NIST Technical Note
NIST TN 2385

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https://doi.org/10.6028/NIST.TN.2385

NIST NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY
U.S. DEPARTMENT OF COMMERCE

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September 2026

U.S. Department of Commerce
Howard Lutnick, Secretary

National Institute of Standards and Technology
Arvind Raman, NIST Director and Under Secretary of Commerce for Standards and Technology

NIST TN 2385
September 2026

Publication History
Approved by the NIST Editorial Review Board on 2025-09-15

How to Cite this NIST Technical Series Publication
Jiann C Yang (2026) On Concrete Spalling – BLEVE or No BLEVE. (National Institute of Standards and Technology, Gaithersburg, MD),NIST Technical Note (TN) NIST TN 2385. https://doi.org/10.6028/NIST.TN.2385

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Abstract

The BLEVE (boiling liquid expanding vapor explosion) hypothesis on fire-induced spalling of concrete was examined using superheated liquid theory. Water trapped within a heated interior region of concrete was used as an idealized system to determine the thermodynamic conditions of water that subsequently would lead to potential occurrence of a BLEVE event. The thermodynamic states that favor BLEVE was identified and delineated in the P–T phase diagram of water and was shown to be highly constrained to narrow ranges of temperature and the amount of water trapped (fill density) in the heated region.

Keywords

Concrete; fire; spalling; superheated liquid; thermodynamics.

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Author Contributions

Author 1: Conceptualization, Methodology, Formal analysis, Writing – Original draft preparation.

1. Introduction

When concrete is exposed to a fire, thermal energy from the fire is transported from the exposed concrete surface to the concrete interior. As the concrete interior is heated, its temperature increases, causing the free water (moisture) in the concrete starts to evaporate, and the resulting water vapor diffuses towards the heated concrete surface where it is further heated and towards the unheated interior regions where it condenses and fills the pores within the concrete. When the interior temperature is high enough, the dehydration of chemically bound water also occurs and generates more water vapor. As this heating process continues, a sudden and at times violent ejection of pieces of surface layers of the heated concrete, termed spalling, could occur. The propensity for spalling depends on many parameters including how the concrete is heated (heating rate), concrete strength and constituents, how concrete is cured, and other factors. Majority of research literature has indicated that spalling results from a highly coupled thermo-hydro-mechanical coupled process occurring in concrete exposed to high temperatures (e.g., fires). Many excellent review articles on various theories and hypotheses that had been used to partially explain the mechanisms of concrete spalling can be found in the literature [1–7].

One of the hypotheses on spalling was attributed to Ichikawa [8], who in passing suggested that the spalling of concrete had been the result of a BLEVE (boiling liquid expanding vapor explosion) event[1]. In this study, superheated liquid theory is used to re-examine Ichikawa's BLEVE hypothesis. Specifically, this study only seeks to answer the question: What are the thermodynamic conditions of the water trapped in a continuously heated interior region of concrete that would potentially trigger a BLEVE event? An idealization is made in the thermodynamic analysis in that there is an interior region of concrete where water is initially trapped. In other words, the amount of water (either liquid, vapor, or liquid-vapor) in the heated region is fixed and is treated as a closed system. How the water is generated, transported, and eventually accumulated in the region within the heated concrete is not the focus of this study.

[1] The AIChE Center for Chemical Process Safety defines BLEVE as "A type of rapid phase transition in which a liquid contained above its atmospheric boiling point is rapidly depressurized, causing a nearly instantaneous transition from liquid to vapor with a corresponding energy release." https://www.aiche.org/ccps/resources/glossary

2. Thermodynamic Limit of superheat

In a series of seminal papers by Reid [9–14], he postulated that superheated liquid theory could be used to explain BLEVE. A superheated liquid is a meta-stable liquid that exists at temperatures beyond its saturation boiling point at the same pressure. These liquids are meta-stable with respect to small thermodynamic perturbations.

From the classical thermodynamic stability theory [15], the metastable state is defined on a P–V phase diagram as

$$\left.\frac{\partial P}{\partial V}\right|_{T,n} = 0 \tag{1}$$

where P, V, T, and n are pressure, volume, absolute temperature, and amount of substance, respectively. If an equation of state (EOS) for the fluid of interest is available, the thermodynamic limit of superheat (T_{sl}), defined as the temperature at which Eq. (1) is satisfied, can be calculated.

Note that one can also estimate the limit of superheat based on kinetic theory models [16]. Since the thermodynamic limit of superheat is based on intrinsic thermodynamic stability criteria, it is a theoretical limit. Therefore, limits of superheat calculated using kinetic theory models are lower than their thermodynamic counterparts [9,16].

