Risk analysis of electrolytic water hydrogen production and ammonia synthesis process based on STAMP-STPA model

Xuan Zhang[a,b], Hao Liu[a,b], Yao Liu[a,b] ,Qingqing Xu[a,b*], Yi Shuai[a,b], Xiaojing Zeng[c], Yu Li[c]

[a]College of Safety and Ocean Engineering, China University of Petroleum, Beijing, China
[b]Key Laboratory of Oil and Gas Safety and Emergency Technology, Ministry of Emergency Management, Beijing , China
[c]No. 5 Oil Production Plant, Qinghai Oilfield Company, PetroChina, Dunhuang, China

Abstract: The rapid development of new energy has brought opportunities and challenges to industries such as petrochemicals, and using green hydrogen as a raw material to replace carbon based fossil fuels in ammonia synthesis has become a new trend. In order to improve the overall safety of the green ammonia process and ensure the safety of process equipment and personnel during operation,a risk analysis of the green ammonia process is conducted in this paper, making the subsequent system hazard analysis and accident cause analysis more comprehensive and complete. Firstly, the STAMP-STPA operation control and feedback model is established,the process of green ammonia and the correlation between equipment to determine the safety requirements and corresponding safety constraints that may cause system accidents is conducted in this paper, and establishes a green ammonia process control and feedback model. Secondly, four potential unsafe control behaviors and key causes of unsafe control have been identified. Finally, the risk of the process is studied, and a comprehensive analysis of the causes of failure is conducted using the FRAM model. The analysis results are visualized in the form of a knowledge graph, making it more intuitive to display. The innovation of this article lies in integrating the model with a knowledge graph, deducing and inferring potential risk factors in a knowledge graph manner, and ultimately achieving the interpretability of the entire model.Research has shown that building a green ammonia process feedback model can make the accident evolution process more clear and the cause sorting clearer. From a system perspective, the causal relationship between risk events in various process environments provides feasible and effective implementation information for the subsequent development of green ammonia processes.

Keywords: Analysis, Electrolytic water hydrogen production, Ammonia synthesis process, STAMP—STPA model

1. INTRODUCTION

Driven by the demand for carbon reduction in the chemical industry under the "dual carbon goals", there is enormous potential for large-scale electrolysis of water for hydrogen production and ammonia synthesis[1]. Electrolysis of water for hydrogen production and synthesis of ammonia is a dynamic, continuous, and nonlinear engineering system that involves complex regulatory requirements for safe collaboration among multiple systems of renewable energy generation, hydrogen production, and synthesis of ammonia. Due to the complexity of its synthetic ammonia production process, especially its high-dimensional nonlinearity and harmful product characteristics, it affects the safety of the green ammonia process[2].

Green ammonia has also experienced multiple accidents during the production process. In September 2014, Ningxia Jiemei Fengyou Chemical Industry experienced an accident where an ammonia liquid mixture sprayed out from the top of the main torch, causing acute ammonia poisoning in 41 people within a 200 meter range[3].In May 2022, Anhui Haoyuan Chemical Industry experienced a major poisoning and suffocation accident during production due to improper operation and safety management loopholes, resulting in toxic gas leakage. With the rapid development of green ammonia technology in China, new safety hazards and risk factors have emerged in the existing green ammonia production system. Therefore, research on green ammonia production is of great significance.

At present, there is very little research on green ammonia both domestically and internationally. Hazard and operability studies,Failure mode effects,criticality analysis and Fault Tree Analysis are usually used to address the safety hazards and risk factors of green ammonia processes.These two methods cannot provide the accident caused by control failure, The STAMP-STAP model has the advantages of identifying system security risks and constraints, defining security control structures, analyzing unsafe control behaviors and key factors in the absence of control information for green ammonia safety analysis. Jie et al. (2022) [[4] constructed a coal mine safety accident causation and control problem model based on the STAMP model, transforming safety issues into safety issues that can be applied to coal mine safety accident analysis, and obtained a detailed process of coal mine safety accident causation analysis. Ceylan et al. (2023) [[5] qualitatively analyzed accidents within the scope of the proposed STAMP model by identifying safety constraints, constructing hierarchical control processes, and specifying the connections between unsafe activities.

