

Preliminary Combustion Risk Analysis of H₂/CO mixture under Severe Accident using Le Chatelier's Law

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1. Introduction

During severe accident (SA), a large amount of hydrogen is possibly generated in reactor pressure vessel (RPV) and released into the containment atmosphere. The released hydrogen is flammable gas which can easily cause combustion reaction with very low ignition energy [1]. It was confirmed that hydrogen combustion can threaten the integrity of containment building through the Fukushima accident. After the accident, nuclear industries in many countries have put tremendous efforts to reduce such potential risk from the hydrogen explosion. i.e. PAR, igniters, etc. Research has been also actively conducted to predict and mitigate hydrogen risk.

On the other hand, another flammable gas carbon monoxide can be generated in the containment building by molten corium-concrete interaction (MCCI) after RPV failure. In fact, pure carbon monoxide is known not to explode in dry air because it needs chain carrier like hydrogen, steam or radical to initiate and sustain combustion reaction [2]. As hydrogen or steam usually exist in the containment atmosphere under SA, carbon monoxide has also a potential risk to explode. However, most of the precedent studies have mainly focused on hydrogen and paid relatively less attention to carbon monoxide [3].

Therefore, the objective of this study is to investigate combustion risk considering carbon monoxide as well as hydrogen for more realistic risk analysis. First, the combustion risk considering hydrogen only was conducted after RPV failure under station blackout (SBO) scenario using MELCOR 1.8.6 code. Next, the combustion risk of H₂/CO mixture was analyzed to estimate effect of carbon monoxide on combustion risk and compared with the former result.

2. Methodology

2.1. Severe accident sequence

Initial event was selected as SBO, which bears the highest transient probability to severe accident. All systems using electricity were assumed to fail during the accident. Operator actions for accident mitigation were also supposed not to be taken. Major accident sequences in SBO are summarized in Table 1.

As soon as the accident starts, the reactor receives trip signal at 0 h. Although the core is cooled by natural

convection, the pressure of primary system increases after steam generator dries out at 1.01 h. When even the core dries out, the fuel around cladding starts to react fast with steam. Due to the zircaloy oxidation, a large amount of hydrogen is produced. As PSV repeats open and close according to the RPV pressure, hydrogen is released from a pressurizer into the reactor drain tank (RDT). The rupture disk in RDT fails when the pressure difference between RDT inside and containment is greater than 0.827 MPa. Then the hydrogen is discharged into the containment atmosphere finally. After RPV failure at 3.75 h, the accident phase progresses into ex-vessel phenomenon. Carbon monoxide as well as hydrogen is additionally generated then due to MCCI. Thus, the combustion risk was investigated after RPV failure (3.75 h).

Table 1. Major accident sequences in SBO

Events	Time (h)
Accident start	0
Reactor trip	0
SG dry-out	1.01
PSV 1 st open	1.38
Core dry-out	1.49
Oxidation start	2.27
Cladding melt	2.65
UO ₂ melt	2.68
Relocation to lower head	2.83
RPV failure	3.75
SIT injection	3.81
SIT exhaust	4.00
MCCI start	4.96
Cavity dry-out	15.65

2.2 MELCOR input for the containment of OPR1000

The OPR1000 constituting a majority of operating nuclear power plants in Korea was selected as a reference NPP. In case of the containment of OPR1000, the detailed modeling was required because checking out the local concentration of combustible gases is challenging with a lumped parameter code. Therefore, a detailed MELCOR nodalization of the containment building OPR1000 was developed, based on the Shin-Kori unit 1&2 Final Safety Analysis Report (FSAR) as shown in Figure 1 [4].

The passive autocatalytic recombiners (PARs), which passively eliminates hydrogen, were modeled in lower area of dome (CV841, CV846) and third floor of

annulus (CV833, CV838) in the input. Although it is known that the PARs remove carbon monoxide as well, its recombination was not modeled in this study.

