RELATIONAL INFORMATION SYSTEM FOR CHEMICAL ACCIDENTS DATABASE (RISCAD) WITH ANALYSIS OF HYDROGEN ACCIDENT

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ABSTRACT

The Relational Information System for Chemical Accidents Database (RISCAD) is based on the fire, explosion, and leakage accident data related to chemical substance, chemical process, high pressure gas, and explosive. These data have been accumulated by the National Institute of Advanced Industrial Science and Technology (AIST). RISCAD has been developed by AIST and the Japan Science and Technology Agency (JST) from 1999 and released on the WWW in October 2002. In RISCAD, accident data can be searched by date, location and free words or keywords by activities, equipment, causes, chemical, and substance names which were hierarchized by the experts. Some accident data are linked relationally to the accident progress flowcharts, hazard information of relevant chemicals and additional information such as the reaction process flowcharts, reaction formula, equipment and facility layout. Additionally, it has the functions to reproduce dynamically thermal analysis (DSC) data and accident statistic data on the Web browser. In this paper, the outline and the functions of RISCAD are introduced. Also, a case study is presented, that is related on hydrogen, with the progress flowchart.

1.0 INTRODUCTION

"Relational Information System for Chemical Accidents Database" (RISCAD; http://www.aist.go.jp/RIODB/RISCAD/), which was developed jointly by the National Institute of Advanced Industrial Science and Technology (AIST) and the Japan Science and Technology Agency (JST), was released on the Web in October, 2002. This paper introduces the outline of RISCAD and a case study on the accident in Japan related on hydrogen in 2005 together with the progress flowcharts.

2.0 CONCEPT OF RISCAD

In the "Material Safety (MS) Seminar", which Professor Terushige Ogawa (Yokohama National University) established, an expert system for the safety assessment of chemical plants is being developed. In this system, the necessity of analysis of past accidents became clear [1-6]. However, regarding the Japanese conventional accident database, it consisted mainly of text information, with only the summary of accidents being recorded, and was lacking in providing were knowledge or lessons. Therefore it was decided to develop an accident database which would serve as a link between accidents and relevant hazard substances, as well as providing information to help in the understanding of accidents.

The database project was started with financial assistance from "The Database Development Program" of JST for three years from October, 1999, and with support from "The Technical Advisory Committee" comprising members of the "MS seminar". RISCAD was released in October, 2002.

How to offer useful information to prevent the recurrence of similar accidents by users of a chemical substance was considered during development. Therefore hazard information relevant to substances related to accidents, classification of accidents by hierarchized keywords, and additional information, such as progress flowcharts, structural formula, figures, etc., were collected. With these, a user of chemical substances can search for accident related information, depending on the substance and operating conditions.

The aim of RISCAD was to fully understand the hazards related to chemical substances and the situation in which an accident had occurred. Thermal hazard data in particular was recorded regarding chemical substances. In addition, thermal analysis (Deferential Scanning Calorimetry: DSC) data was collected and the function equipped so that a user could analyze DSC data on the Web browser dynamically.

Experts constructed a system whereby accidents are classified by hierarchized keywords : final events, activities, equipment, probable causes and damage. And a search function using hierarchized keywords for the each category was installed.

Additional image information, except for text information, such as chemical reaction process flow, devices and facilities layout, schematic diagrams of the device at which an accident occurred, and reaction formula etc., was recorded.

It was also equipped with a display chart showing accident search results, and was also equipped with function which could change the parameters of the chart on the Web browser dynamically.

Concerning the analysis of each accident, an accident progress flowchart which extracted a lag from the normal state that triggered an accident was made by experts.