Regarding the green ammonia process, Zhao et al. (2022) [6] used the chain of emergency events and their secondary events to describe the complete evolution process of the scenario of casualties caused by liquid ammonia leakage from three dimensions: disaster, disaster bearing body, and emergency management. Schmitz et al. (2021) [7] links organizational factors to account for processes and their barrier systems, Using the bowtie method. It is shown that organizational factors directly affect accident processes as they strongly influence the quality or trustworthiness of the barrier systems. Liu et al. (2021) [8] proposed an intelligent quantitative risk assessment method (DYN-LSTM-QRA) based on the dynamic mechanism model of the ammonia synthesis process, which evaluates the risks of multiple conditions and their dynamic hazard ranges to ensure the safe operation of the process. And it was applied to leakage accidents in the ammonia synthesis process, and its effectiveness and reliability were verified through dynamic simulation. Ge et al. [9] (2023) calculated the concentration distribution of the model based on existing probabilistic risk assessment formulas. Quantitative analysis of ammonia process leakage using the revised formula, and analysis of different state parameters to identify hazardous leakage points in the ammonia process system. However, there are relatively few analyses of accident failures, and the green ammonia process has certain risks.

The traditional causal model assumes that accidents are caused by a chain of failed events [10]. In the event chain, each failure will lead to the next failure in the event chain. Traditional causal models only involve simple failure event chains, and event based models are prone to missing interactions in complex failure events and completely ignoring components that are not involved. STAMP-STPA extends the definition of accident causation beyond failure events and establishes an accident causation mechanism that includes interaction between system components, operators, and organizational management. The interaction between system components, operators, and organizational management in the green ammonia system makes the risk factors more complex. STAMP-STPA can better identify system risks.

This article uses the STAMP-STPA model to analyze the process flow of electrolysis water for hydrogen production and ammonia synthesis, determine safety requirements and constraints, and establish four safety barriers. At the same time, a comprehensive analysis of the causes of failure is conducted using the FRAM model, and the analysis results are visualized through a knowledge graph. Innovatively integrating models with knowledge graphs, deducing and inferring potential risk factors through knowledge graphs, ultimately achieving interpretability of the entire model.

2. OVERVIEW OF THE PRINCIPLES OF THE STAMP-STPA MODEL

STAMP views security as a characteristic presented by the interaction of various related components within the system, and security depends on the execution of the constraints on the behavior of system components and the potential interactions between components [11]. By applying security constraints to control the system, the security analysis of the system is transformed into a control problem, the system is divided into different levels of control structures, and a model is constructed based on the control relationships. A complete STAMP model typically consists of three parts: security constraints, hierarchical control structure, and process model, STAMP believes that only by complying with safety constraints, effective control, and timely and accurate information feedback can the safe operation of the system be ensured. STPA is a safety analysis method based on STAMP, which can be referred to as "pre accident investigation". By identifying potential accident causes, i.e. loss scenarios, hazards are eliminated or controlled in design and operation before accidents occur. This method establishes a system safety control feedback loop composed of controllers, sensors, actuators, controlled objects, etc., analyzes the unsafe situations of the behavior of each component and the interaction behavior between components in time, space, and logic during the controlled process, and more comprehensively identifies the unsafe control behavior of the system.

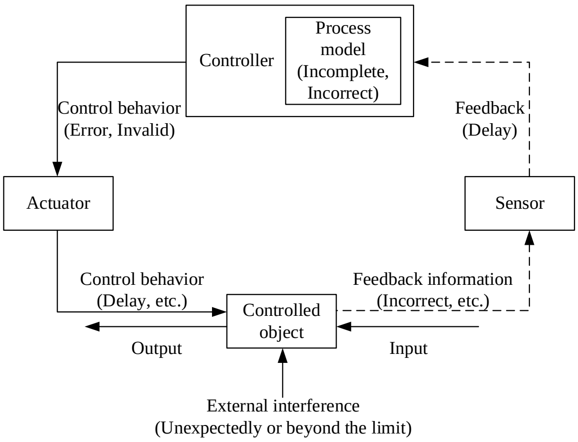

Fig. 1 STAMP model

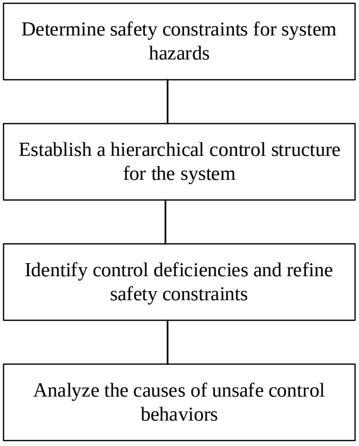

Fig. 2 Steps of STPA analysis method

3. CONSTRUCTION OF FORWARD MODELING FOR GREEN AMMONIA PROCESS ACCIDENTS

Similar to other security analysis methods, The STAMP-STPA method mainly identifies the risks existing in the system, but the difference is that it can consider the interaction between different devices, and identify unsafe control behaviors in the system control loop by analyzing the safety requirements and constraints of the system, and identifying unsafe control behaviors during accident evolution. Safety analysis is conducted from the perspective of system control and constraints. Using the STAMP-STPA method to construct an accident forward model can intuitively illustrate the process of accident occurrence and ensure the systematic integrity of the accident forward model.

