수소생산시설에서의 요오드-황 공정에 대한 안전성 평가연구

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Safety Assessments for the IS(Iodine Sulfur) Process in a Hydrogen Production Facility

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Abstract : A substitute energy development has been required due to the exhaust of the fossil fuel and an environmental problem. Consequently, possible technologies producing hydrogen from water that does not release carbon is a very promising technology. Also, Iodine-Sulfur(IS) thermochemical water decomposition is one of the promising processes that are used to produce hydrogen efficiently using the high temperature gas-cooled reactor(HTGR) as an energy source that is possible to supply heat over 900℃. In this study, to make a initiating events identification for the IS process, Master Logic Diagram(MLD) is used and 9 initiating events that cause a leakage of the chemical material are identified. Also, 6 events are identified among 9 initiating events above and are quantified using event tree.

초 록 : 화석연료의 고갈과 환경문제로 인해 대체에너지 개발의 필요성이 대두되고 있다. 이에 거론되고 있는 대체에너지 중에서 물로부터 수소를 생산하는 기술은 탄소발생이 없는 매우 장래가 유망한 기술이다. IS 열화학적 물분해 공정은 거론되는 방법 중 매우 유망한 기술로 에너지원으로 900℃ 이상의 열을 공급할 수 있는 고온가스냉각로(HTGR)를 사용하여 매우 능률적으로 수소를 생산할 수 있는 방법이다. 본 연구에서는 IS공정의 초기사건을 도출하기 위해 주논리도(MLD)방법이 사용되어 화학물질의 유출을 야기할 수 있는 초기사건 9가지가 도출되었다. 또한 도출된 9가지 초기사건 중 6가지를 선정, 사건수목을 이용하여 정량화하였다.
Key Words : iodine-sulfur process, master logic diagram, initiating events identification, event tree analysis

1. Introduction

Hydrogen is very attractive as a future secondary energy carrier, considering environmental problems. It is important to produce hydrogen from water by use of carbon free primary energy source. The thermochemical water decomposition cycle is one of the methods for the hydrogen production process from water[1]. Japan Atomic Energy Research Institute(JAERI) has been carrying out an R&D on the IS(iodine - sulfur) process that was first proposed by GA(General Atomic Co.) focusing on demonstration the "closed-cycle" continuous hydrogen production on developing a feasible and efficient scheme for the HI processing, and on screening and/or developing materials of construction to be used in the corrosive process environment[2]. The successful continuous operation of the IS-process was demonstrated and this process is one of the thermochemical processes, which is the closest to being industrialized[3].

Currently, Korea has also started a research about the IS process and the construction of the IS process system is planned. In this study, for risk analysis of the IS process and improvement of IS process safety, initiating events of the IS process are identified by using the Master Logic Diagram(MLD) that is method for initiating event identification. Also, 6 events are

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identified among 9 initiating events above and performed quantification of events using event tree. This study will contribute to improvement of safety in pre-conceptual design of IS process in a hydrogen production facility.

2. Methodology

2.1. IS process

A scheme of the IS process is shown in Fig. 1 The process is composed of the following chemical reactions;

$$I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4 \text{ (Bunsen reaction)} \quad (1)$$

$$2HI = H_2 + I_2 \ (200\sim500℃) \quad (2)$$

$$H_2SO_4 = SO_2 + 0.5O_2 + H_2O \ (800℃) \quad (3)$$

The so-called Bunsen reaction(1) is an exothermic sulfur dioxide gas-absorbing reaction in an aqueous phase. The hydriodic acid and the sulfuric acid formed are separated by a liquid - liquid phase separation phenomenon that occurs in the presence of an excess of iodine. The separated hydriodic acid dissolves the iodine and is denoted as the HIx phase. After purification, hydriodic acid is separated from iodine by distillation. The HI is then decomposed to produce hydrogen(2). Similarly, the separated sulfuric acid denoted as the sulfuric acid phase is purified, concentrated, vaporized and decomposed to produce oxygen. Here, the decomposition reaction(3) proceeds endothermically in two stages; firstly, the sulfuric acid decomposes spontaneously into sulfur trioxide and