3.0 OUTLINE OF RISCAD

3.1 Recorded Accidents

The duration of accidents collected is from October 28, 1949 to December 12, 2004, and the number was over 4,350 as of the end of April, 2007

The sources of accident records are those of "The Hazard and Accident Database" (http://www.aist.go.jp/RIODB/cgi-pub019/DB019_top_jpn.cgi), which is one of "The Research Information Databases (RIO-DB)" of AIST (about 4,000 records), a book of "Reaction Hazard - Accident and Analysis - " [7], accident reports of hazardous substances related with The Japanese "Fire Service Law" and The Japanese "Industrial Safety and Health Law", news reports of recent accidents, and originally collected accidents by the "MS seminar".

"The Hazard and Accident Database" records many accidents related to high pressure gas and explosives, and RISCAD was designed in consideration of these accidents.

The thermal hazard data relevant to accident related substances was based on information from "Bretherick's Handbook of Reactive Chemical Hazard" [8] and the "Handbook of Mixture Hazard of Chemical Substances" [9]. The thermal analysis (DSC) data were provided by Yokohama National University, The University of Tokyo, and AIST.

3.2 Characteristics

RISCAD has a search by date function, location, and an accident summary (full text search by free words) like that of general accident databases.

In addition, RISCARD has the following characteristics.

(1) A search function by keywords hierarchized by experts, such as final events, activities, equipment, probable causes and damage.

For example hierarchized keywords concerning probable causes are shown in Tables 1. The following discussions were carried out concerning keywords about probable causes. "Human Factor" and "Organization Factor" were established as the 1st categories in order to separate the simple mistakes of operators and root causes related to organizations. "Substance Factor/Reaction Factor", which were important as causes of chemical accidents were established as the 1st category. And in that category, "Formation of Inflammable Gaseous Mixture" and "Contact with Impurity" were established as sub categories, because they became causes in many accidents. "Impurity" in that keyword was defined as including the air and the moisture which there must not be in the system. To prevent similar chemical accidents, classification by trigger events was important, therefore "Stimulus Factor" was established as the 1st category.

Table 1. Hierarchized keywords about probable causes.

1st_category	2nd_category	3rd_category
Human factor	Unsuitable action/operation	Mistake of information communication
		Operation mistake/Work mistake
		Judgment mistake/Mistake of determination
		Loss of operation capability/Lack of operation capability
		Other unsuitable actions/operations
	Other human factors	
Organization factor	Safety control defect	Training is insufficient/Education is insufficient
		Management technique mistake
		Defect of an organism system
	Design mistake	Prior evaluation is insufficient.
		Equipment design mistake
		Condition setting mistake
	Other organization factors	
Substance factor/Reaction factor	Mixed system reaction	Incorrect mixture
		Reaction by contacting impurities
	Self-reaction	Decomposition
		Polycondensation
		Ignition
	Formation of inflammable gaseous mixture	

1st_category	2nd_category	3rd_category
Equipment factor	Poor control system	Computer incorrect operation/Computer fault
		Inadequate in control/Poor control
	Poor apparatus	Electric failure
		Malfunction
		Functional loss
	Material damage	Fatigue
		Corrosion
		Deterioration
		Other material damages
	Other equipment factors	
External factor	Natural disaster	Abnormal weather
		Earthquake
		Other natural disasters
	Traffic accident	
	Intentional cause	Terrorism
		Arson
	Domino effect	
	Utility stop	
	Other external factors	
Stimulus factor	Mechanical force	I mpact
		Friction
		B ombardment
	E lectro-explosive device	Flame
		Sparks
		High temperature object
		Static electricity
	Light	
	Accumulation	
	Other stimulus factors	
Uncertain cause		

(2) Search function by other names (synonyms) of chemical substances.

The "Japanese Chemical Substances Dictionary" (JCHEM), which JST developed was used in RISCAD. The following are examples of synonyms by JCHEM. Synonyms of "Ethanol"; ethyl alcohol, alcohol, ethane-1-ol, methyl carbinol, ethyl hydrate, spirit, and wine spirit.

(3) Dynamic statistical analysis on the Web browser.

RISCAD has the function to show the search results of accidents dynamically on the Web browser. A choice is possible from a pile bar chart, a side bar chart, a line chart, a pie chart, and a distribution map of Japan. A RISCAD chart choice screen is shown in Figure 1.