For the present discussion, it suffices to use the thermodynamic limits of superheat to explain the potential occurrence of BLEVE since they can be easily calculated using an EOS. The Peng-Robinson EOS [17] was used to obtain the thermodynamic limit of superheat of water as a function of pressure. This EOS has the following form:

$$P = \frac{RT}{v - b} - \frac{a}{v(v+b) - b(v-b)} \tag{2}$$

where $v = V/n$ is the molar volume, R is the universal gas constant, $a(T) = a(T_c) \times a(T_r, w)$, ω is the acentric factor, T_c is the critical temperature, $T_r = T / T_c$, $a(T_c) = (0.45724 R^2 T_c^2) / P_c$, P_c is the critical pressure, $\sqrt{a} = 1 + k\left(1 - \sqrt{T_r}\right)$, $k = 0.37464 + 1.54226w - 0.26992w^2$, and $b(T) = b(T_c) = 0.07780 RT / P_c$.

Taking the partial derivative of Eq. (2) with respect to V at constant T and n and using the stability criterion described in Eq. (1), one can solve for T, which is the thermodynamic limit of superheat (T_{sl}), and obtain

$$T_{sl} = \frac{2a(v+b)(v-b)^2}{R(v^2 + 2bv - b^2)^2} \tag{3}$$

The following iterative procedure is used to calculate T_{sl} at a given P:

1. Guess a $T_{\mathrm{sl,guessed}}$.
2. Solve for v using Eq. (2) with $T_{\mathrm{sl,guessed}}$ and P.
3. Calculate T_{sl} using Eq. (3).
4. Check if $\left|T_{\mathrm{sl}} - T_{\mathrm{sl,guessed}}\right|$ is less than the user-defined convergence criteria. If not, assign $T_{\mathrm{sl,new}} = (T_{\mathrm{sl}} + T_{\mathrm{sl,guessed}}) / 2$.
5. Go to Step 2 and repeat until the convergence criteria has been reached.

The critical properties and the acentric factor of water used in the calculations were obtained from the NIST REFPROP database [18]: T_c = 641.7 K, P_c = 22.064 × 10^6 Pa, ρ_c = 322 kg/m^3, and ω = 0.3443. The calculated thermodynamic limits of superheat T_{sl} as a function of pressure are plotted together with the water vapor-pressure curve (data also taken from REFPROP) in Fig. 1. Superheated meta-stable liquid water exists in the region between the vapor pressure curve and the locus of the limits of superheat (the so-called spinodal curve).

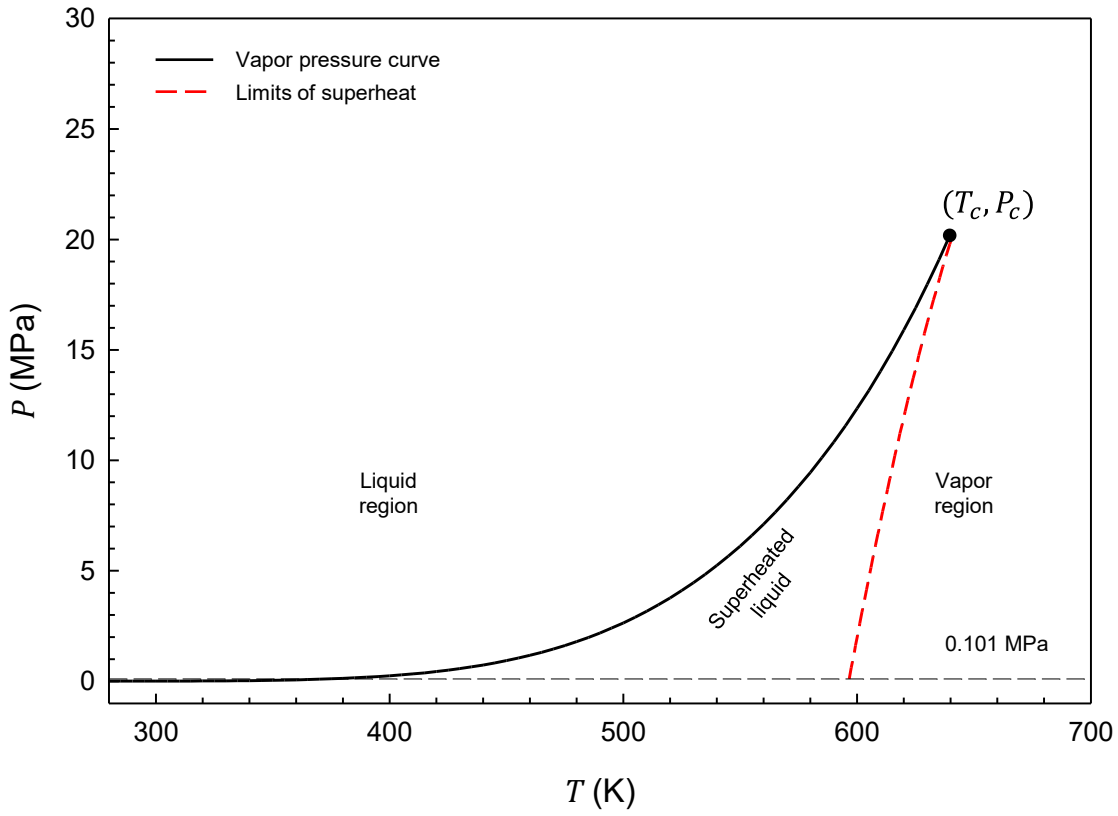

Fig. 1. Vapor-pressure curve and locus of limits of superheat of water.

