Countermeasures						
Education	Educate risk management for non-routine works and changes. (Risk assessment, KY, etc.)		Educate about safe work management and MOC. (Rules, case studies, etc.)			
Engineering						
Enforcement	Confirm risk assessment is executed for non-routine works and changes. Strengthen risk management system through education and personnel development.		Establish system to ensure risk assessment is conducted before operation, issuance of operating instructions and its approval routes, etc. Review MOC system			Review risk evaluation scope and check sheet usage for MOC.
Environment						
Example			Prepare general examples for MOC			

(Table 6-2) 6M-5E analysis for background of accident contributing factors and recurrence prevention countermeasures (4)

Contributing factor c) Inadequate tank control temperature setting
Contributing factor d) Inadequate tank temperature detection

Background of accident contributing factors	Man	Machine	Method	Material	Measurement	Management
V-3138 temperature control	Compare to the main process equipment, there was relatively little awareness of the need for quantitative temperature control in V-3138. Risk information associated to DAA formation was not widely shared.	The temperature of main process units in acrylic acid plant need to be precisely controlled. The V-3138 liquid could be cooled by the cooling coil. Hence the precise control of temperature was not necessary.		With regard to V-3138 liquid, there are concerns of acrylic acid freezing and sludge precipitation at low temperatures and polymerization at high temperatures but the liquid has high contents of inhibitors. Inhibitors and the atmosphere condition are not able to prevent formation of DAA, whereas the temperature has a big impact.	The tank temperature has to be maintained within a range.	
Necessity of instrument installation	When the need for temperature control is assessed as low, temperature will not be monitored continuously.	When intermittent detection is sufficient, thermometers will not be installed.	The need to install a thermometer and how to use it is established based on matters such as the necessity of temperature control, the temperature monitoring cycle and legal requirements. The plant has no standard on means of temperature monitoring.			Assessment for the need of temperature control and monitoring was carried out by each plant individually. This has created variation in the assessment and awareness of temperature control and monitoring.

(Table 6-2) 6M-5E analysis for background of accident contributing factors and recurrence prevention countermeasures (4)

Contributing factor c) Inadequate tank control temperature setting
Contributing factor d) Inadequate tank temperature detection

Background of accident contributing factors	Man	Machine	Method	Material	Measurement	Management
V-3138 thermometer: design and construction stages		Thermometer installation was not planned at the V-3138 design stage. Thermometer nozzle was added as the project moved into detailed design and construction stages.				There were no records available that can accurately identify the intention on how to use the nozzle or the existence of a thermometer when the equipment commissioned.
About the V-3138 thermometer: relation to lateral deployment following a trouble	Even though V-3138 was found of not having thermometer installed, it was not included in the lateral deployment scope.	After polymerization trouble occurred in another acrylic acid intermediate tank (in April 1994), the proposed countermeasures included implementing continuous temperature monitoring and installing external heat exchangers similar tanks other than the tank where the trouble occurred.	The equipment subject to the lateral deployment was tanks that receive column bottom liquid at 80～100°C.		The bottom temperatures of T-108 columns were only about 65～70°C. (T-5108 had not yet been constructed at that time).	The causes investigation and countermeasures implementation for this trouble were concluded only within the involved department. There was no system in place to involve participation of other departments likes Technology in investigation for preventing similar trouble in other areas.
Perspectives of Countermeasures						
Education		Educate operators the new development in V-3138 (V-3138 and its associated equipment)	Educate operators the new development in V-3138 (Operating instructions, control standard, etc.).	Educate operators the new development in V-3138 (Liquid properties, DAA behavior, etc.)	Educate operators the new development in V-3138 (Test run results)	
Engineering	Develop engineer and improve technical capabilities through trouble investigation involvement.	Study the specifications of V-3138 and its associated equipment (new installation) (Control temperature, means to control, etc.) Risk assessment for new installation.	Update the P&ID, etc. around V-3138.	Study the specifications of V-3138 and its associated equipment (new installation) (reconfirmation of liquid properties). Explain the details of DAA formation.	Confirm the operating conditions, status, etc. through test run.	Evaluate specification propriety of V-3138 and its associated equipment

(Table 6-2) 6M-5E analysis for background of accident contributing factors and recurrence prevention countermeasures (4)

Contributing factor c) Inadequate tank control temperature setting
Contributing factor d) Inadequate tank temperature detection

Background of accident contributing factors	Man	Machine	Method	Material	Measurement	Management
Perspectives of Countermeasures						
Enforcement		Standardize tank temperature monitoring (thermometer installation).	Develop the operation manuals for glacial acrylic acid production facilities.			Reflect methods to control intermediate tank in operation manuals. Review the system of lateral deployment following a trouble
Environment		Prepare site signage for new installation.				
Example		Establish methods and supplementary measures to control the tank temperature. Review the equipment based on above establishment.	Review design standards for tank associated equipment			

(Table 6-2) 6M-5E analysis for background of accident contributing factors and recurrence prevention countermeasures (5)

Contributing factor e) Unable to control the temperature within normal range
Contributing factor f) Unable to cool down the temperature below the upper limit
Contributing factor g) Unable to avoid abnormal situations

Background of accident contributing factors	Man	Machine	Method	Material	Measurement	Management
Acrylic acid safety measures overall		In acrylic acid plant, if any abnormality is detected and prevent the normal operation to continue, the plant will be shutdown through interlock system.	Emergency criteria and response procedures were not established for the abnormal situations which cannot be controlled even if the equipment is shutdown.			Conventionally, the safety measures focused on measures to prevent trouble.
V-3138	It was not possible to detect the temperature has exceeded until the equipment has been shut down or some sort of actions had been taken.	(Inadequate temperature detection). There was no equipment to handle the abnormal situations.	(Inadequate control temperature setting). There were no criteria and means for handling abnormal situations established.			
Perspectives of Countermeasures						
Education	Maintain and improve the emergency response capabilities through training.	Educate and train operators on response procedures for V-3138 abnormal situations. (Specifications, design conditions, etc.).	Educate and train operators on response procedures for V-3138 abnormal situations. (Operating instructions, control standard, etc.).	Educate and train operators on response procedures for V-3138 abnormal situations. (Handling of emergency inhibitors).	Confirm the required time of response procedure for abnormal situations by training.	Implement the planned emergency response drills

(Table 6-2) 6M-5E analysis for background of accident contributing factors and recurrence prevention countermeasures (5)

Contributing factor e) Unable to control the temperature within normal range
Contributing factor f) Unable to cool down the temperature below the upper limit
Contributing factor g) Unable to avoid abnormal situations

Background of accident contributing factors	Man	Machine	Method	Material	Measurement	Management
Perspectives of Countermeasures						
Engineering	Develop engineer and improve technical capabilities through analyzing external incidents.	Evaluate response procedures for V-3138 abnormal situations (Temperature criteria, emergency inhibitor equipment, etc.) Evaluate response procedure for abnormal situations for equipment handling acrylic acid (Temperature criteria, equipment specifications, etc.) Conduct risk assessment on response procedures for abnormal situations.	Evaluate response procedures for V-3138 abnormal situations (Operating instructions, control standard, etc.) Evaluate response procedure for abnormal situations for equipment handling acrylic acid (Operating instructions, control standard, etc.) Develop the criteria for judging abnormal symptom and the basic concepts of the response procedures.	Evaluate response procedures for V-3138 abnormal situations (Selection of emergency inhibitors and understand its properties, etc.) Evaluate response procedure for abnormal situations for equipment handling acrylic acid (Selection of emergency inhibitors and understand its properties, etc.)		Evaluate the propriety of V-3138 abnormal situations criteria, response procedures. Evaluate the propriety of equipment handling acrylic acid abnormal situations criteria, response procedures. Review equipment based on the design concepts.
Enforcement	Strengthen the implementation of daily hazard evaluation		Develop V-3138 manuals and other documentations. Review operation manuals of equipment handling acrylic acid.			
Environment		Prepare site signage for equipment installation.				
Example						Collect and make full use of the external incident case studies and technical information.