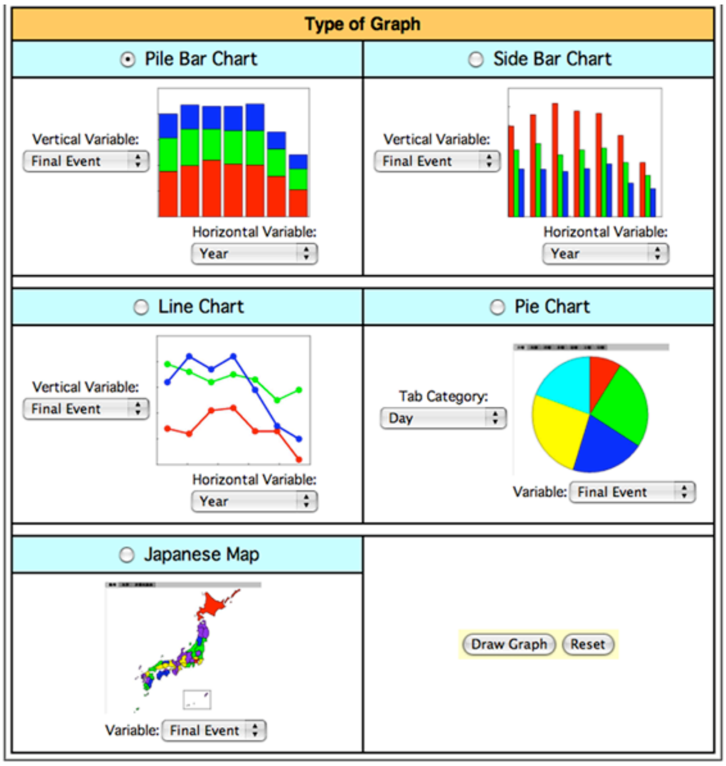

Figure 1. Chart types to show statistical analysis on RISCAD.

(4) Link to thermal hazard data relevant to chemical substance accidents.

The thermal hazard data screen shows the following information : Substance ID, CAS number, JCHEM number, substance name, other names (synonyms), chemical formula, rational formula, boiling point (˚C), flash point (˚C), condition of flash point, ignition point (˚C), condition of ignition point, lower explosion limit (%), upper explosion limit (%), mixture hazard, classification of thermal hazard, and United Nations hazard classification. The classification of thermal hazard was developed by the "MS seminar".

(5) Dynamic analysis of thermal analysis (DSC) data on the Web browser.

(6) Link to images of additional information.

The images of additional information are those such as the chemical reaction process flow, the devices and facilities layout, the schematic diagram of the device at which an accident was occurred, reaction formula, etc. Examples of additional information are shown in Figure 2.

(7) Link to the accident progress flowchart.

The accident progress flowchart was analyzed by time series, and the trigger events or causes were extracted so as to be able to fully understand the accident. Finally, we extracted and learn lessons from the accident progress flowchart.

