

2.11 Passive Auto-Catalytic Recombiners

Passive autocatalytic recombiners (PARs) are a passive hydrogen removal device for used in post-accident conditions that chemically combine hydrogen and oxygen gas molecules on catalytic surfaces into water vapor. Each PAR consists of an open-ended stainless-steel box with catalyst-coated elements inside, and a cover to protect the elements from water sprays [Reference 34]. The catalytic reaction can take place at ambient temperature and significantly low hydrogen concentration (~1 vol.%). The resulting reaction heat induces a chimney flow which provides self-start and self-feeding of the device. These properties make PARs a passive safety device. Typical removal rates per PAR unit are in the order of 60 m³ hydrogen per hour, which correlates to a heat contribution of approximately 180 kW [Reference 45]. The basic technical ability of PARs to reduce the amount of hydrogen in the containment atmosphere has been proven in several studies over the last two decades Blanchat [Reference 4], and OECD/NEA [Reference 39]

According to Reineke [Reference 45], PARs have a quick start. However, water deposited on the catalyst as well as other air-borne substances—which are expected to be numerous during a severe accident—may slow down the initial startup process. The catalysts used are not strictly selective for hydrogen and oxygen, and consequently may influence or may be influenced by atmospheric components. Recent research by (OECD/NEA, 2010) also indicates that PAR operation can dissolve previously formed stratified layers prior to PAR operation. There is also a possibility of local combustion initiated by hot catalyst sheets at high hydrogen concentrations leading to a pressure rise inside the containment and significantly change the composition and thermal conditions of the containment atmosphere.

The potential poisoning effect of PAR was also investigated by the OECD research (OECD/NEA, 2010). As described by Reineke (2012), PAR was exposed to excessive aerosol concentrations of insoluble tin oxide (SnO₂) representing insoluble aerosols, highly hygroscopic and sticky lithium nitrate (LiNO₃) solution droplets, steam and iodine, a potential catalyst poison. The results showed that even under such challenging conditions, PAR recombination efficiency remained in the range of 50-70 %. This is comparable to the results of the THAI HR series with similar thermal-hydraulic conditions, but without aerosols and iodine. Also, the onset of recombination occurred at hydrogen concentrations comparable to corresponding tests from the HR series. No major negative effects of aerosols and/or iodine on PAR performance could be observed.

There was an attempt to define the failure probability of PARs among Probabilistic Risk Analysis (PRA) engineers working in new nuclear plant designs. But it has been difficult to find a failure mode for PARs. As a general rule supported by experiments, however, these PARs do not fail. There are no moving parts whatsoever. The natural convection of containment forces air through the slats and the rest is a chemical process.

2.12 Relationship to Containment Failure Mechanisms

Hydrogen combustion could be a potential threat to containment integrity because of the increase in pressure and temperature during the event. The pressure has two components; the dynamic load and the static load. For slow deflagrations, the dynamic load is zero. For accelerated deflagrations there is a continuous increase in dynamic pressure. Theoretical predictions of detonation pressures

are shown in Figure 2-12. The static pressure load on the containment is bounded by the AICC pressure. The actual static pressure is generally lower due to heat transfer to structures during the event and in some cases due to incomplete combustion. The dynamic load during a detonation lasts only for a period of milliseconds and may be unable to cause containment failure, though equipment damage may still be possible. Because flames may accelerate during a deflagration, equipment damage may occur due to a local impulse loading. The deflagration temperature load is rather insignificant, in general, because it only lasts from tens of seconds to a few minutes, with a brief peak and sharp decay. An impulse (integral of pressure over time) analysis is required for dynamic pressures. The existence of a combustion event does not automatically imply containment failure. The combustion pressure must be compared against a containment failure criteria. The containment failure criteria should include the pressure versus impulse curves for the containment failure modes and the maximum pressure and impulse available from combustion, if detonation impacts need to be evaluated.

3.0 Methodology

The methodology for determining the potential and the effect of hydrogen combustion within the containment consists of:

1. Evaluation of the impact of non-detonative slow combustion on containment overpressure
2. Evaluation of local hydrogen accumulation beyond 10% in volume in the vicinity of hydrogen release sources
3. Evaluation of the potential for local and global occurrence of DDT.