(Table 6-2) 6M-5E analysis for background of accident contributing factors and recurrence prevention countermeasures (6)

Contributing factor h) Unable to avoid crisis situations

Background of accident contributing factors	Man	Machine	Method	Material	Measurement	Management
Past trouble		Himeji Plant has not experienced a tank ruptured or explosion due to acrylic acid polymerization. Acrylic acid polymers have been discovered during tank internal inspection and basic measures to prevent polymerization have been implemented for each tank.	Measures taken when acrylic acid polymerized in the tanks included two instances of spraying water onto the tank and one instance of charging water and inhibitors from the manhole. Other measures which have taken included charging cooling water into the tank jacket.			
Activities relating to responses to abnormal phenomena	Other than the complex-wide disaster prevention trainings, each of the various workplaces will also implement its own planned disaster prevention exercises. One of these trainings is the fire fighting exercises which include a yearly fire fighting competition.	To improve the disaster prevention capabilities, the plant has also building up a good supply of the disaster prevention equipment.	Immediate response procedures for abnormal phenomena have been developed in the Plant's Emergency Response Plan but none of these covered for runaway reaction. (In the training materials relating to abnormal phenomena and alerting procedure (in the process for approval), there was illustration to cool the tank by spraying water as a way of responding to runaway reaction).			With the aim of improving the disaster prevention capabilities in the HMI division (safety team), various activities have been conducted together with the RC activities since Year 2007.

(Table 6-2) 6M-5E analysis for background of accident contributing factors and recurrence prevention countermeasures (6)

Contributing factor h) Unable to avoid crisis situations

Background of accident contributing factors	Man	Machine	Method	Material	Measurement	Management
Status of rules development			There was no manual to standardize each plant criteria for abnormality and its respective response procedures.			The role and responsibility on providing information to public fire department was not clearly defined in self disaster prevention team.
Responses during this accident	Tank cooling was judged to be necessary based on the V-3138 conditions and hence the tank was sprayed with water. The intention was to cool and to absorb the acrylic acid vapor.	Operators sprayed water from six fire hydrants (each at 400 liters/min.). Later, the self disaster prevention team sprayed additional water (3,100 liters/min) from the fire engine.	Since acrylic acid vapor was being released, additional measures such as charging water and inhibitors inside V-3138 could not be taken. There was no means to control the abnormal situations progress other than spraying water.	V-3138 was insulated and it was assumed that water spraying did not have much cooling effect to the tank liquid but may have prevented vapor cloud explosion.		
Perspectives of Countermeasures						
Education	Maintain and improve the emergency response capabilities through training.	Provide education and training based on crisis management/ self disaster prevention manual (Specifications, design conditions, etc.)	Provide education and training based on crisis management/ self disaster prevention manual. (Improve immediate actions, etc.)	Re-educate the hazards of handle materials.	Confirm the required time of response procedure for abnormal situations by training.	Implement plans for education and training.
Engineering	Develop engineer and improve technical capabilities through analyzing external incidents.	Evaluate the response procedures for crisis situations (Temperature criteria, specifications, etc.) Conduct risk assessment on response procedures.	Evaluate the response procedures for crisis situations (Operating instructions, control standard, etc.)			Evaluate the propriety of response procedures.

(Table 6-2) 6M-5E analysis for background of accident contributing factors and recurrence prevention countermeasures (6)

Contributing factor h) Unable to avoid crisis situations

Background of accident contributing factors	Man	Machine	Method	Material	Measurement	Management
Perspectives of Countermeasures						
Enforcement			Develop crisis management manual Review self disaster prevention manual Review operation manuals			
Environment		Review disaster prevention equipment.				
Example						Collect and make full use of the external incident case studies and technical information.

Afterword

The explosion and fire that occurred in the Nippon Shokubai's Himeji Plant occurred from a chain of events, starting with an increase in the amount of liquid stored in the intermediate tank that was used to temporarily store the bottom liquid of the glacial acrylic acid rectifying column in the acrylic acid production facilities. In spite of the increase in stored liquid, the Recycle to Top was not commissioned, so that the cooling was insufficient in the tank. This accelerated the reaction to form acrylic acid dimer and caused the temperature to rise, which in turn triggered an abnormality by which the polymerization of acrylic acid occurred. Deficiencies in the temperature detection and temperature monitoring of the liquid stored in the tank led to the explosion and fire.

Nippon Shokubai must take to its heart that the accident at the Himeji Plant triggered significant casualties and return to its fundamental corporate commitment of “Safety takes priority over production” and work on restoring the company to regain public trust as a chemical company. To achieve this, the company must make certain to implement the recurrence prevention countermeasures recommended by the Accident Investigation Committee. At the same time, it is strongly recommended that Nippon Shokubai practically carried out the activities by third party evaluation in order to develop an effective framework for safety management.

The recurrence prevention countermeasures recommended by the Accident Investigation Committee should be considered to implement in the other Plants in addition to Himeji Plant. We urge the company to laterally deploy these countermeasures at other production facilities, in order to improve the overall framework for safety management at Nippon Shokubai.

Additionally, we hope that the accident investigation report will be utilized to prevent accidents in similar and other processes and contribute in some way to improve the safety of the chemical industry.

Finally throughout the progess of investigating the accident, I would like to express my deep gratitude to the members of the Accident Investigation Committee for their valuable input and the persons who conducted the active investigation. I also wish to thank the following people and organizations for their efforts in investigating the sequence of events that led to the explosion and fire and the impact of the accident: Toyo Engineering Corporation for their assistance with fluid analysis, IHI Corporation for their assistance with structural analysis and blast pressure investigation and Dr. Yoshio Nakayama of the National Institute of Advanced Industrial Science and Technology (AIST) for verifying the validity of the investigation and analysis results.

My deepest gratitude also goes to the personnel of the Fire and Disaster Management Agency, National Research Institute of Fire and Disaster and Himeji City Fire Department for their extensive advice in helping us to wrap up the accident investigation and accident investigation report.

March 2013
Masamitsu Tamura
Chairman
Accident Investigation Committee
Nippon Shokubai Co., Ltd.

Appendix 1 Confirmation by Adiabatic Reaction Test

(1) Purpose: Confirmed the following items concerning V-3138 liquid (T-5108 bottom liquid) using adiabatic reaction test facilities.

- a) Liquid composition curve at start temperatures of 80℃, 90℃, and 100℃.
- b) Behavior of runaway reaction at start temperature of 90℃.
- c) Difference in temperature curves due to start temperature and atmosphere

(2) Test methods and conditions

Tests were conducted by both the Nippon Shokubai laboratory and enclosed testing room in Asa Plant of Kayaku Japan Co., Ltd. In both tests, sample was placed in an insulated container inside hot air oven and the sample was heated to raise its temperature. The oven temperature was tracked in order to simulate the adiabatic condition. (Temperature difference between the sample and the oven was kept within 1℃.) Refer to Appendix 4/15 to 6/15 for the details of respective tests equipment and conditions.

- a) Test at Nippon Shokubai laboratory (for purposes: a) and c))
- ◆ Analyzed the initial and progressive liquid sample compositions took from the sampling nozzle. To prevent any abnormal reaction, an emergency used solvent was added to the insulated container when the sample temperature reached 130℃ and stopped the test.
- b) Tests at the enclosed testing room in Asa Plant of Kayaku Japan Co., Ltd. (for purpose: b) and c))
- ◆ The enclosed testing room cannot be entered for safety reasons when sample temperatures reached above 140℃, hence the oven temperature was not able to raise beyond this point. (oven temperature unable to follow the rise in sample temperature)

(3) Test results (Acrylic acid: AA, acrylic acid dimer: DAA, acrylic acid trimer: TAA)

- a) Liquid composition curve at start temperatures of 80℃, 90℃, and 100℃
- ◆ Start temperature: 100℃ (under M-Gas, N2 atmospheres)
  - There were slight differences in AA, DAA, and TAA composition but no polymers were formed.
  - There was little change in MQ concentration but PTZ concentration decreased over time for both cases.
- ◆ Start temperature: 90℃ (under N2 atmosphere)
  - There was little change in AA, DAA, and TAA composition at the end of the test, compared to the test with start temperature of 100℃. A little amount of polymers formed at the end of the test.
  - Inhibitor behavior was the same as the test with start temperature of 100℃ but the PTZ concentration at the end of the test was lower than the test with start temperature of 100℃. Probably this was due to the longer elapsed time.
- ◆ Start temperature: 80℃ (N2 atmosphere)
  - Same as the others tests, the DAA and TAA concentrations increased over time. However, the DAA concentration peaked at about 40wt% and the TAA concentration increased to about 13wt%.