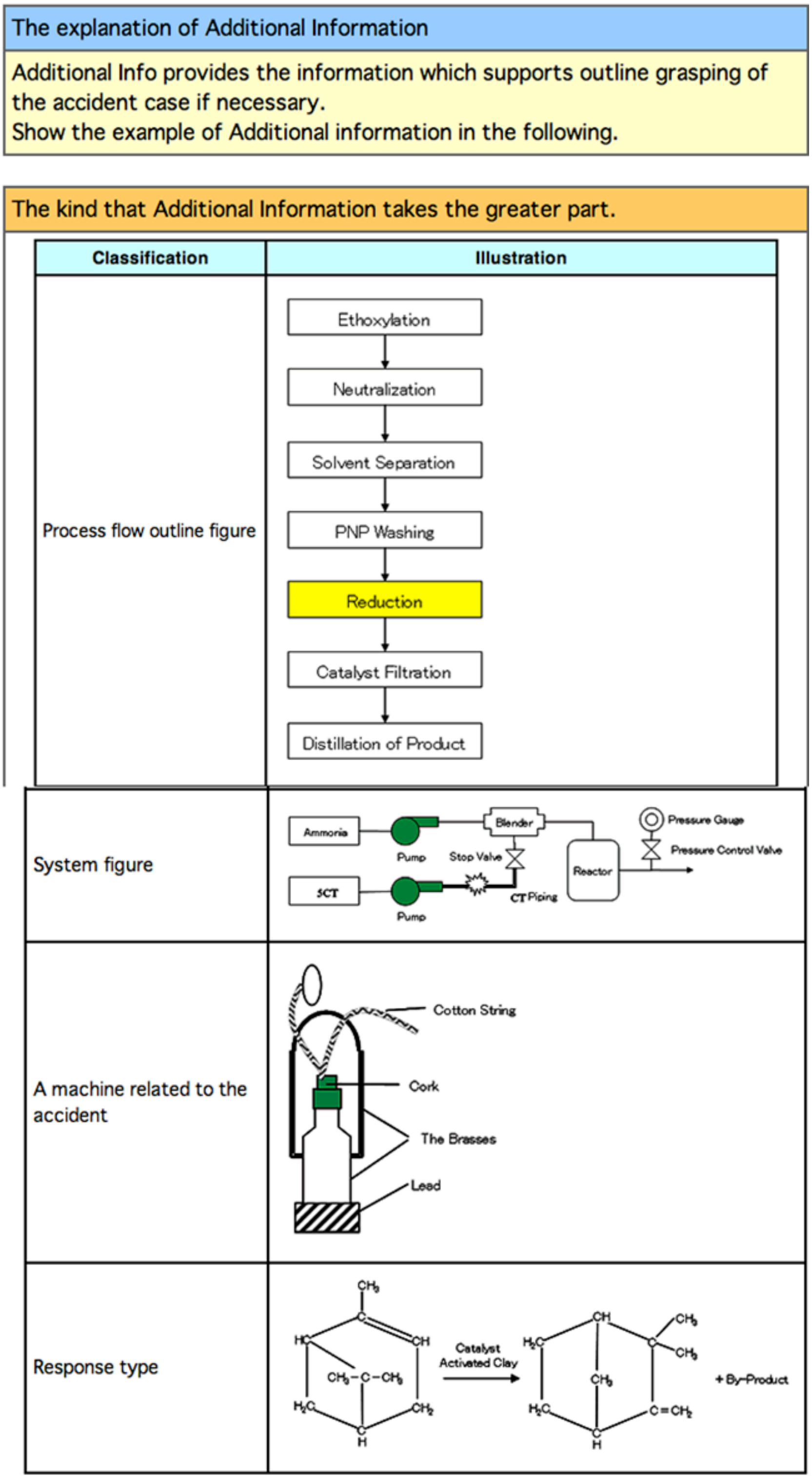

Figure 2 Examples of additional information.

(8) Search function of hazard information by substance name.

At first, RISCAD could show hazard information only for substances relevant to the searched accidents. So, a function to search for and show hazard information by substance names was added in compliance with database users. By this function, a hazard information database, mainly mixture hazard, comprising more than 4.000 substances recorded in RISCAD, became available to database users.

4.0 CASE STUDY

Case studies were carried out on an accident related hydrogen by making progress flowchart. At first, one of our investigation team investigated an accident report alone and made a draft progress flowchart. Then, all investigation team members discussed about the accident, for example, the root causes that were not written in the accident report, and updated the progress flowchart.