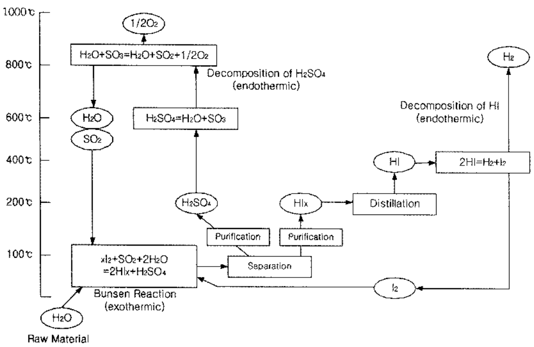

Fig. 1. Reaction scheme of the IS process.

gaseous water at ca. 400℃, and secondly, at higher temperatures, the sulfur trioxide decomposes into sulfur dioxide and oxygen in the presence of a solid catalyst. Thus, these three reactions make a chemical cycle that is an energy converter from heat to hydrogen[4].

2.2. Initiating event identification using the MLD in IS process

The Master logic diagram technique is a basic approach for initiating event identification. It is a logic diagram that resembles a fault tree but without the formal mathematical properties of the latter. It starts with a "Top Event" which is the undesired event(like "Leakage of the chemical material") and it continues decomposing it into simpler contributing events in a way that the events of a certain level will in some logical combination, cause the events of the level immediately above. The development continues until a level is reached where events directly challenging the various safety functions of the plant are identified.

The starting point of MLD development is beginning by defining the top event. In this study, top event is defined to containment failure that can induce the stopping of the system and cause risk. And then, the deductive decomposition is carried out through the following step.

2.2.1. Identification of critical areas

A critical area of the plant is one containing an each other different chemical material.

(1) Bunsen Reaction Step
(2) H_2SO_4 Decomposition Step
(3) HI Decomposition Step
(4) H_2 Step

These four sections have been identified as possible sites of chemical material release. A schematic representation of the division of the IS process plant in the four sections is given in Fig. 2. This process needs only H_2O, and it will be changed to H_2, O_2 gases.

The first level of decomposition is along the four possible sites of chemical material release as shown Fig. 3. There is 4 events of chemical material leakage events in Is process as top events of MLD.

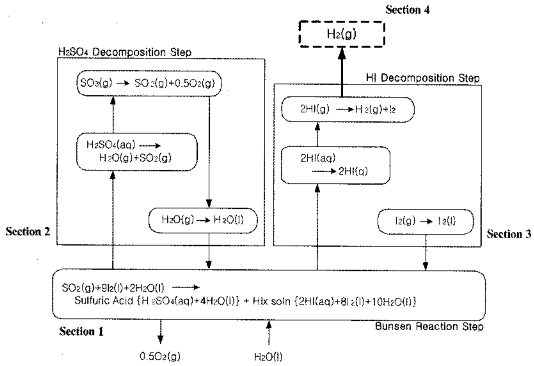

Fig. 2. Schematic diagram of the IS process.

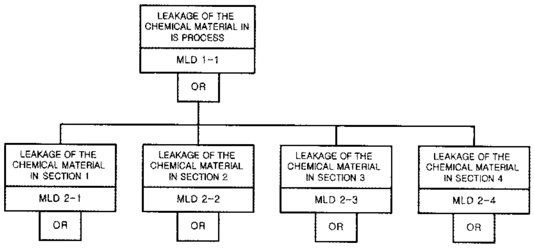

Fig. 3. MLD of the IS process.

2.2.2. MLD of the Bunsen reaction section as an example

Fig. 4 gives MLD of the Bunsen reaction section. The reasons that Bunsen reaction section may fail have structure failure and bypass. Structure failures occur in corrosion by H_2SO_4, overpressure, external loading and high temperature. Overpressure in Bunsen reaction may occur in fire and run-away reaction. An earthquake is the only natural phenomenon considered which might cause loss of containment. All the others flooding and high wind have been neglected, because this particular system is surrounded to the outside building. High temperature may occur in external fire.

Bypass in the Bunsen reaction happens due to the failure of the pump to provide the water.