- Upon reaching 90℃, DAA has already reached about 21wt%. The behavior after this point differed from the test with start temperature of 90℃ (The same observation as the test with start temperature of 100℃).
- The PTZ concentration decreased significantly and polymers gradually formed starting from the end stage of the test. Probably this was due to the elapsed time was much longer than other tests (There was little change in the MQ concentration).

b) Behavior of runaway reaction at start temperature of 90℃.

◆ Temperature curves and their comparison
- The temperature curve up to 130℃ was almost the same as laboratory test results.
- After this point, the temperature increased sharply but the rise in temperature stopped at about 190℃ and began to decrease.

◆ Changes in composition and weight before and after test

	Weight [g]	Analyzed Composition [wt%]				Inhibitor Concentration [ppm]	
		AA	DAA	TAA	Polymers	PTZ	MQ
Before	1,503	98.8	3.2	0.0	0.0	215	1,527
After	1,439	20.1	22.2	16.6	41.7	30	937

Weight decreased by 64g ⇒ 4.3% compared with weight before the test

- The weight decreased before and after the test was presumed to be due to the evaporated sample released out from the system.
  # It is presumed there was no pressure increased within the actual testing facilities because any evaporated vapor due to temperature rise in sample is released out of the system from the exhaust vent.
- After the test, about 40wt% of polymers was formed. Although the rise in temperature stopped at about 190℃, it was obvious that polymerization itself has progressed.
- There were black and white polymers floating in the Dewar flask. Also polymers had adhered to the vent tube and lid due to polymerization of condensate.

◆ Observations
- From the composition and weight of the contents after the tests, the sample will reach an estimated temperature of 260~270℃ if the heat generated from the reaction is entirely used for increasing the temperature of sample itself.
- Reasons of the rise in temperature stopped before reaching the above temperatures was presumed to be due to the reaction heat being consumed by the following factors.
  - Heat dissipation at temperature range above 140℃
  - Latent heat of liquid evaporation
    # The released samples due to evaporation were 4.3% of the initial prepared amount. Since condensate and its polymer were found in the vent tube, it is assumed that the heat was consumed by the condensate returning to the Dewar flask and re-evaporating

into the vent tube.

c) Difference in temperature curves due to start temperature and atmosphere

- Difference in temperature curves due to starting temperatures
  - Although there were slight differences at each start temperature, the values calculated from the actual temperatures and compositions curves were mostly matched.
  - The required times to reach 130℃ were as follows:
    - Start temperature 100℃: 7~8 hours
    - Start temperature 90℃: about 24 hours
    - Start temperature 80℃: about 63 hours

  ⇒ Up to 130℃, the increased temperature was assumed to be mainly due to heat of formation from DAA and TAA.

- Difference in temperature curves due to atmosphere (N2 atmosphere, M-Gas atmosphere)
  - In the Kayaku Japan's test, there was almost no difference in temperature curves for both atmospheres beyond 130℃.
  - In the Nippon Shokubai laboratory's test, there was almost no difference in temperature curves for both atmospheres. Hence the reproducibility was considered good.

  ⇒Through a series of reactions, it has not found any difference in temperature curves due to different atmospheres. Therefore, it is presumed that the atmosphere inside the tank did not influence the accident in the Himeji Plant.

Nippon Shokubai Adiabatic Reaction Laboratory Test Equipment

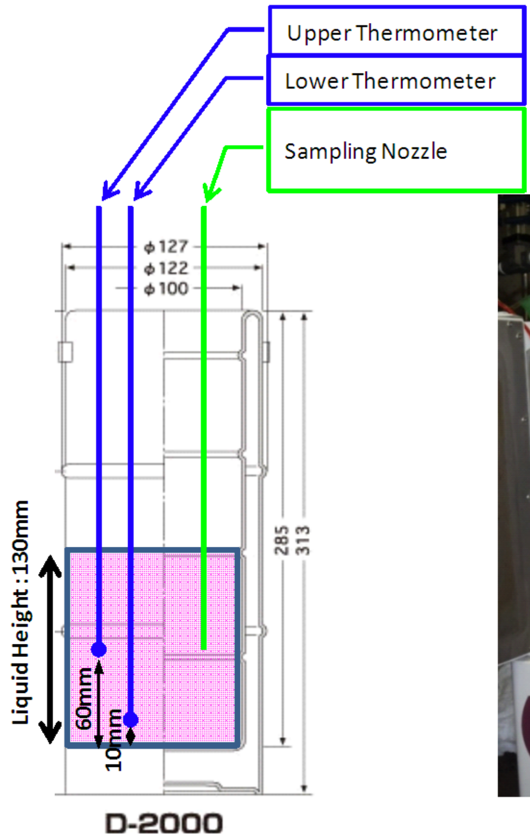
A. Thermostat equipment: Laboratory Constant Temperature Oven, DK240S by Yamato Scientific Co., Ltd.

B. Adiabatic container: Dewar flask, D-2000 (2 liter) by Thermo Scientific

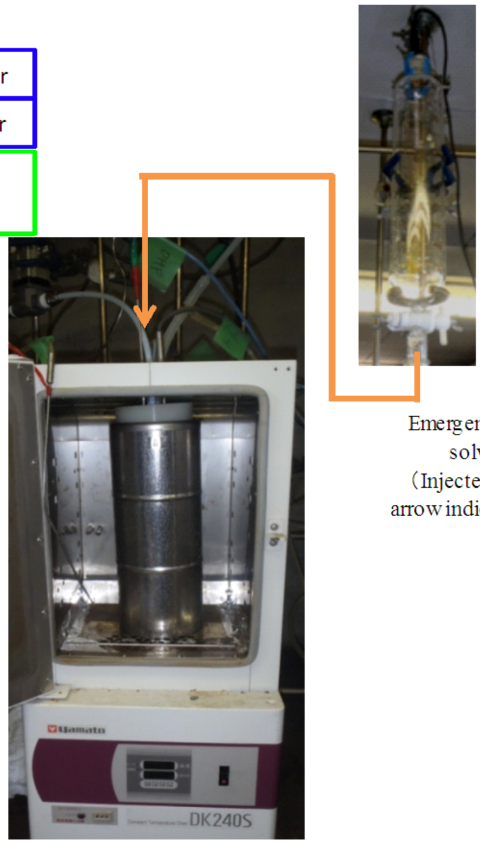
*whenever sample temperature increased by 1℃, the oven internal temperature is also tracked and increased by 1℃ （ΔT: Within 1℃)

C. Container lid

D. Thermometer　 Resistance temperature detector (Pt)



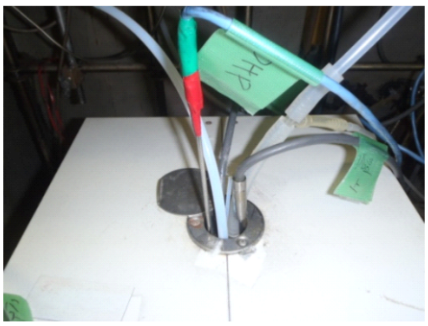
Dewar flask by Thermo
Capacity : 2ℓ



Emergency used solvent
（Injected through arrow indicated line）

Oven Internal

Oven Internal Dimensions (mm): $240^{W} \times 250^{D} \times 340^{H}$
Oven Internal Capacity: about 20 liters