Explosion at the High-compressed Hydrogen Energy Generator (HHEG)

Date : December 7, 2005, **Time** : 13:22, **Place** : Fukuoka, Japan,

Final Event : Explosion, **Damage** : Human - No Injury, Physical - Accident Institution, Five Cars,

Probable Cause : Reaction of Titanium Electrode and/or Combustion of Hydrogen/Oxygen Mixture,

Involved Substances : Hydrogen, Oxygen, Titanium, Fluorine, etc.,

Outline of the accident :

An explosion occurred during the operation of the High-compressed Hydrogen Energy Generator (HHEG) in the verification test facilities of the hydrogen station within an university campus. The electrolysis cell in the HHEG burned down, pipes bursted and the peripheral equipments scattered all over the facilities. The liquid blown out from the bursted pipes and the gas release valve, and glass fragments were scattered within 10 meter radius. The water splash caused microscopic corrosion on the windows and hoods of five cars. There was no injuries. The titanium electrode in the electrolysis cell of the HHEG and/or hydrogen were burned, then water containing hydrogen flowed to the oxygen pipe. At that time, the metal fragments flowed in the oxygen pipe then it caused an explosion and the pipe bursted.

The Progress flowchart of this accident is shown in Figure 3.

Lessons Learned :

Risk assessment on test operation : Risk assessment should be done to know the risk of the operation and to take safety measures even if the operation is under testing or temporary.

High pressure oxygen can burn metals : Under high pressure oxygen, even metals could burn. If equipment is contacted with oxygen, it should be made of material that is well examined under ordinary operating condition.

Pressure rises at the closed end of pipe : If pressure wave happens in a pipe, it may cause excessive pressure than the strength of the pipe at the closed end of pipe and it will burst.

Safety management system at institutes : Institutes, including university, should organize the safety management system, even if they do only test or temporary operations.

Summary	Accident ID, Date, Location

12/7/2005, 13:22, Fukuoka, Japan
An explosion occurred during the operation of the High-compressed Hydrogen Energy Generator (HHEG) in the verification test facilities of the hydrogen station within an university campus. The electrolysis cell in the HHEG burned down, pipes bursted and the peripheral equipments scattered all over the facilities. The liquid blown out from the bursted pipes and the gas release valve, and glass fragments were scattered within 10 meter radius. The water splash caused microscopic corrosion on the windows and hoods of five cars. There was no injuries. The titanium electrode in the electrolysis cell of the HHEG and/or hydrogen were burned, then water containing hydrogen flowed to the oxygen pipe. At that time, the metal fragments flowed in the oxygen pipe then it caused an explosion and the pipe bursted.

Background

August 28, 2003, an explosion occurred in the test operation of the old HHEG test model. Hydrogen flowed in the oxygen separation tank by water decrease between that tank and the electrolysis cell tank. It exploded for some ignition sources. The fire likely spread to the electrolysis cell. They had increased the holding water volume in the electrolysis cell for this new HHEG. The operation of this new HHEG started November 15, 2005. In the operation, the pressure of hydrogen had been slightly increased with checking the performance of the peripheral equipments. On November 24, 2005, the HHEG achieved generating 40 MPa hydrogen, and the next day, it generated hydrogen at 30 Nm3/hour at the pressure of 40 MPa. Then, the new operation, supplying hydrogen to the accumulator, had just started on the day of the accident.
Weather : fair, Temperature : 7.3 'C, Wind Direction : Northwest, Wind Velocity : 3m/s