3.1 Methodology for Non-Detonative Slow Combustion Evaluation

The methodology for the evaluation of the potential of containment failure due to non-detonative slow combustion of hydrogen is to compute the AICC pressure resulting from burning a containment-wide uniformly mixed hydrogen-air-steam mixture containing an equivalent amount of hydrogen as would be generated from 100% fuel clad metal-water reaction during an accident and compare its values to the ultimate pressure capacity of the containment. The AICC pressure is the bounding combustion pressure when hydrogen in the containment burns in a slow deflagration mode for any given initial conditions.

The computed AICC pressure is higher if the initial preborn pressure is higher. The highest AICC pressure is achieved when the pre-burn condition corresponds to the condition of a gaseous mixture with highest steam mole fraction that is barely, but still, flammable. On the flammability limit curves for hydrogen-air-steam mixtures, this point would correspond to the farthest tip of the curves along the steam axis. If the containment can survive the highest AICC pressure, the containment will survive any slow burns at all possible preburn conditions. Then, the containment would not be vulnerable to overpressure failure due to non-detonative slow deflagrations.

3.2 Methodology for Local Hydrogen Accumulation Evaluation

A containment-wide uniformly mixed hydrogen-air-steam mixture assumed in the calculation of AICC pressure would normally not be achieved during a progression of severe core melt accident in which a rapid hydrogen release is occurring from inside the RCS to the compartment where the release point is located. The rapid hydrogen release can lead to a significant local accumulation of hydrogen with concentrations much higher than other downstream compartments. Hence, the issue here is whether the local hydrogen accumulation is severe enough to lead to the conditions favorable to the occurrence of local DDT.

The methodology for the evaluation of local hydrogen accumulation beyond 10% in volume is to use the MAAP4 code with sufficient nodes representing compartments of the containment to analyze various "hydrogen" accident scenarios that represent the entire spectrum of hydrogen-significant accident sequences. Here, the 10% hydrogen volume fraction is taken as a criterion for determining whether the accumulation should be further considered for DDT evaluation. The 10% hydrogen volume fraction is the value identified in the USNRC regulation as the upper bound for a uniformly distributed hydrogen concentration during and following an accident that releases an equivalent amount of hydrogen as would be generated from a 100% fuel clad metal-water reaction. The result from this evaluation is not an end by itself, but rather is used as an input to the DDT evaluation.

3.3 Methodology for DDT Evaluation

The occurrence of DDT can potentially produce significant dynamic pressure loads at least 9 to several tens times initial pressure (Figure 2-12). Comparing the possible range of DDT dynamic pressure magnitude to the ultimate pressure capacity of the containment usually leads one to the conclusion of high probability of containment failure. Hence, for the DDT evaluation, it is considered reasonably sufficient (based on the current knowledge of DDT) to quantitatively evaluate whether the conditions that support the onset of DDT exist during the progression of all possible accident sequences without having to estimate the associated dynamic pressure.

The methodology for the evaluation of the potential of DDT is based on the method proposed by the expert group in the "OECD State of the Art Report (SOAR) on Flame Propagation and Deflagration-to-Detonation Transition in Nuclear Safety" issued in 2000 [Reference 6]. There are two main criteria established by the SOAR; the flame acceleration (FA) criterion also known as "the σ criterion," and the detonation cell width criterion that is also known as "the 7λ criterion." The two criteria are considered necessary conditions for DDT and are described in Sections 3.3.1 and 3.3.2 below.

3.3.1 Criterion for Flame Acceleration

The criterion for flame acceleration according to the SOAR [Reference 6] is based on the observation of a large amount of experimental data that correlates the expansion ratio of burned gas mixture to the occurrence of flame acceleration. It was found that there is a (minimum) critical value for the expansion ratios (later on to be referred to as σ_{critical}) required to support flame acceleration. The critical expansion ratio is a function of temperature. The critical expansion ratio decreases with increasing temperatures. This is one of the necessary conditions for DDT purely based on the thermodynamic properties of the mixture. There is no geometric factor in this criterion. The criterion can be stated as follows:

- 1) If $\sigma_{index} < 1$, no FA is possible
(3-1)
- 2) If $\sigma_{index} \geq 1$, FA is possible
(3-2)