The construction process of the control and feedback model for the electrolysis water hydrogen production and ammonia synthesis process based on STAMP-STPA is shown below.

3.1. Clarify the green ammonia process flow

Through investigation and research, determine the research subject, clarify the process flow of green ammonia, and confirm the functions of various equipment and facilities in the overall process flow and their interrelationships. Among them, the green ammonia process flow is shown in Figure 3.

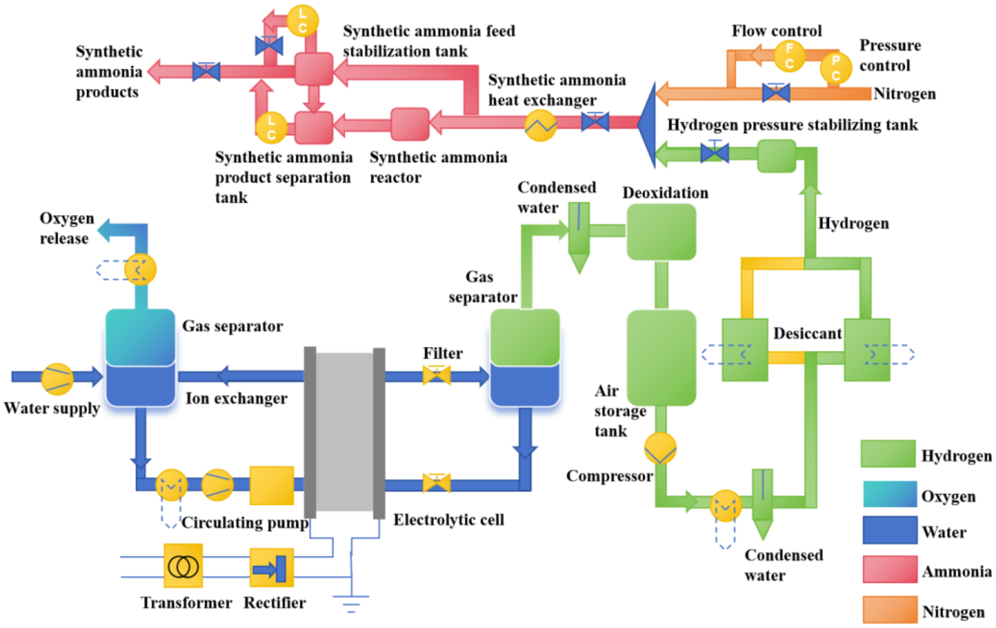

Fig. 3 Green ammonia process flow

3.2. Analyze security requirements and security constraints

Using the normal parameters of the intelligent information monitoring system and control system as safety constraints for failure accidents in the green ammonia process system, control the measurement point parameters of the two systems through corresponding constraint barriers and threshold alarm devices. The failure accident of the green ammonia process system refers to the phenomenon of system failure caused by equipment failure, design defects, and other reasons that prevent the generation of ammonia products, as well as abnormal pressure, flow rate, liquid level indicators and toxic gas release during the process. Before conducting green ammonia production, operators inspect the equipment and facilities to ensure that the production system does not experience any leaks, blockages, etc. This is the first layer of constraint barrier to prevent the failure of the green ammonia production system. In the production process of green ammonia, the intelligent information monitoring system and control system ensure the normal operation of the production system by monitoring parameters such as temperature, pressure, and gas concentration, which is the second layer of constraint barrier to prevent the failure of the green ammonia production system. In the process of green ammonia production, the auxiliary decision-making system provides timely information feedback on the system's operation, which is the third layer of constraint barrier to prevent the failure of the green ammonia production system.

3.3. Establish a control and feedback model for green ammonia process

In the control and prevention of production accidents in the green ammonia process, the control of process temperature, pressure, flow rate, liquid level, and gas monitoring during the production process is the key. Therefore, monitoring of important parameters in the process is particularly important. Using a monitoring controller to monitor these 5 parameters in the production system, control the pressure to prevent structural damage to equipment and facilities caused by overpressure during the production process. According to the feedback control loop in Figure 1 and the STPA process in Figure 2, the management personnel in the green ammonia production process are used as controllers; Use the inspection of the pump and equipment, as well as the operators and manual central control system responsible for executing the production process, as actuators; Technicians, control systems, intelligent information monitoring systems, and auxiliary decision-making systems serve as sensors.