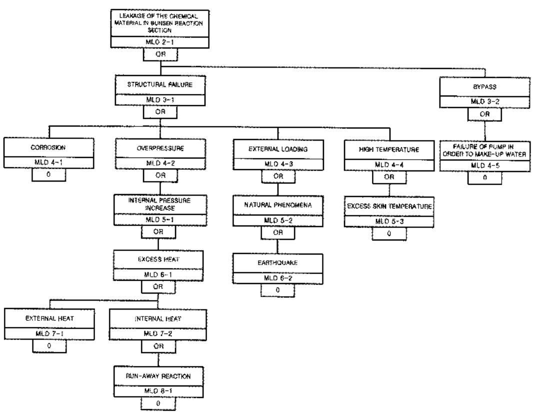

Fig. 4. MLD of the Bunsen reaction section.

2.3. Initiating events identification

The most important initiating events, which are identified with the application of the master logic diagram to the IS process, are the following;

(1) Pipebreak owing to corrosion, thermal stress, hydrogen embrittlement and hydrogen induced cracking
(2) Overpressure owing to run-away reaction in the Bunsen reaction
(3) Vapor pressure increase from a temperature control failure
(4) Direct pressure increase from evaporated gas
(5) Clogged pipe by I2 concentration control failure
(6) Overfilling in storing hydrogen
(7) Failure of check valves and molecular seals
(8) Bypass accident of a water supply pump
(9) Earthquakes
(10) Fire

3. Quantitative analysis of accidents

3.1. Identification of accidents

In this study, following 6 types of accidents are chosen among 10 initiating events according to the probability of occurrence events and whether there is a concrete concept of design.

(1) Pipebreak owing to corrosion and thermal stress
(2) Break of a pipe that contains an inflammable gas
(3) Vapor pressure increase from a temperature control failure
(4) Bypass accident of a water supply pump
(5) Earthquakes
(6) Fire

3.2. Quantitative analysis of pipebreak owing to corrosion and thermal stress as an example

Event tree of pipebreak owing to corrosion and thermal stress is shown below Fig. 5.

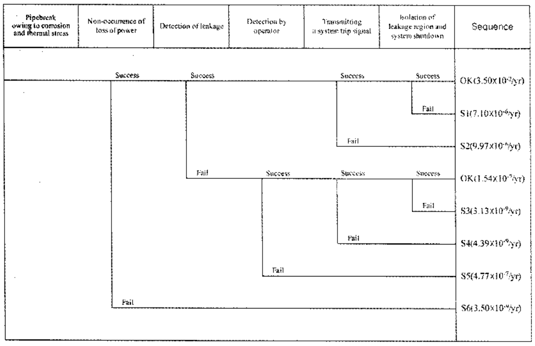

Fig. 5. Event tree of the pipebreak accident.

Because H_2 Plant is a kind of chemical plant, frequency of pipebreak is fixed by accident risk data from U.S. hazardous chemical facilities[5]. Data of failure rate is composed of a database for general chemical plant. And it refer to JAERI-Tech 2004-051, Nureg/CR-4550, IEEE Std 500-1984, WASH-1400, PSA report for Ulchin unit 5 and 6[6)10)].

As a result, the leakage probability of pipebreak is 1.0×10^{-5} which is lower than the important criteria of CDF of nuclear power plants(1×10^{-4}).

4. Conclusion

Initiating event identification use both formed techniques based on systematic and logical method and experienced techniques using former data[11] The MLD technique is a deductive tool using a top-down approach, which can do a formal and logical identification of initiating events. In this paper, initiating event identification of the IS process is carried out by using MLD. Also, 6 events are chosen and event tree method that is broadly used in order to evaluate safety of nuclear power plant is carried out for quantification. As a result, a sum of each event is 1.22×10^{-4} that is similar to the value of CDF of nuclear power plant(1×10^{-4}). But, plant that will be built later on requires much higher safety since it is operated in the condition of high pressure. Therefore, for the safety enhancement of hydrogen production facility, early detection after leakage and studies that enables to limit amount of leakage by block and removal are required. More over, studies of safety device and consideration are need in aspect of system design.

Also, 6 events are chosen and event tree method that is broadly used in order to evaluate safety of nuclear power plant is carried out for quantification.

It is considered to contribute to more safe development of hydrogen production facility by future study of sensitivity analysis, uncertainty analysis, interface risk assessment between high temperature gas supply system and hydrogen production facility using IS process, reflection plan of risk assessment result at the stage of IS process facility design and etc.

Finally, the result of this study is considered to contribute to improvement of safety in pre-conceptual design and also to the safety management.

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