Top of the Oven

＜Top of the Oven＞
- Thermometers for measuring sample's temperature: 2pcs
- Thermometers for preventing overheating
- Sampling nozzle
- Open air vent
  （N_2 injected 100mm from top : 1ℓ/min）
- Line for injecting emergency used solvent

＜Bottom of the Oven＞
- N_2 injected for preventing explosion: 1ℓ/min

Kayaku Japan Co., Ltd. Adiabatic Reaction Test Equipment

A. Thermostat equipment: Laboratory Constant Temperature Oven, DK240S by Yamato Scientific Co., Ltd.

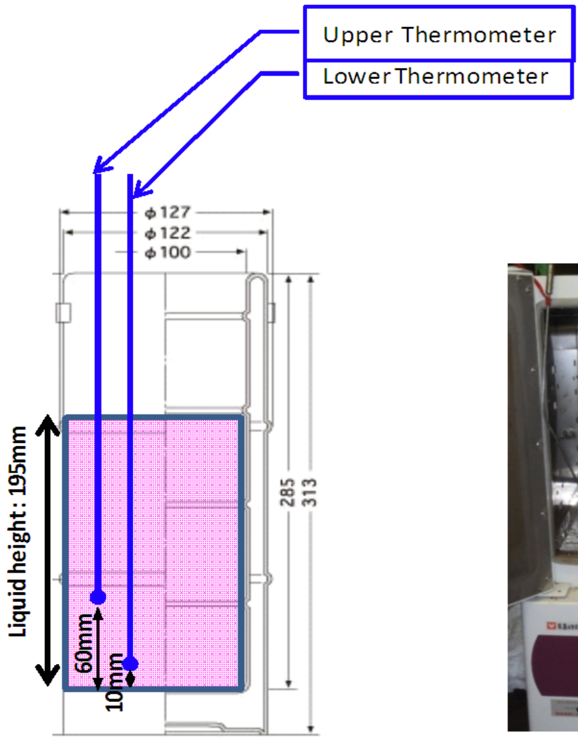
Weight: 23 kg,   Power consumption: AC100V 4.5A (15A)

B. Adiabatic container: Dewar flask, D-2000 (2 liter) by Thermo Scientific

*whenever sample temperature increased by 1℃, the oven internal temperature is also tracked and increased by 1℃ (ΔT: Within 1℃)

C. Container lid

D. Thermometer   Resistance temperature detector (Pt)



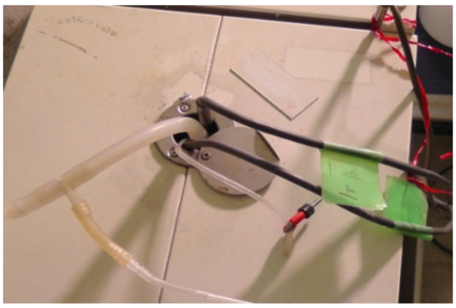
D-2000

Dewar flask by Thermo
Capacity : 2ℓ

Secured by wire

Oven Internal

Oven Internal Dimensions (mm): $240^{W} \times 250^{D} \times 340^{H}$
Oven Internal Capacity: about 20 liters



Top of the Oven

<Top of the Oven>

・Thermometers for measuring sample's temperature: 2pcs
・Open air vent
（N_2 injected 100mm from top : 1ℓ/min）

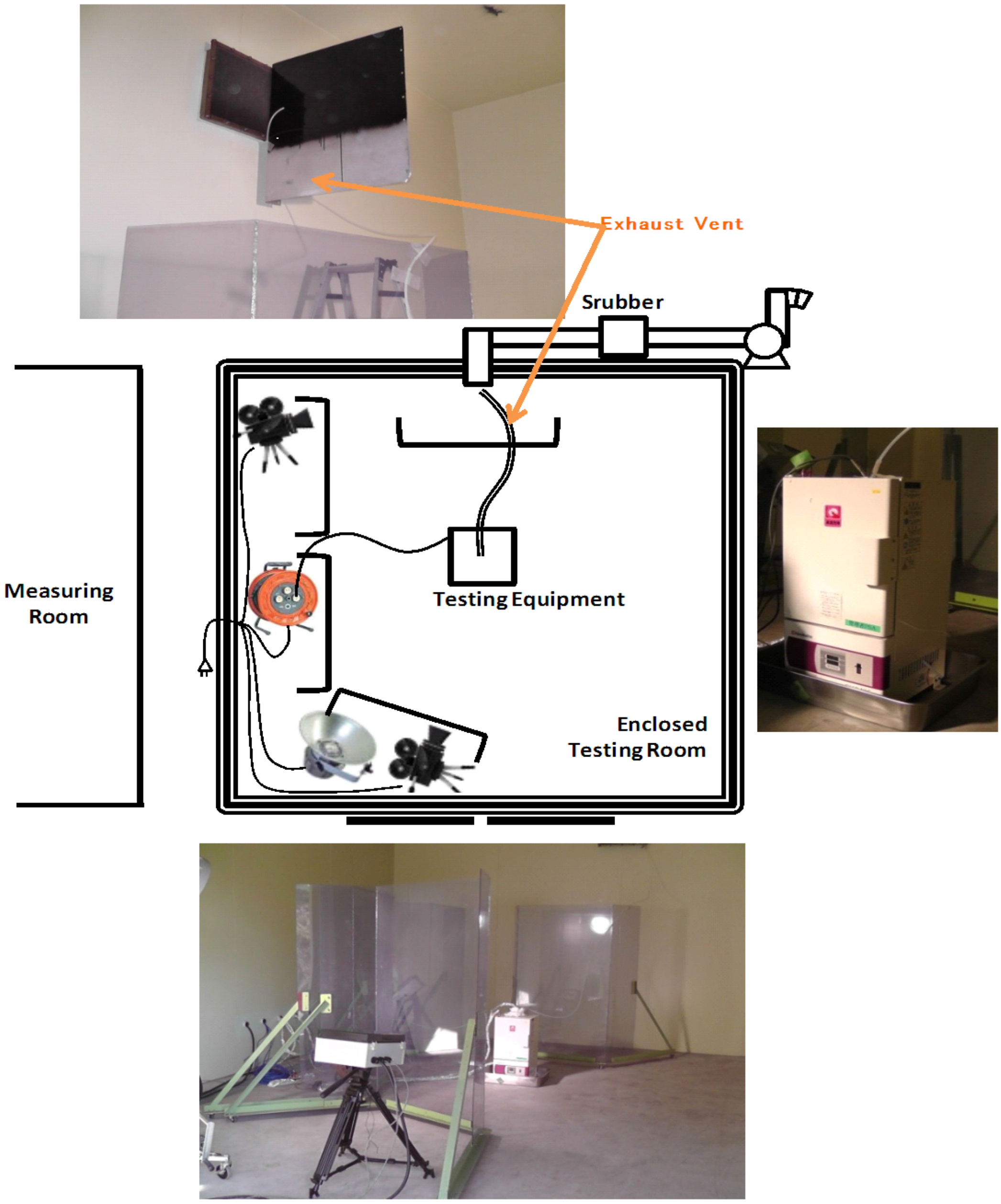
<Bottom of the Oven>

・N_2 injected for preventing explosion: 1ℓ/min

Facility Layout of Kayaku Japan Co., Ltd. Adiabatic Reaction Test

A. Thermostat Equipment Testing Facility:	Enclosed testing room in Asa Plant of Kayaku Japan Co., Ltd.
B. Thermostat equipment:	Laboratory Constant Temperature Oven, DK240S by Yamato Scientific Co., Ltd.
C. Adiabatic container:	Dewar flask, D-2000 (2 liter) by Thermo Scientific
D. Other equipment:	Video camera, lighting equipment, protection board, ventilation equipment, etc.