Based on the STAMP model and the relevant equipment of the green ammonia production system, establish a control and feedback model for the green ammonia process, as shown in Figure 4. When management personnel convey command information, operators input commands and collect feedback information from the manual control center system, while technical personnel share collaborative information to provide technical support to the production system. Firstly, adjust the inlet system to achieve an appropriate level of inlet water volume and inlet water speed. In the oxygen separation system, the electrical energy from the substation unit enters the alkaline electrolysis tank for water electrolysis to produce hydrogen. Electrolytic separation controls the anode electrolysis of the electrolytic cell, and after gas separation operation, oxygen gas liquid separation is carried out. According to the comprehensive washing plan, release oxygen. Secondly, in the hydrogen separation system, a portion of the hydrogen gas at the cathode of the electrolytic cell enters the buffer tank to stabilize the pressure and then enters the compressor to compress it to the required pressure for synthetic ammonia. The other portion enters the hydrogen storage device for consuming upstream hydrogen or supplementing downstream hydrogen. Subsequently, in the synthetic ammonia product system, fresh hydrogen compressed by the compressor is cooled by a hydrogen cooler, stabilized in a hydrogen pressure stabilizing tank, mixed with external nitrogen and synthetic ammonia circulating gas, preheated by a synthetic ammonia heat exchanger, and then separated by gas-liquid in the feed stabilizing tank of the synthetic ammonia. The gas phase enters the outlet gas of the synthetic ammonia reactor and is cooled before being separated by gas-liquid in the synthetic ammonia separation tank. The liquid phase enters the synthetic ammonia separation tank to stabilize the pressure and is completed in the form of liquid ammonia. Finally, throughout the entire process, the intelligent information monitoring system monitors the temperature, gas concentration, and pressure in the production process. The abnormal information is transmitted to the threshold alarm by the process ESDS, and the pressure is relieved to the atmosphere by the pressure relief valve and control valve. In the control system, flow control valves and liquid level control valves control the flow and liquid level of the system. The auxiliary decision-making system records and historical calls information, makes auxiliary decisions, and provides information feedback to the manual control center.