Category	Cause	Accident Progress Flow			Notes
Progress		1	2005/12/7 9:25	The HHEG operation started.	New operation to supply hydrogen to the accumulator
	Lack of risk assessment of new/test operation Lack of sharing information of new technology Lack of safety management system				
		2	11:14	Hydrogen pressure was regulated at about 40 MPa.	Abnormalities was not found.
		3	12:43	Hydrogen supplying operation from the HHEG to the pressure accumulator started.	Hydrogen pressure was at about 39 MPa steadily.
	Expose titanium to oxygen at high pressure and high temperature / Leak oxygen into hydrogen				Peeling off platinum coating on titanium, reaction with fluorine from the membrane filter / Generating oxygen bubble, failure of the membrane filter, etc.
		4		Burning of titanium electrode and/or reaction between hydrogen and oxygen in the electrolysis cell occurred.	
		5	13:22:36	Abnormal reaction occurred in the partial electrolysis cell.	Voltage of the electrolysis cell dropped from 179.4 V to 161.5 V. Electric current rose from 992.5 A to 1002.6 A.
		6		Pressure increased in the electrolysis cell.	The range-over alarm of the measurement device went off.
		7		The gas blew out from the hydrogen pipe joint.	
		8		Safety valve on the oxygen pipe worked.	
		9		Cell fragments, reaction products from cell, hydrogen and water flowed in the oxygen separation tank and reminded in the pipe.	
	Lack of risk assessment on plant design				
		10	13:22:38	Pressure in the electrolysis cell tank and the oxygen separation tank increased.	Temperature of circulating water at the electrolysis cell tank outlet rose. Liquid level in the electrolysis cell tank rose. Circulating water pipe got discolored and caused plastic deformation.

Cause	No.	Time	Event	Details
	11		The differential pressure regulating bypass was opened. Electric current of the electrolysis cell was shut down. Emergency release, emergency depressure, hydrogen supply shut-down were carried out.	The electrolysis cell tank and the oxygen separation tank were directly opened through by both the circulating water pipe and the differential pressure regulating bypass.
Lack of risk assessment on control of chemical reaction				
	12		The reaction continues even after the electrolysis was stopped.	
	13	13:22:40	Liquid level in the oxygen separation tank rose to the outlet. Hydrogen temperature within the electrolysis cell rose.	Temperature of hydrogen exceeded 100 'C in 5 seconds, then it was estimated to exceed to 400 'C. Vapor escaped from the hydrogen release pipe.
	14	13:22:45	Pressure in the oxygen separation tank and the electrolysis cell reached the maximum.	Pressure was at more than 55 MPa. (estimate : approximately 100 MPa)
Lack of risk assessment on safety devices				
	15	13:22:50	Safety valve shut down.	Pressure decreased below 42 MPa by safety valve activating.
	16	13:22:55	Water circulating pump was shut down.	Water containing hydrogen and the product from electrolysis cell could flow through the differential pressure regulating bypass into the oxygen separation tank.
	17		The abnormal reaction spread all over the electrolysis cell.	
	18	13:22:59	Safety valve worked again.	Vapor blew out from the safety valve
	19	13:23:00	Pressure in the oxygen separation tank and the electrolysis cell rose again.	The electrolysis cell burned down. Pressure is at above 45 MPa.
	20		Cell fragments, reaction products from cell, hydrogen and water flow into the oxygen separation tank through the differential pressure regulating bypass.	
	21		Cell fragments and hydrogen flew into the oxygen pipe.	
Friction or impact between cell fragments and pipe and/or high temperature of cell fragments and reaction products from cell				
	22		Deflagration occurred in the oxygen pipe.	
Lack of risk assessment on design of piping and venting				
	23	13:23:17	It blew out from the leak vent of the safety valve on oxygen pipe	
	24		Pressure rose locally at the end of pipes.	Oxygen was remained at the end of pipes.
	25	13:23:18	Oxygen pipe bursted.	Flash was seen immediately on the monitor.