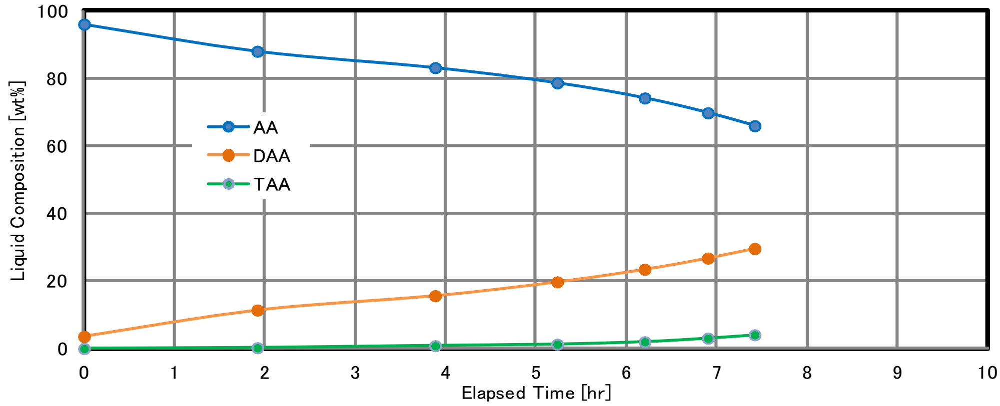
Testing method and conditions



i. Adiabatic Reaction Test Results (Composition Curves)

1. Start temperature: 100℃, M-Gas atmosphere

＊ Sample: T-5108 bottom liquid (sample on 2012/10/22)

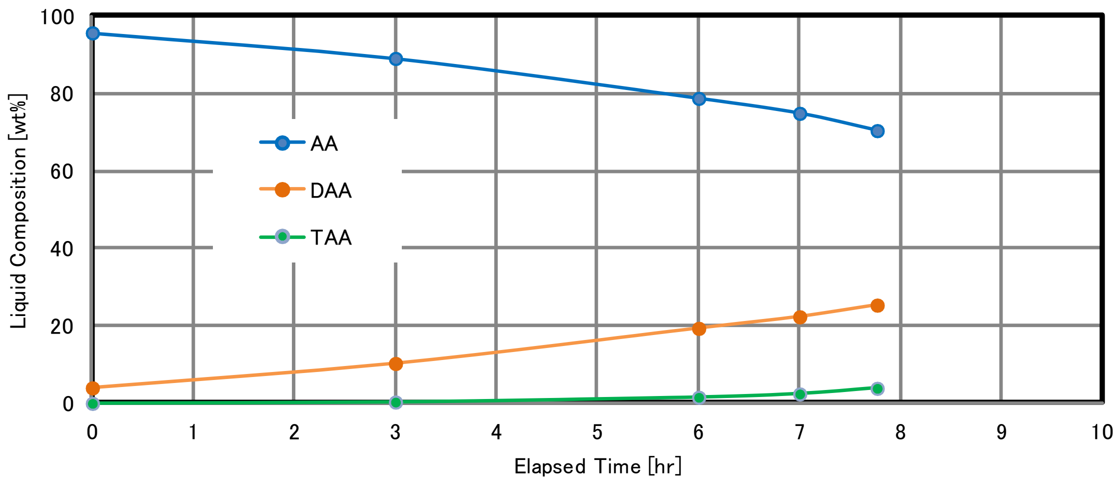


Elapsed Time		Internal Temp.[℃]		AA	DAA	TAA	Polymers	PTZ	MQ
[min]	[hr]	Top	Bottom	[wt%]	[wt%]	[wt%]	[wt%]	[ppm]	[ppm]
0	0.0	101.4	101.8	96.2	3.6	0.0	0.0	224	1525
115	1.9	104.4	105.0	88.1	11.4	0.3	0.0	217	1531
233	3.9	109.5	110.0	83.3	15.7	0.9	0.0	200	1529
314	5.2	114.4	115.0	78.8	19.8	1.3	0.0	192	1535
372	6.2	119.3	120.0	74.3	23.5	2.0	0.0	186	1544
414	6.9	124.2	125.1	69.9	26.8	3.1	0.0	180	1483
445	7.4	129.3	130.1	66.1	29.7	4.1	0.0	172	1537

※Polymers: molecular weight 5,000～50,000

2. Start temperature: 100℃, N_2 atmosphere

＊ Sample: T-5108 bottom liquid (sample on 2012/10/22)

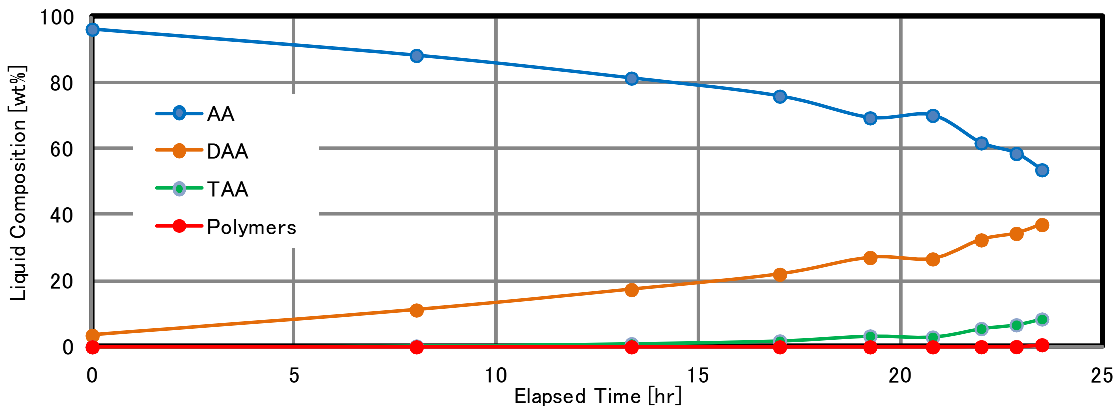


Elapsed Time		Internal Temp. [℃]		AA	DAA	TAA	Polymers	PTZ	MQ
[min]	[hr]	Top	Bottom	[wt%]	[wt%]	[wt%]	[wt%]	[ppm]	[ppm]
0	0.0	96.7	101.8	95.7	4.0	0.0	0.0	218	1763
180	3.0	104.6	105.2	89.1	10.3	0.4	0.0	201	1759
360	6.0	117.0	117.6	78.8	19.4	1.6	0.0	187	1793
420	7.0	123.0	123.6	74.9	22.4	2.5	0.0	174	1790
466	7.8	129.4	130.0	70.5	25.4	3.9	0.0	170	1910

※Polymers: molecular weight 5,000～50,000

3. Start temperature: 90℃, N_2 atmosphere

＊Sample: T-5108 bottom liquid (sample on 2012/10/22)

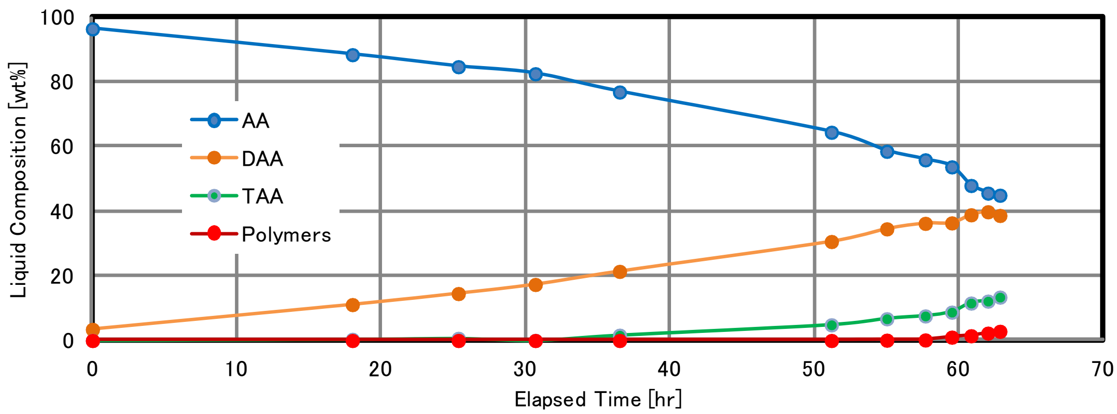


Elapsed Time [min]	Elapsed Time [hr]	Internl Temp. [℃] Top	Internl Temp. [℃] Bottom	AA [wt%]	DAA [wt%]	TAA [wt%]	Polymers [wt%]	PTZ [ppm]	MQ [ppm]
0	0.0	89.8	90.2	96.3	3.5	0.0	0.0	215	1527
481	8.0	94.5	95.0	88.4	11.2	0.3	0.0	208	1524
800	13.3	99.4	100.0	81.5	17.4	1.0	0.0	193	1522
1020	17.0	104.5	105.0	76.0	22.0	1.8	0.0	180	1518
1154	19.2	109.5	110.0	69.4	27.1	3.3	0.0	164	1519
1247	20.8	113.9	115.0	70.2	26.7	3.0	0.0	156	1585
1319	22.0	118.9	120.0	61.8	32.4	5.5	0.0	148	1609
1371	22.9	123.8	125.0	58.6	34.4	6.7	0.1	141	1558
1409	23.5	128.8	130.1	53.7	37.1	8.4	0.6	140	1521