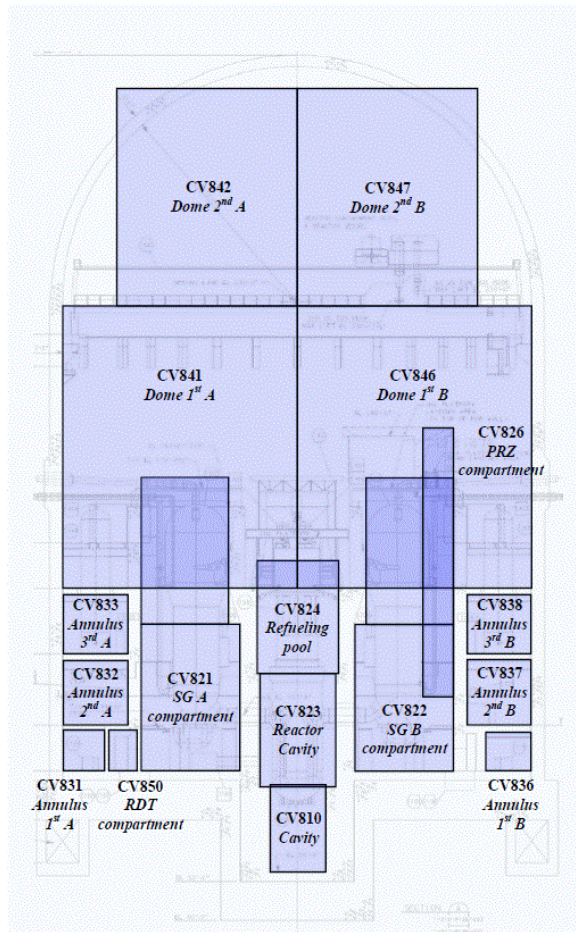


Figure 1. Control volumes for OPR1000 containment of the MELCOR nodalization [4]

2.3. Definition of Lower flammability limit

Lower flammability limit (LFL) is the limiting concentration of a combustible gas in air where flame propagates independently. It is usually experimentally-determined in air at specified temperature and pressure. If the concentration of combustible gas in a compartment is maintained lower than the value, a gaseous explosion can be prevented in the compartment. In the opposite case, the gas is regarded flammable, which means the compartment is classified as the combustible region.

Through a simple comparison of the concentration with the LFL, it can be easily judged whether the gas in the compartment is flammable. Therefore, when conducting combustion risk analysis considering only hydrogen, the LFL was used as a criterion. The criterion is also contained in MELCOR BUR package.

As the LFL of hydrogen in air at normal temperature and pressure is known as 4.1 vol. %, the flammability criterion of hydrogen can be described like **inequity (1)**.

$$X_{H_2} > 0.041 \quad (1)$$

2.4. Le Chatelier's law

Le Chatelier's law is the widely used method to estimate the LFL of binary or ternary fuel when the LFL and fraction of each flammable component are known. The LFL of the fuel mixture is defined like the **equation (2)** according to Le Chatelier's law. Where y_i is the fraction of the combustible species i in binary or ternary fuel and N is the number of combustible species in gas mixture.

$$\frac{1}{LFL_{mix}} = \sum_i^N \frac{y_i}{LFL_i} \quad (2)$$

For example, a mixture containing 20% hydrogen, 20% carbon monoxide and 60% air will have LFL value of 6.2 vol. %. It has been confirmed that the law is reasonably accurate for binary fuel mixtures containing hydrogen and carbon monoxide at normal temperature and pressure according to Jaimes, D. J. et al [5]. In addition, ASTM E681 also suggested when predicting the LFL of multi-component fuel in mixture.

Thus, the law was applied when judging the flammable of H_2/CO mixture during accident progress. The LFL of the binary fuel mixture calculated according to the law was required to confirm the flammability. In other words, if the summation of mole fraction of the combustible component is larger than the LFL of mixture like the **inequity (3)**, the mixture is considered flammable. Where X_i is mole fraction of the combustible species i .

$$X_{H_2} + X_{CO} > LFL_{mix} \quad (3)$$

However, both left and right-hand side terms of **inequity (3)** are variable as the gas composition changes during the accident progress. If assigning the **equation (2)** into the **inequity (3)**, it is modified like the **inequity (4)**, which fixes a right-hand side term at constant value.

$$X_{H_2} + X_{CO} \frac{LFL_{H_2}}{LFL_{CO}} > LFL_{H_2} \quad (4)$$

The right-hand side in **inequity (4)** is not the H_2/CO mixture concentration but rather the converted concentration of hydrogen weighted by the LFL of hydrogen and carbon monoxide. As the LFL of carbon monoxide is 12.5 vol. %, **inequity (4)** is also described as **inequity (5)** with the value assigned properly.

$$X_{H_2} + 0.328 X_{CO} > 0.041 \quad (5)$$

With the **inequity (5)**, the compartment vulnerable to H_2/CO mixture was classified. The left-hand side of the **inequity (5)**, is defined as the converted mixture concentration, in this study.

It is true that when carbon monoxide is considered in combustion risk analysis, the LFL of the mixture decrease. But through the simple transformation, converted carbon monoxide term was added in the left-hand side in **inequity (5)**, fixing the right-hand side term at constant hydrogen LFL. Therefore, although carbon monoxide was considered in the study, the concentration of flammable gases was compared with only the LFL of hydrogen, not the H₂/CO mixture.