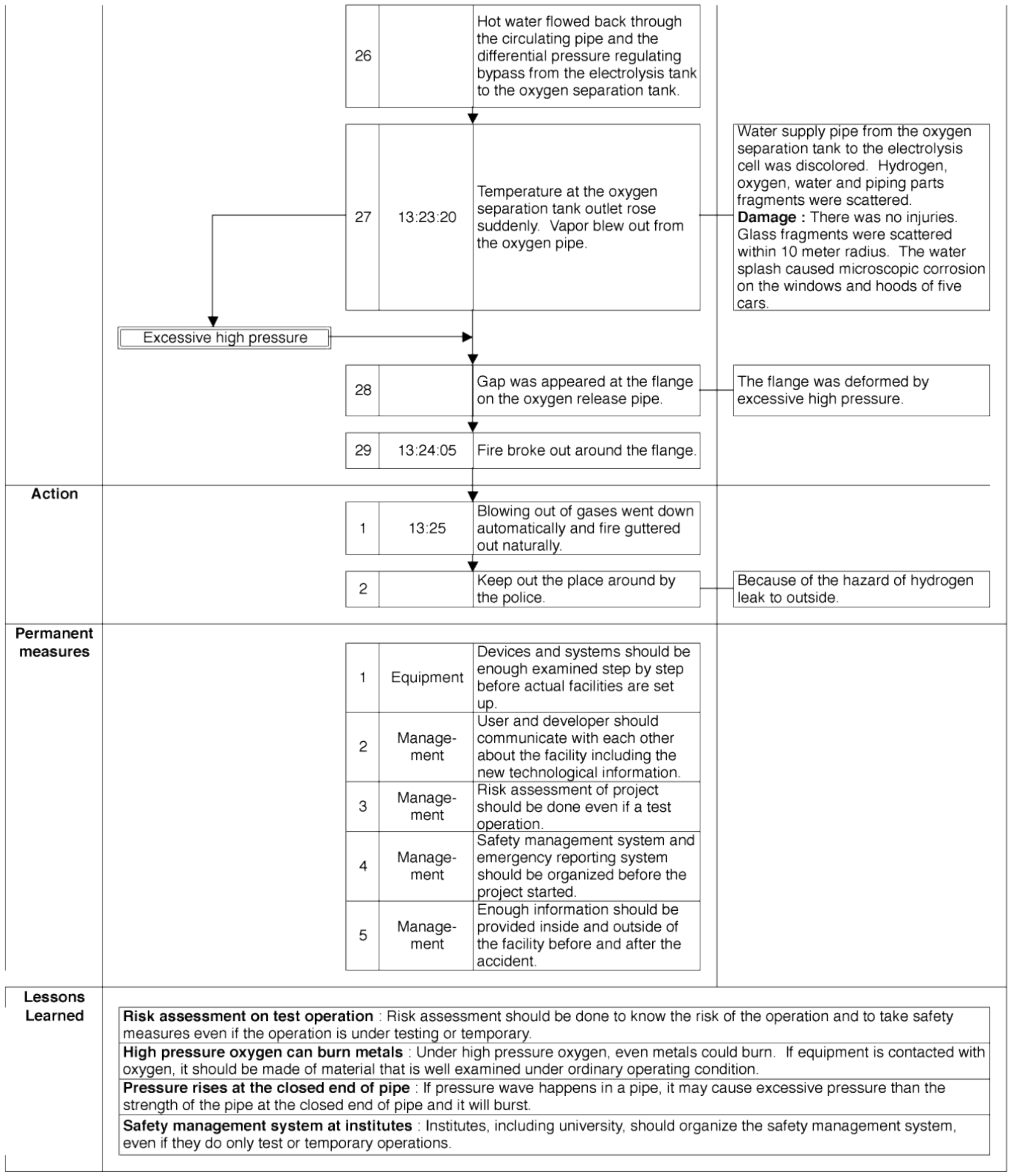

Figure 3. Progress flowchart of the accident at the HHEG.

5.0 CONCLUSION

A chemical accidents database with many useful functions for database users who want to prevent the recurrence of a similar accident as those in the past and who want to know the hazards of chemical substances which they plan to use, was released as RISCAD on the Web. One of the characteristics of RISCAD is its link to the accident progress flowchart analyzed by experts. To make a progress flowchart and discuss an accident with it, it is very useful for understanding an accident and drawing lessons from it. And to learn about an accident by RISCAD with the progress flowchart will also be helpful to database users in understanding an accident and clarifying how to prevent it happening.

By a case study of an accident related on hydrogen, it proved a necessity and importance of risk assessment on every operation even if it is a test operation or a temporary operation.

Anyone can use RISCAD free of charge via Internet. RISCAD will be improved in compliance with database users' requests.

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