Here, σ_{index} is defined as the ratio of the expansion ratio σ to the $\sigma_{critical}$

$$\sigma_{index} = \frac{\sigma(\bar{X}_{H_2}, \bar{X}_{H_2O}, \bar{X}_{O_2}, T)}{\sigma_{critical}(\bar{X}_{H_2}, \bar{X}_{O_2}, T)}$$

(3-3)

The expansion ratio σ is defined as the ratio of density of unburned gases to the density of burned gases. The expansion ratio is a function of averaged concentrations of hydrogen (\bar{X}_{H_2}), steam (\bar{X}_{H_2O}) and oxygen (\bar{X}_{O_2}), and temperature (T) of the compartment. On the other hand, the critical expansion ratio is a function of temperature for lean mixtures and is constant for rich mixtures as shown in Table 3-1 below.

Table 3-1 lists values of critical expansion ratios [Reference 6] that were used in the GASFLOW code [Reference 67] developed by FZK of Germany. These values can be fitted by a quadratic equation (in Table 3-2) that was developed by AECL and used in their DDTINDEX code [Reference 10].

Table 3-1 Critical Expansion Ratio as a Function of Initial Temperature

Temperature(K)	$\sigma_{critical}$	
	$X_{H_2} < 2X_{O_2}$	$X_{H_2} > 2X_{O_2}$
300	3.75	3.75
400	2.80	3.75
500	2.25	3.75
600	2.10	3.75

Table 3-2 Fitting Equation for Critical Expansion Ratio [Reference 10]

Temperature(°C)	$\sigma_{critical}$	
	$X_{H_2} < 2X_{O_2}$	$X_{H_2} > 2X_{O_2}$
T	$3.75 - 0.0115(T - 25) + 0.00002(T - 25)^2$	3.75

As an example for a typical range of the values of the expansion ratios as a function of concentrations and temperatures for hydrogen-steam-air mixtures, Figure 3-1 shows expansion ratios calculated using STANJAN code, a well-known chemical equilibrium code developed at Stanford University [Reference 46]. Also shown is the critical expansion ratios above which flame acceleration is possible. It can be seen that at 300 K temperature, a gaseous mixture with steam not greater than 40% would meet the FA condition with hydrogen concentration in the range of 12-13%. At 400 K, the required hydrogen concentrations reduce to 10-11%.

3.3.1.1 MAAP4 Calculations of Expansion Ratios

An expansion ratio is not a variable in the MAAP4 code, but it can be calculated from other variables in the MAAP4 code. The expansion ratio is defined as the ratio of the density of unburned gas mixture (ρ_u) to the density of burned gas mixture (ρ_b);

$$\sigma = \frac{\rho_u}{\rho_b} \quad (3-4)$$

If one writes an ideal gas equation for an initial burned gas mixture, and then writes another ideal gas equation for the burned gas mixture at the same pressure as the unburned gas, i.e. undergoing an isobaric process, the density ratio derived from these two equations becomes:

$$\frac{\rho_u}{\rho_b} = \frac{T_b}{T_u} \frac{n_b}{n_u} \quad (3-5)$$

where T_b is flame temperature, T_u is unburned gas temperature, n_b is number of moles of gases after burn, and n_u is number of moles of gases before burn.

On the other hand, the AICC pressure P_{AICC} is a calculated quantity in MAAP4 and it is calculated from:

$$P_{AICC} = P_0 \frac{T_{AICC}}{T_u} \frac{n_b}{n_u} \quad (3-6)$$

Multiplying and dividing the right hand side of Eq. 3-6 with T_b , one obtains:

$$P_{AICC} = P_0 \frac{T_{AICC}}{T_b} \frac{T_b}{T_u} \frac{n_b}{n_u} \quad (3-7)$$

The right hand side of Eq. 3-5 can be seen as part of the right hand side of Eq. 3-7. Hence by substituting part of the right hand side of Eq. 3-7 with Eq. 3-5, the expansion ratio is then given by:

$$\sigma = \frac{\rho_u}{\rho_b} = \frac{P_{AICC}}{P_0} \frac{T_b}{T_{AICC}} \quad (3-8)$$