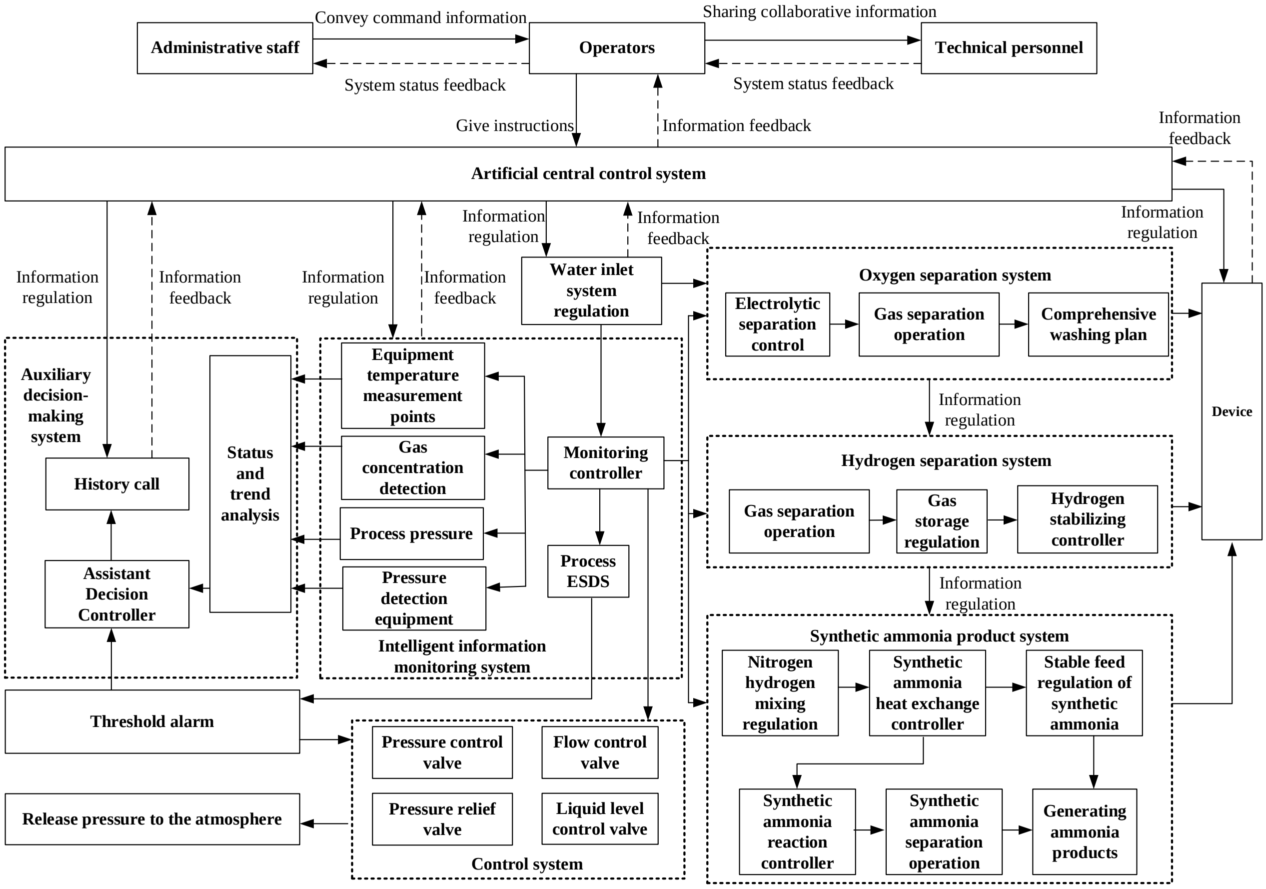

Fig. 4 STAMP-STPA control and feedback model for green ammonia process

3.4. Identify unsafe control behaviors

Based on the control and feedback model of the green ammonia process, analyze the risks present in the green ammonia production process from four perspectives: failure to provide control behavior, incorrect or unsafe control behavior, early/delayed occurrence of control behavior, and premature/prolonged end of control behavior. Table 1 Identified Unsafe Control Actions, CA)， Can be converted into safety constraints for the normal operation of green ammonia production systems. To prevent accidents caused by the failure of the green ammonia production system, it is necessary to ensure that the system control behavior complies with safety constraints during production operations.

3.5. Identify unsafe control behaviors

Based on the control feedback model and the basic control deficiencies proposed by STAMP-STPA, summarize the key reasons for unsafe control behaviors leading to green ammonia production accidents: insufficient execution of actions, incorrect or insufficient feedback information. Among them, inadequate control behavior execution includes:

a) Insufficient execution of control instructions by operators due to physical or psychological reasons, resulting in operational errors.
b) After the green ammonia production operation command was issued, the manual central control system was not fully executed and equipment maintenance was not carried out regularly.

Feedback errors or deficiencies include:

a) Technical personnel: Failure to provide timely feedback on fault information or incorrect feedback.
b) Control system: Incorrect or insufficient feedback information from flow control valves, liquid level control valves, pressure control valves, and pressure relief valves.
c) Intelligent information monitoring system: The monitoring controller failed to provide timely feedback on monitoring information, and the process ESDS did not reach the threshold alarm threshold and triggered an alarm, resulting in decision-making errors in the auxiliary system.

d) Auxiliary decision-making system: Error in historical record call, resulting in biased information feedback.