※Polymers: molecular weight 5,000～50,000

4. Start temperature: 80℃, N_2 atmosphere

＊Sample: T-5108 bottom liquid (sample on 2012/10/22)



Elapsed Time [min]	Elapsed Time [hr]	Internl Temp. [℃] Top	Internl Temp. [℃] Bottom	AA [wt%]	DAA [wt%]	TAA [wt%]	Polymers [wt%]	PTZ [ppm]	MQ [ppm]
0	0.0	80.5	81.0	96.4	3.4	0.0	0.0	210	1510
1080	18.0	84.3	84.7	88.4	11.1	0.4	0.0	211	1358
1520	25.3	86.1	86.6	84.7	14.5	0.7	0.0	201	1519
1840	30.7	87.8	88.2	82.5	17.3	0.0	0.0	188	1517
2190	36.5	90.0	90.5	76.8	21.4	1.6	0.0	179	1549
3070	51.2	99.3	99.9	64.4	30.6	4.8	0.0	154	1594
3300	55.0	104.4	105.1	58.5	34.5	6.7	0.1	119	1625
3460	57.7	109.4	110.0	55.9	36.2	7.6	0.2	105	1567
3570	59.5	114.2	114.8	53.7	36.4	8.8	1.0	109	1552
3650	60.8	118.8	119.5	47.9	38.9	11.6	1.5	121	1563
3720	62.0	124.4	125.0	45.6	39.8	12.2	2.3	99	1554
3770	62.8	129.7	130.3	44.9	38.7	13.4	2.9	92	1565

※Polymers: molecular weight 5,000～50,000

Behavior of Runaway Reaction

1. Test conditions

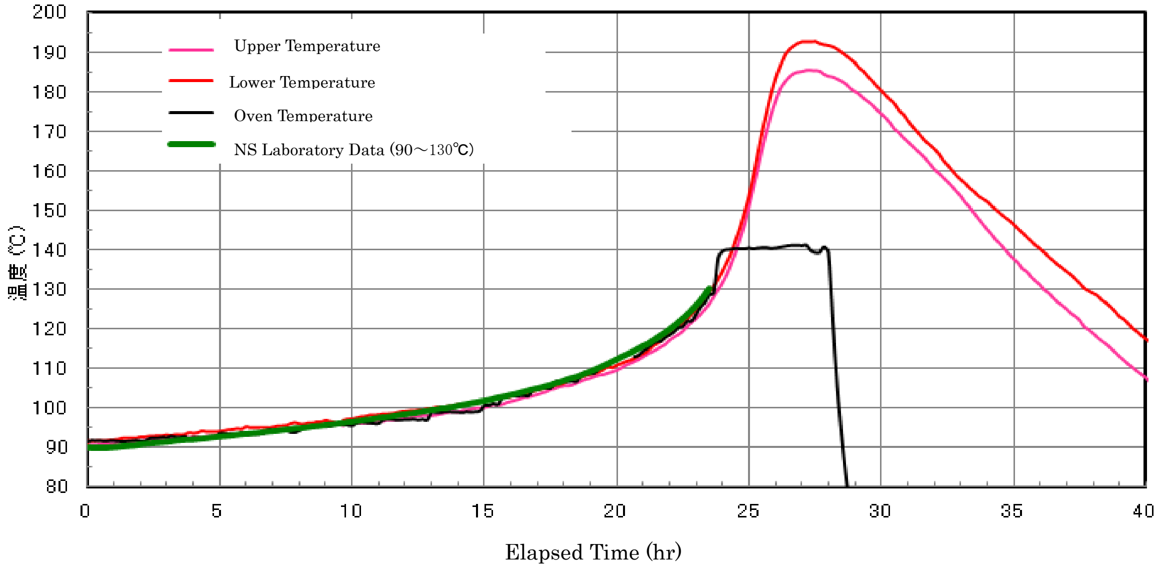
A Sample: T-5108 bottom liquid (sampled on October 22, 2012) B. Liquid amount: 1503 g

C. Start temperature: 90℃ D. Atmosphere: N_2

The enclosed testing room cannot be entered for safety reasons when sample temperatures reached above 140℃, hence the oven temperature was not able to raise beyond this point.

2. Test results

A. Comparison for the temperature curves



B. Weight and liquid compositions before and after the test

	Analyzed Composition [wt%]				Weight
	AA	DAA	TAA	Polymers	[g]
Before	98.8	3.2	0.0	0.0	1,503
After	20.1	22.2	16.6	41.7	1,439

Weight Decreased: 64g or 4.3% (compare to before test)

C. Conditions of Polymers Adhesion after the Test

Internal of Dewar Flask

Floating Polymers (black, white): 31g

Exhaust vent

Condensed Polymers

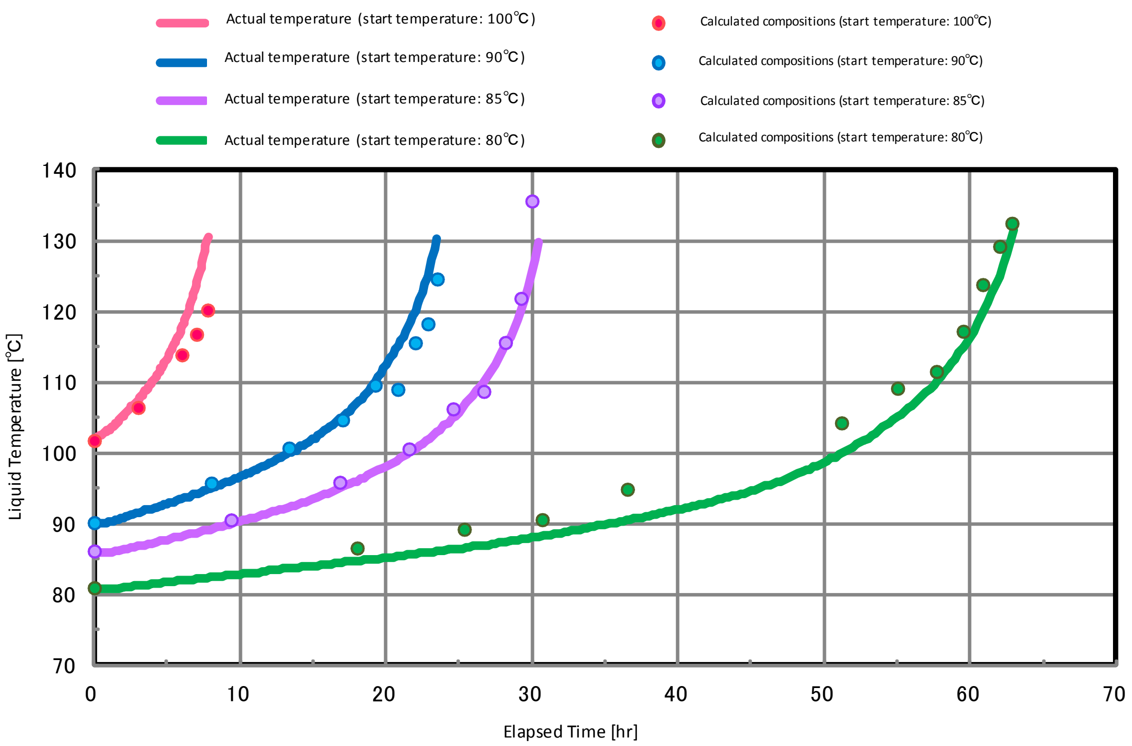
Lid of Dewar Flask (silicone stopper)