All four variables on the right hand side of Eq. 3-8 are MAAP4 variables. Hence, the expansion ratio can be calculated simultaneously in MAAP runs by defining the following term for a containment node in the input:

$$\sigma = \frac{\rho_u}{\rho_b} = \frac{PAICC(I) TFLRB(I)}{PRB(I) TAICCB(I)} \quad (3-9)$$

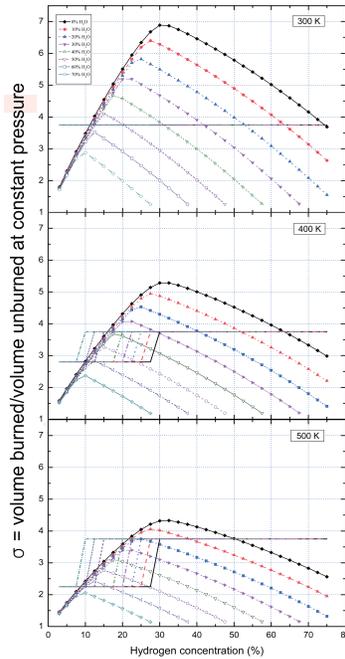


Figure 3-1 Example of Expansion Ratio Calculated by STANJAN Code

3.3.2 Criterion for Deflagration-to-Detonation Transition Potential

For the potential of DDT, the “7λ criterion” proposed in the SOAR [Reference 6] is used for evaluation. This criterion represents another necessary but not sufficient condition in addition to the flame acceleration criterion discussed in Section 3.3.1. The criterion requires that the characteristic length of the compartment is greater than 7 times the detonation cell width. This criterion is generally in good agreement with experimental data over a wide range of scales and mixture compositions [Reference 6].

The 7λ criterion can be stated as follows:

1) If $7\lambda_{index} < 1$, DDT not possible (3-10)

2) If $7\lambda_{index} \geq 1$, there is possibility of DDT (3-11)

where the $7\lambda_{index}$ is a characteristic length index defined as the characteristic length divided by 7 times averaged detonation cell width λ as shown below:

$$7\lambda_{index} = \frac{\text{Characteristic Dimension}}{7 \times \text{Averaged Detonation Cell Width}} = \frac{L}{7\lambda} \quad (3-12)$$

Overall DDT Criteria

Since flame acceleration is a prerequisite to the onset of DDT, the flame acceleration criterion represented by σ_{index} in Eq. 3-2 must also be satisfied. This criterion implicitly implies that the mixture composition meets the downward flammability limits to support flame propagation in all directions.

Hence the overall DDT criteria to be used for this analysis require the following 2 criteria - 7λ criterion, and flame propagation criterion, to be satisfied simultaneously;

- 1) DDT condition - possible

$$\text{DDT index} = 7\lambda_{\text{index}} \times \sigma_{\text{index}} \geq 1 \quad \text{if } 7\lambda_{\text{index}} \geq 1 \text{ and } \sigma_{\text{index}} \geq 1 \quad (3-13)$$

- 2) DDT condition - not possible

$$\text{DDT index} = 0 \quad \text{if one of 2 conditions not satisfied} \quad (3-14)$$

The DDT index is used in the MAAP analysis to indicate whether DDT condition is possible or not possible by using a value of either 0 or ≥ 1 as an indicator.

3.3.2.1 Correlation for Detonation Cell Width

Detonation cell width is a length that characterizes the reactivity of the mixture. A smaller detonation cell width indicates that the mixture is more reactive. The detonation cell width can be calculated with an empirical correlation (function B67p) presented in Appendix D of the SOAR report [Reference 6] and is shown in Equation (3-15). According to this equation, the detonation cell width can be calculated with just four input parameters (i.e., hydrogen concentration, steam concentration and initial temperature and pressure). The calculation of this correlation is simple and can be conveniently applied in the MAAP include file for MAAP4 runs. The correlation (which is also used in the GASFLOW code) is adopted for this analysis and is expressed as follows:

$$\log_{10}(\lambda) = \left[a - m + \left[\frac{b}{(A - k/T)^f} + h \cdot (A - g \cdot T)^2 + i \cdot (A - g \cdot T) \right] \cdot \left[1 + d \cdot C + e \cdot T \cdot C^2 \right] \cdot \frac{j}{T} \right] \cdot [P - c] \cdot \left[\frac{1}{0.1 - c} + n \cdot (P - 0.1) \right] + m \quad (3-15)$$