Table 1. Unsafe control behavior

Unsafe control behavior	Risks caused	Security constraint
No control behavior provided	(1) The pressure control valve fails, resulting in overpressure in the process system;	Regularly inspect and maintain various safety valves and pumps;
	(2) The pressure relief valve fails, resulting in pressure exceeding the threshold and failing to relieve pressure;	
	(1) The flow control valve fails, resulting in abnormal flow in the process system	Set up automatic protection devices for high and low liquid levels and flow rates. When the liquid level and flow rate are abnormal, an alarm will be triggered and the filling of raw materials will be suspended through interlocking;
	(2) The liquid level control valve fails to control the liquid level;	
	(1) The pressure detection equipment did not detect any abnormal pressure;	Regularly inspect and repair pressure, temperature, gas concentration and other monitoring devices to improve the accuracy of monitoring and early warning;
	(2) The gas concentration detection equipment failed to detect the leaked gas;	
	(3) The temperature abnormality is not alarmed by the equipment temperature measurement point;	
	(1) There is a malfunction in the electrolytic separation control, resulting in abnormal electrolysis;	Regularly inspect various equipment and facilities, and establish a sound regular maintenance system;
	(2) The hydrogen pressure stabilization control fails, resulting in abnormal hydrogen pressure	
	(3) The synthetic ammonia reaction controller is abnormal and cannot carry out normal reactions	
Control behavior errors or unsafe	(1) The gas concentration detection equipment detects an abnormality;	Technicians should complete the product quantity calculation for the green ammonia process in advance and submit the calculation report to management and operators for inspection and verification of the production report to ensure the accuracy of the efficiency of the green ammonia production system.
	(2) Misregulation of flow and liquid level control valves;	
	(3) Temperature measurement error at the equipment temperature point;	
	(4) Process ESDS false alarm;	
	(5) The pressure threshold is not reached, and the pressure relief valve leaks pressure by mistake;	
	(6) wrong decision-making by the assistant decision-maker;	
Control the behavior to occur in advance/delay	(1) The information is transmitted to the pressure control valve and the pressure relief valve control fails, and cannot be opened in time, resulting in damage to equipment and facilities;	Regularly inspect valves and equipment, and repair and update them. At the same time, set reasonable thresholds for temperature, pressure, concentration, liquid level, and flow rate.
	(2) The minimum flow and liquid level control valves did not open the circulation in time, resulting in damage to equipment and facilities;	
	(3) The feedback of temperature, pressure, and concentration measurement facilities is not timely;	
	(4) Alarm system alarm delay;	
	(1) The delay in the separation operation of oxygen and hydrogen leads to incomplete separation;	Check the operating status of each device, make timely central adjustments, strengthen fault diagnosis by technical personnel, and make timely decisions by management personnel.
	(2) The reaction in the synthetic ammonia reactor is advanced, and the raw materials have not fully entered, resulting in insufficient reaction;	
	(3) The separation operation of synthetic ammonia is not timely, resulting in impure ammonia products;	
	(4) In the process of assisting decision-making, the delay in accessing historical records can lead to decision-making errors;	
Control behavior ends too early/lasts	(1) The control of pressure, temperature, concentration, flow rate, and liquid level is	Before production, determine the status of each parameter.

too long	prematurely terminated;	
	(2) The hydrogen storage regulation ended prematurely, resulting in some hydrogen leakage;	
	(3) The comprehensive washing process is prematurely ended, resulting in impure oxygen and hydrogen;	

4. COMPARATIVE ANALYSIS

4.1. FRAM model analysis

This article constructs a FRAM model based on the feedback process of green ammonia process control, as shown in Figure 5. This model divides the green ammonia process into multiple modules according to function. After the management personnel convey instructions, each executing unit operates the corresponding equipment to execute the specified actions, until the action command of "production stop" is issued. In Figure 5, the corners I (Inputs) of the hexagon represent the inputs of the functional module, P (Preconditions) represent the prerequisites for the operation of the functional module, R (Resources) represent the manpower and other resources required for the operation of the functional module, T (Time) represents the time required for the functional module, C (Control) represents the control conditions during the operation of the functional module, and O (Outputs) represents the output of the functional module [12].

From the FRAM model shown in Figure 5, the execution routes of different functional modules in the emergency response process can be sorted out, and the causes of emergency response failure can be obtained, including: 1) untimely information feedback; 2) Abnormal monitoring of equipment parameters; 3) Control system response delay; 4) Improper macroeconomic regulation by management personnel; 5) The pressure relief valve did not release pressure in a timely manner; 6) Abnormal manual control system; 7) Emergency training is inadequate, and personnel lack equipment operation skills.