White polymers at the back of the lid

iii. Difference in temperature curves due to start temperature and atmosphere

＊Sample: T−5108 bottom liquid (sample on 2012/10/22)

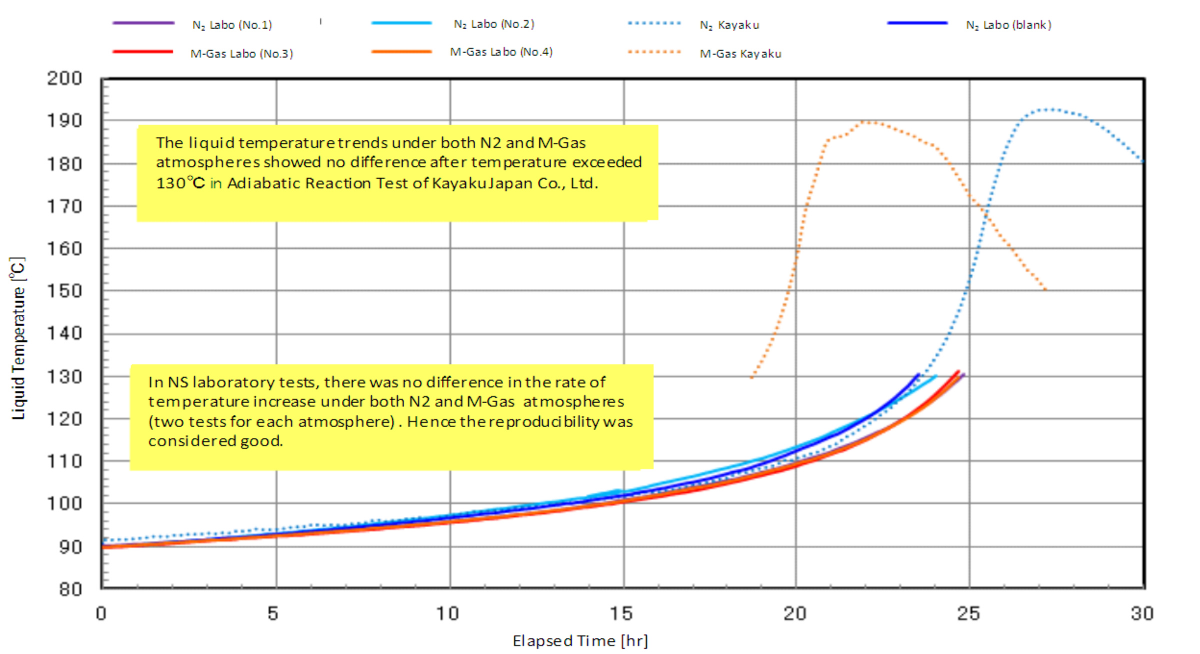
1. Difference in temperature curves due to start temperature and atmosphere



※ During the liquid storing operation in V−3138, it took about 60 hours to reach 60 m3 from 25 m3 and about 80 hours to discover the white smoke. The experiment data with comparatively long elapsed time (start temperature: 80℃) was used to estimate the tank internal temperature.

2. Difference in temperature curves due to atmosphere

＊T−5108 bottom liquid: Test started from 90℃



Appendix 2　Estimated Tank Internal Temperature and Pressure Based on Reaction Analysis

(1)　Estimation results

Estimated internal pressure at the time that crack initiated on tank: about 0.274MPaG (structural analysis result: 0.24 to 0.29MPaG)

(2)　Premises for the calculation

-1)　The temperature of the upper portion liquid above the coil was assumed to increase and the composition and temperature were assumed to be evenly distributed.

-2)　It was assumed that after the tank liquid volume reached 60m^3, DAA formation has caused the upper portion liquid above the coil to reach an average temperature of 120℃. After which the polymerization has caused the temperature to rise.

-3)　At the point when the tank internal temperature reached 120℃, the DAA concentration was set at 60wt% and AA concentration at 40wt%.

-4)　The amount of heat generated associated with polymerization was estimated based on the rate of increased temperature which corrected the adiabatic reaction test results. Also, the amount of polymers formed was calculated by dividing the heat of polymerization into amount of heat generated calculated from the rate of increased temperature.

-5)　The vapor pressure of the liquid inside the tank was presumed to be the vapor pressure of mixed AA/DAA liquid. The tank internal pressure was calculated from the pressure drop of the generated vapors which pass through the tank's vent and sealed gas piping (seal pot).

-6)　Confirm the presence of choke flow

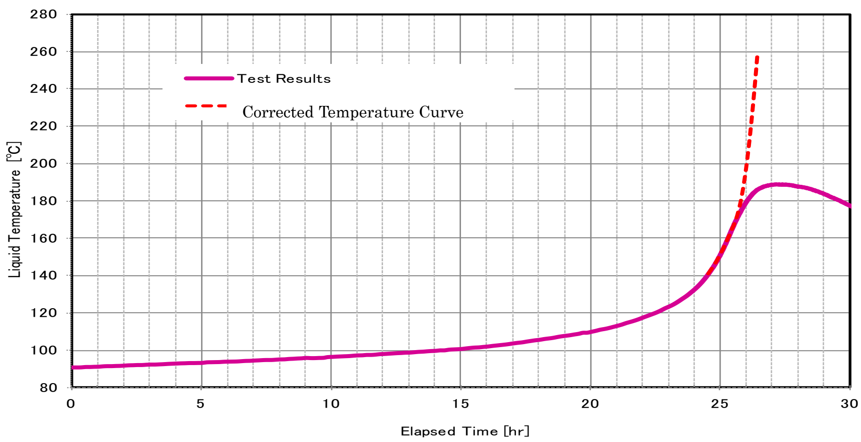
Choke flow refers to phenomenon when the gas flow rate released from the vent reached and maintained at sonic velocity, the pressure at the vent outlet increased. Choke flow will significantly affect the calculation results and hence we need to confirm its presence.

> ⇒ The gas velocity at the vent outlet when the tank ruptured was estimated at 248m/sec. On the other hand, the sonic velocity of acrylic acid gas at temperature of 233℃ was estimated at 250m/sec. We therefore confirmed that it was not within the range of affecting the estimated internal pressure.

-7)　Correction of adiabatic reaction test data

The highest temperature reached during the tests was about 190℃ but the reaction rate (temperature rise) has slowed down before reaching 190℃. This was presumed to be due to the heat loss during the adiabatic reaction tests. The time to reach the corrected temperature was calculated by the compositions after tests. Under no heat loss situation, this time was faster than the time to reach the highest temperature recorded during the tests.

> ⇒ The correction range for the rate of temperature increased was calculated right up to the point that the reaction has slowed down.