where A is dry hydrogen volume fraction of hydrogen-steam-air mixture (vol%), i.e.,

$$[H_2]_{\text{dry}} = \frac{[H_2]}{[H_2] + [\text{air}]} \quad (3-16)$$

- T is initial temperature (K),
- C is steam volume fraction (vol%),
- P is initial pressure (MPa),
- λ is detonation cell size (cm),

and various constants in the correlation:

a	-1.13331E+00
b	4.59807E+01
c	-1.57650E-01
d	4.65429E-02
e	3.59620E-07
f	9.97468E-01
g	-2.66646E-02
h	8.74995E-04
i	-4.07641E-02
j	3.31162E+02
k	-4.18215E+02
m	2.38970E+00
n	-8.42378E+00

Examples of typical range for the values of detonation cell width are shown in Figure 3-2 and Figure 3-3 where both correlation results are compared with experiment data. Figure 3-2 shows detonation cell width as a function of hydrogen concentration for a mixture with no steam at various temperatures. The detonation cell width becomes smaller when the temperature is higher at the condition with same hydrogen and steam concentrations. Figure 3-3 shows that at any fixed hydrogen concentration, the detonation cell width increases with increasing steam concentrations. As shown in Figure 3-4, maps of the constant cell widths at 2 different pressures plotted in $[H_2]_{dry}$ - $[H_2O]$ plane using Eq. 3-15 show that the detonation cell width is not sensitive to an increase in pressure.

3.3.2.2 Other Correlation for Detonation Cell Width

There is another method for calculating detonation cell width reported in the SOAR [Reference 6]. This method based on chemical kinetics was suggested by Gavrikov of Russian Research Center (RRC). It was developed from the Zeldovich-von Neumann-Döring (ZND) model for detonation. It is a semi-empirical approach to correlate the relation between a characteristic reaction zone width (δ) and the detonation cell width (λ). The Gavrikov correlation is as shown below:

$$\log_{10}(\lambda/\delta) = Y \cdot (a \cdot Y - b) + X \cdot [c \cdot X - d + (e - f \cdot Y) \cdot Y] \\ + g \cdot \ln(Y) + h \cdot \ln(X) + Y \cdot (i/X - k \cdot Y/X^m) - j \quad (3-17)$$

where, $X = E_a / RT_{ps}$, $Y = T_{vn} / T_0$, in the range of $3 < X < 16$ and $1.5 < Y < 8$, and other constants are

a	-0.007843787493
b	0.1777662961
c	0.02371845901

d	1.477047968
e	0.1545112857
f	0.01547021569
g	1.446582357
h	8.730494354
i	4.599907939
j	7.443410379
k	0.4058325462
m	1.453392165

It is not easy to apply the Gavrikov correlation. Some parameters are required to be pre-calculated with chemical kinetic theory. Gavrikov used the CHEMKIN-II code (the version of Prof. J. Shepherd of Caltech) for kinetic pre-calculations. This code, which can be executed in a command window, was developed with two types for hydrogen-steam-air mixture and C-H-O-N mixture respectively. The Gavrikov method is not used here because of its complexity. Its example calculation of detonation cell width are compared with results from Eq. 3-15 for standard air-hydrogen mixture ($T=375$ K, $p = 1$ bar) in Figure 3-5. The two correlations give slightly different results. For the same gas compositions, Eq. 3-15 give smaller detonation cell widths than the Gavrikov correlation. Hence the use of Eq. 3-15 to determine detonation widths in the 7λ criterion is a conservative approach.

3.3.2.3 Detonation Cell Width for CO

The correlation for detonation cell width using Eq. 3-15 is only valid for mixtures composed of air, hydrogen and steam. It is not applicable to gaseous mixtures in the containment during a severe accident involving generation of CO and CO₂ from Molten Core Concrete Interaction (MCCI). However, in order to estimate detonation cell widths for such mixtures, a conservative approach may be taken by assuming one mole of CO is as reactive as one mole (or a fraction of a mole) of hydrogen in the correlation of Eq. 3-15 while the presence of CO₂ would be treated as if it is nitrogen. A one-to-one mole assumption is believed to be a very conservative approach since CO is not as reactive as H₂. No detonation could be initiated in stoichiometric CO-O₂ mixture [Austin & Shepherd, 2000]. The lower flammability limit for CO in air is much higher than that of H₂, i.e. 12.5% for CO vs. 4% for H₂ [Reference 35].