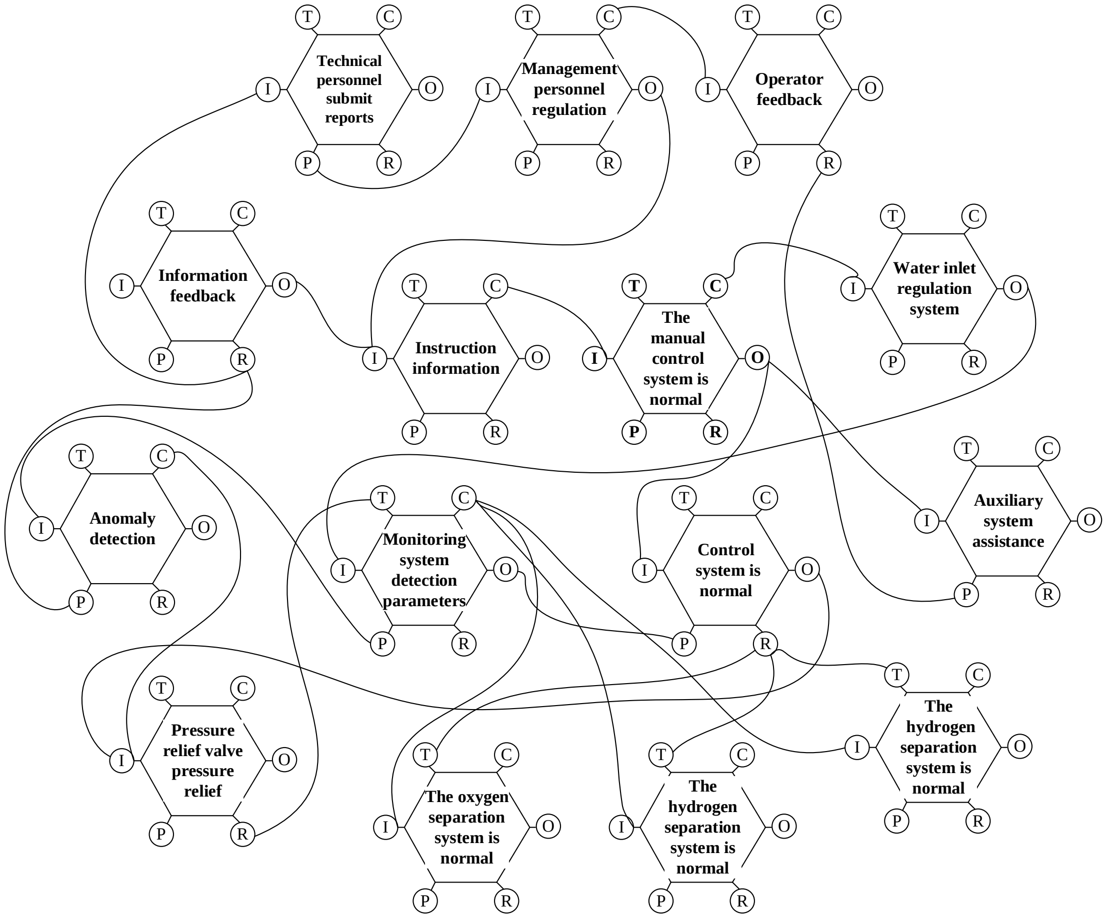

Fig. 5 FRAM Model Analysis of Green Ammonia Process

4.2. Knowledge Graph Analysis

For the knowledge graph of green ammonia process accidents, a reasonable description of the relationship between hazard evolution and protective measures can not only help managers understand the relationship between hazard evolution in a timely manner, but also provide corresponding handling measures for managers, reduce hazard risks, and ensure the normal progress of green ammonia production [13]. This article establishes an accident related knowledge graph for the green ammonia process, as shown in Figure 6. It can be found that the problems and causes in this system include:

a) The gas concentration monitoring system did not generate an alarm message, and there are two reasons for this safety issue: 1) the detection device itself fails; 2) The design of the detection device has defects.

b) The sensor at the temperature measurement point of the green ammonia equipment is abnormal, and there are two reasons for this safety issue: 1) The sensor itself fails or its function is incomplete; 2) The design of the detection device has defects, that is, it cannot detect abnormal temperature at the leakage point.

c) The feedback from the process pressure monitoring equipment is not timely, and the reasons may include: 1) insufficient sensitivity of the pressure monitoring equipment itself; 2) The overall control system has defects; 3) Monitoring system malfunction.

d) Maintenance personnel may have work loopholes, which may be due to: 1) poor physical or psychological condition of the staff on the day; 2) The safety management system regulations are incomplete.

e) The failure of process flow and liquid level control valves may be due to: 1) defects in the control system; 2) Insufficient sensitivity of the device; 3) The system feedback is not timely.

f) The response plan is not complete, and the reasons may include: 1) the daily maintenance and repair system of personnel is not perfect; 2) Delay in auxiliary decision-making system; 3) Inadequate protective measures.