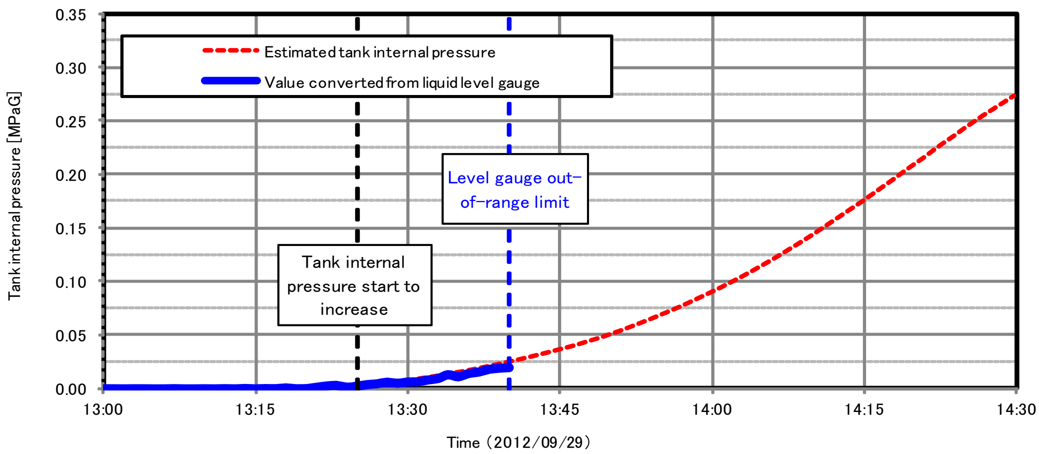
(3) Calculation results

※The estimated liquid temperature was calculated by using Aspen Plus

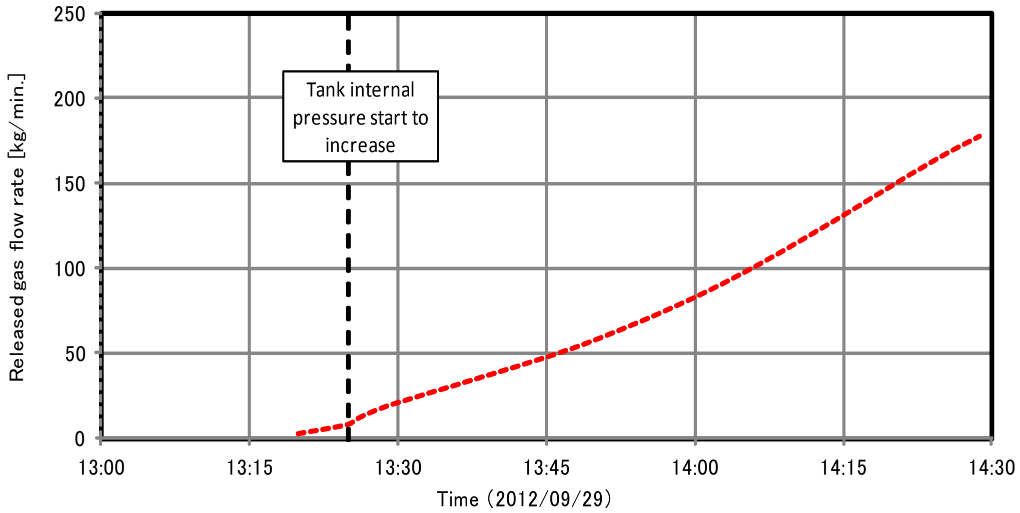
		Analysis Starting Point		Reched Boiling Point		Level Gauge Reached Out-of-Range Limit		Cracks Appeared on Tank's Shell Plate
Time		To About 10:00	⇒	About 13:20	⇒	About 13:40	⇒	To About 14:35
Estimated liq. temp.	℃	120	⇒	167	⇒	175	⇒	233
Estimated press.	MPaG	–	⇒	0	⇒	0.025	⇒	**0.274**
Estimated liq. composition (upper section on above coil)								
AA	wt%	40	⇒	35.7	⇒	34.2	⇒	17.0
DAA, etc.	wt%	60	⇒	53.8	⇒	52.8	⇒	46.2
Polymers	wt%	0	⇒	10.6	⇒	13.0	⇒	36.8
Polymers Amount	kg	0	⇒	4,248	⇒	5,178	⇒	12,814
Evaporation Amount	kg	0	⇒	59	⇒	420	⇒	5,522
Vent gas linear velocity	m/sec	0	⇒	20	⇒	86	⇒	248

i. Estimated tank internal pressure

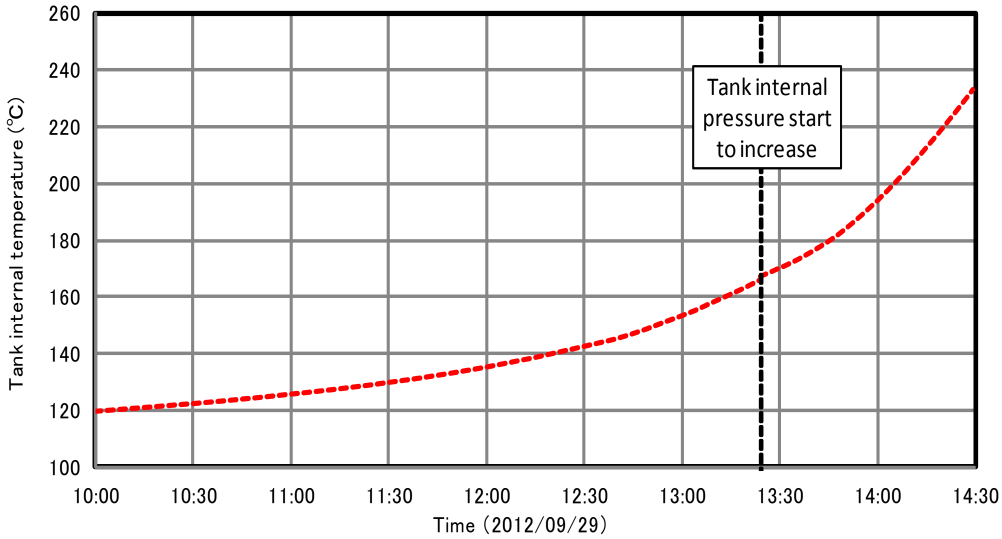
※About 14:35, cracks initiated on tank



ii. Estimated released gas flow rate ※About 14:35, cracks initiated on tank



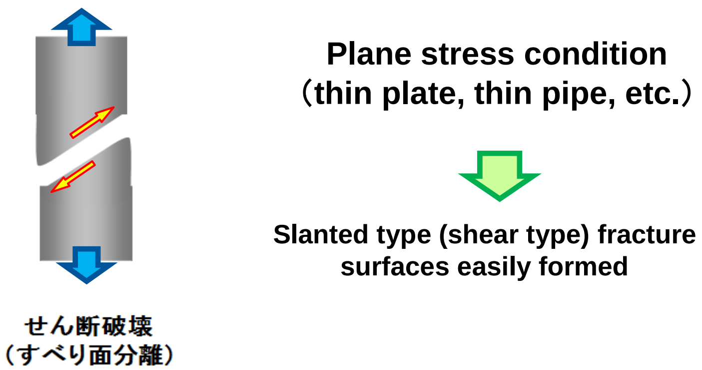
iii. Estimated tank internal temperature ※About 14:35, cracks initiated on tank



Appendix 3　Observation of V-3138 Fracture Surfaces

(1)　Extensive observation of the fracture surfaces at the V-3138 fractured sections.

As shown in the figures below, the fracture surfaces are slanted to the through-thickness direction and formed through shear destruction caused by glide plane decohesion were extensively observed. The fact that shear fracture was extensively observed did not contradict the presumption of V-3138 destruction were developing at a fast rate.



(2) Observation of fracture surfaces at cooling water coil outlet nozzle

As shown in the amplified photos, the dark gray areas seen in the outer surface resemble ductile fractures that are formed from voids linkage when there is destruction from tensile deformation of ductile metallic materials. Also, the fine veined patterns in the through-thickness direction observed in light gray areas are assumed to be traces, when the crack formed due to ductile destruction propagated in the through-thickness direction with the increased load.

Based on the above observations, it is presumed that crack initiated due to ductile destruction on the exterior of flange outer circumference of cooling water coil outlet nozzle. The crack propagated vertically on the shell plate escaping from the flange outer circumference.

Outlet nozzle of cooling water (observed from outside)

Ductile fracture surfaces without shear fracture (dark area)
⇨ Fracture surfaces formed due to tensile deformation (voids linkage)

Veined pattern in through-thickness direction
⇨ Fracture surfaces due to crack propagation