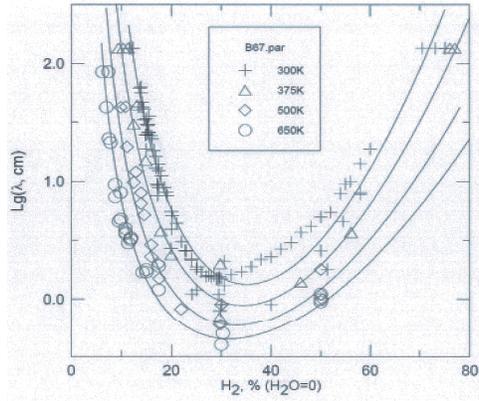


Figure 3-2 Calculation Results of Detonation Cell Width from Eq. 3-15 vs. Experimental Data as a Function of Hydrogen Concentrations at Various Temperatures [Reference 6]

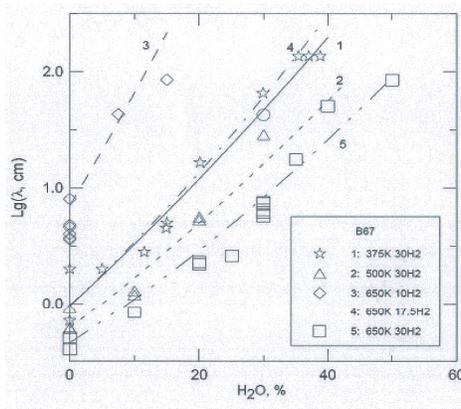


Figure 3-3 Calculation Results of Detonation Cell Width from Eq. 3-15 vs. Experimental Data as a Function of Steam Concentrations at various hydrogen concentrations [Reference 6]

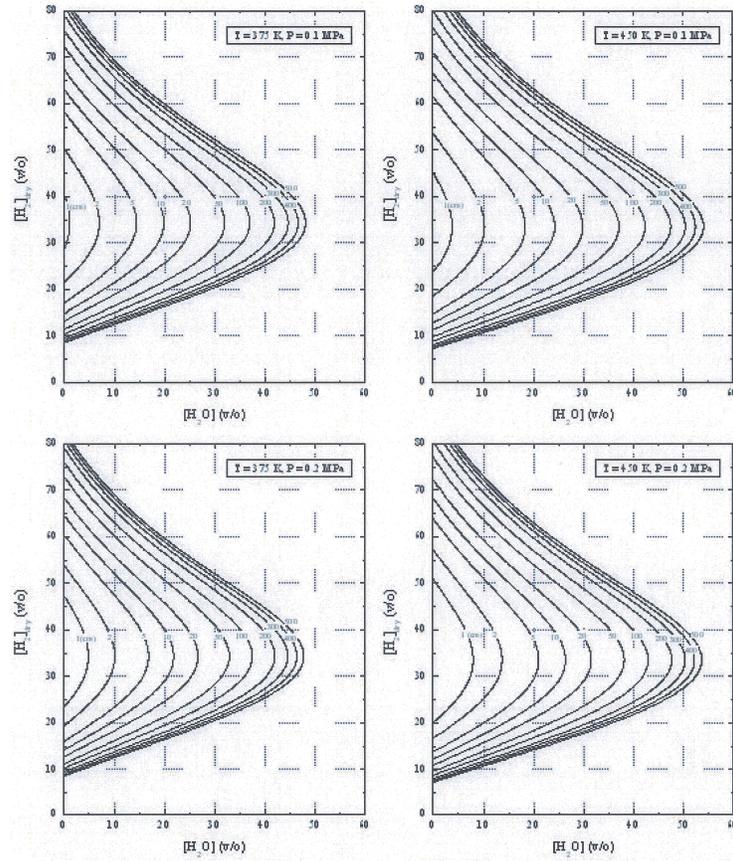


Figure 3-4 Detonation Cell Width (cm) plotted in $[H_2]_{dry}$ - $[H_2O]$ Plane using Eq. 3-15