3. Results and Discussion

As a result, 7 compartments were vulnerable to the combustion risk whether carbon monoxide is included or not in the analysis. But the flammable duration time and its number increased in 3 compartments due to additional consideration of carbon monoxide; cavity, cavity door and regenerative heat exchanger room. In this section, the combustion risk was assessed for these three flammable compartments.

3.1 Flammability in Cavity (CV810)

Figure 2 shows mole fraction of hydrogen, carbon monoxide and mixture calculated according to Le Chatelier's law in cavity. After RPV fails at 3.75 h, hydrogen is released into the containment building. The mole fraction of hydrogen increased rapidly to 0.20 accordingly. But it reduced rapidly soon and repeated increase and decrease again from 3.76 to 4.67 h due to gas flow from RPV. As the mole fraction of hydrogen was greater than the LFL then, the cavity is possibly classified as the compartment vulnerable to hydrogen for 0.91 h.

However, water in cavity can extinguish the fire caused by combustion easily. When the cavity was flooded, the region was excluded on hydrogen risk analysis conducted in FSAR. Thus, the existence of water should be checked at the same time. **Figure 2** also describes the water level in cavity. It increases rapidly due to cavity flooding after RPV failure and decreases gradually due to evaporation. Cavity dries out at 15.65 h finally. In conclusion, the hydrogen risk was not identified from 3.76 to 4.67 h due to water.

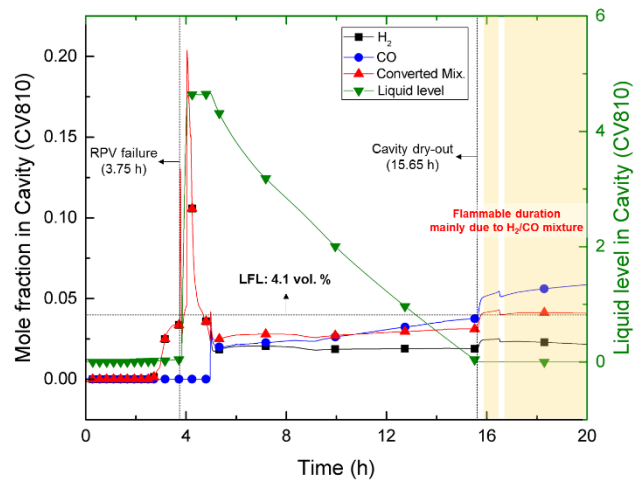


Figure 2. Mole fraction of flammable gases and mixture and water level in cavity (CV810) under SBO scenario

While hydrogen mole fraction maintains a relatively constant value after MCCI, mole fraction of carbon monoxide increases rapidly at 4.96 h due to MCCI and gradually hereafter. To consider the effect of carbon monoxide on the risk estimation, the concentration of mixture was calculated according to Le Chatelier's law. As the term is composed with the sum of hydrogen and converted carbon monoxide mole fraction, it has the same value with hydrogen until RPV fails at 3.75 h. After carbon monoxide starts to be generated, it is maintained larger than hydrogen due to the contribution of carbon monoxide.

Therefore, there exist three flammable duration times when it exceeds the LFL, which cannot be checked out with hydrogen only. The first duration interval is from 4.98 to 4.99 h, for 30 s. As the cavity is filled with water then, it was concluded that it is not vulnerable to combustion. Another interval is from 15.86 to 16.51 h, for 2340 s and from 17.16 to 19.61 h, for 8820 s as shown in **Figure 3**. As no water exist then, the cavity can be regarded as the compartment vulnerable to H₂/CO mixture for the time.

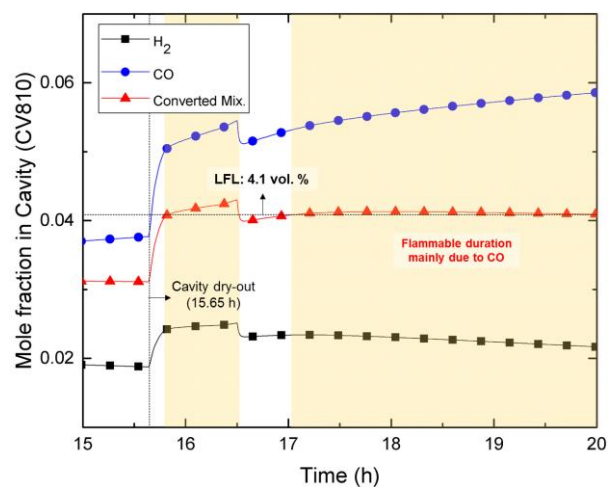


Figure 3. Mole fraction of flammable gases and mixture in cavity (CV810) after cavity dry-out under SBO scenario

3.2 Flammability in Cavity door (CV812) and Regenerative heat exchanger room (CV825)

Figure 4 describes mole fraction of flammable gases and mixture in cavity door and heat exchanger room. Although there is a slight difference in maximum mole fraction, they show similar variation with **Figure 2**.