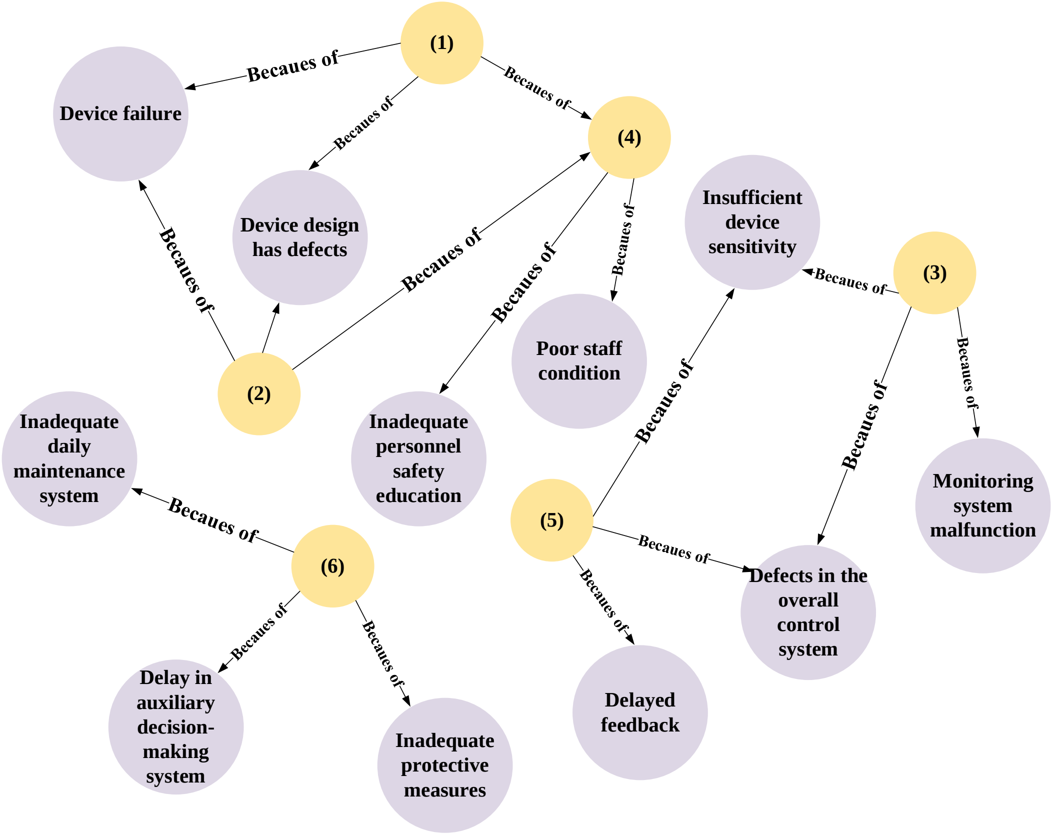

Fig. 6 Knowledge graph of accident correlation in green ammonia process

Table 2. Comparative analysis of results

Analysis results of the STAMP model	Analysis results of the FRAM model	Analysis results of knowledge graph
(1) The pressure control valve fails, resulting in overpressure in the process system;	(1) Information feedback is not timely;	(1) The gas concentration monitoring system did not generate an alarm message;
(2) The pressure relief valve fails, resulting in pressure exceeding the threshold and failing to relieve pressure;	(2) Abnormal monitoring of equipment parameters;	(2) The sensor at the temperature measurement point of the green ammonia equipment is abnormal;
(3) The comprehensive washing process is prematurely terminated, leading to impure oxygen and hydrogen;	(3) The control system has a delayed response;	(3) The feedback from the process pressure monitoring equipment is not timely;

(4) The flow and liquid level control valves fail to control the effect;	(4) The management personnel have made improper macro-control;	(4) Maintenance personnel have work loopholes;
(5) The gas concentration detection equipment fails to detect the leaked gas;	(5) The pressure relief valve did not release pressure in time;	(5) Process flow and liquid level control valves fail;
(6) The temperature abnormality is detected by the equipment temperature measuring point but no alarm is given;	(6) Abnormal manual control system;	(6) The response plan is not perfect.
(7) Failure in the control of electrolytic separation leads to abnormal electrolysis;	(7) Emergency training is not in place, and personnel lack equipment operation skills.	
(8) Failure of hydrogen pressure stabilization control leads to abnormal hydrogen pressure		
(9) The synthetic ammonia reaction controller is abnormal and cannot carry out normal reactions		
(10) Process ESDS false alarm;		
(11) The auxiliary decision-making device makes a wrong decision;		
(12) The comprehensive washing is prematurely ended, resulting in impure oxygen and hydrogen.		

4. CONCLUSION

(1) The control and feedback model of green ammonia process based on STAMP-STPA proposed in this article focuses on the characteristics of the green ammonia process. By defining the safety control model and identifying system risks and constraints, effective identification of unsafe control behaviors and deep excavation of key reasons are achieved.

(2) The control and feedback model of green ammonia process based on STAMP-STPA overcomes the problems of traditional safety analysis methods not being able to consider the internal correlation of complex systems, ignoring component interaction and macro control, making system hazard analysis and accident cause tracing more comprehensive and complete.

(3) A comprehensive analysis of the cause of failure was conducted using the FRAM model, and the results were visualized in the form of a knowledge graph to make the display more intuitive. The failure cause identification ability of the STAMP-STPA model is improved by 171 compared to the FRMA method, as measured by the number of failure causes ultimately obtained by the system analysis method 4%.

Acknowledgements

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