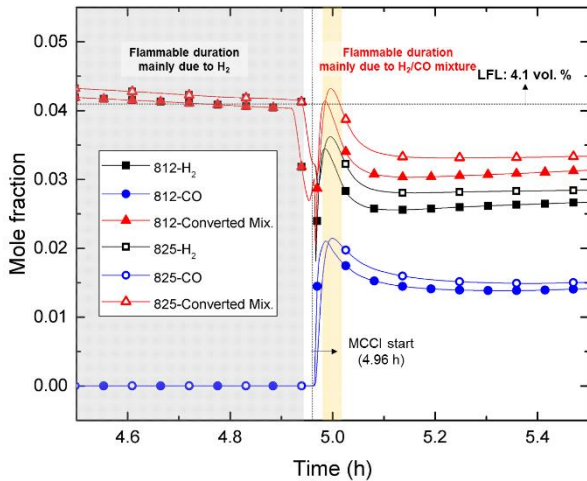


Figure 4. Mole fraction of flammable gases and mixture in cavity door (CV812) and regenerative heat exchanger room (CV825) under SBO scenario

As yellow region in **Figure 4** shows, the regenerative heat exchanger room was identified flammable around at 5 h, for 90 s. Although the duration cannot be confirmed with the criterion considering hydrogen only, the value excess of LFL is not so large and lasts a very short time. In addition, the flammable duration time due to the H₂/CO mixture is not largely different from that to hydrogen. This tendency is similar for cavity door.

4. Conclusions

In this research, hydrogen risk analysis was conducted for OPR1000 after RPV failure under the SBO scenario using the MELCOR 1.8.6 code. In addition, combustion risk including carbon monoxide as well as hydrogen was also predicted for the conservative analysis with LFL. As a result, the cavity was identified as the most vulnerable compartment to H₂/CO mixture after RPV failure. Major findings and future works can be summarized as below.

- (1) In hydrogen combustion risk analysis, 7 combustible compartments were identified as vulnerable to the explosion under SBO scenario.
- (2) In the risk analysis of H₂/CO mixture, 7 compartments were regarded combustible as well. However, not only the flammable duration time increased, but also its number were additionally found in 3 compartments: cavity, cavity door and regenerative heat exchanger room. The cavity was considered

the most vulnerable to H₂/CO mixture among them.

- (3) In most compartments in containment building, it seems sufficient to assess the combustion risk with hydrogen only. However, in case of the cavity, where the carbon monoxide is mainly generated, it is noted that the analysis should be conducted with H₂/CO mixture.
- (4) The LFL used in this research was determined at NTP. But it is known that it depends on ambient thermodynamic conditions. As temperature and pressure in containment under SA increase above 100 °C and 4 atm, the LFL reflecting ambient conditions should be applied for more reliable results. In a future work, the LFL calculated using CNAFT model developed by Jeon et al. will be used in the risk analysis [6].
- (5) Although PARs eliminate carbon monoxide as well, only hydrogen recombination was modeled in this study. If carbon monoxide recombination reaction is modeled, the combustion risk of H₂/CO mixture in cavity may be reduced. Therefore, as a future work, combustion risk considering carbon monoxide elimination by PAR needs to be conducted for more reliable results.

REFERENCES

- [1] Karim, G. A. (2003). Hydrogen as a spark ignition engine fuel. *International Journal of Hydrogen Energy*, 28(5), 569-577.
- [2] Cohen, N. (1992). "Flammability and explosion limits of H₂ and H₂/CO: a literature review" (No. TR-92 (2534)-1). AEROSPACE CORP EL SEGUNDO CA TECHNOLOGY OPERATIONS.
- [3] Kumar, R. K. *et al.* (2000). Carbon monoxide-hydrogen combustion characteristics in severe accident containment conditions. Organisation for Economic Co-operation and Development, Paris, France, Report No. NEA/CSNI
- [4] Kim, N. K. *et al.* (2018). "Systematic hydrogen risk analysis of OPR1000 containment before RPV failure under station blackout scenario". *Annals of Nuclear Energy*, 116, 429-438.
- [5] Jaimes, D. J. *et al.* (2017). Determination of lower flammability limits of mixtures of air and gaseous renewable fuels at elevated temperatures and pressures (Doctoral dissertation, UC Irvine).
- [6] Jeon, J. *et al.* (2018). Development of Calculated Non-Adiabatic Flame Temperature Model to Predict Flammability Limits of H₂-Air-Diluent Mixtures Based on Heat Transfer Mechanism