From Fig. 1, the metastable state can be attained from isobaric heating or isothermal decompression of the liquid. When the meta-stable superheated liquid reaches its limit of superheat, it can no longer be sustained as a liquid. A rapid phase-transition from liquid to vapor occurs. If the perturbation is sufficiently large, superheated liquids will partially vaporize and form a final, more stable state, usually consisting of vapor and residual liquid Reid [14]. In the context of fire-induced spalling, isothermal depressurization is the likely scenario.

3. Thermodynamic behavior of water in a closed system when heated

Depending on the initial amount of water (liquid and vapor) in the closed system, the P–T behavior differs when the water is heated [19]. Given an initial fill density ρ_{fill}, defined as the ratio of the initial mass of water to the system volume, there are three scenarios to be considered: (a) $\rho_{\text{fill}} > \rho_c$, (b) $\rho_{\text{fill}} = \rho_c$, and (c) $\rho_{\text{fill}} < \rho_c$. Figure 2 is used to illustrate the heating processes under these three filling conditions. The data used to generate Fig. 2 was obtained from the NIST REFPROP database [18].

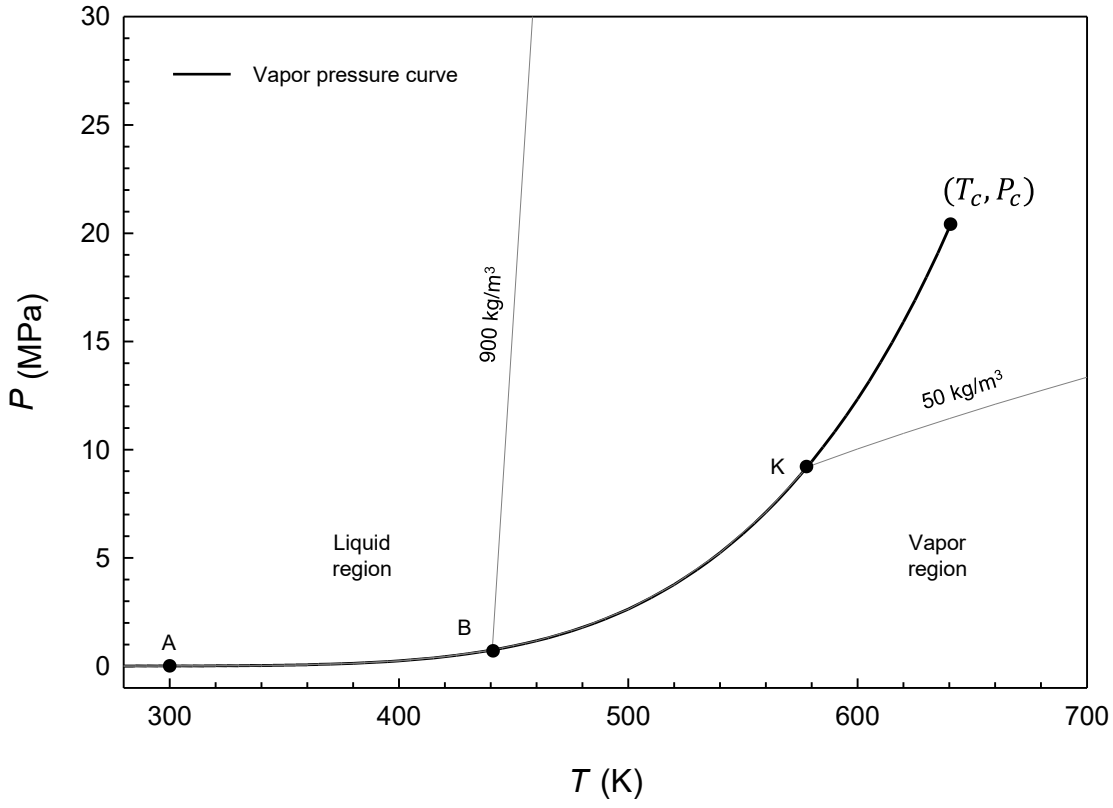

Fig. 2. Heating water initially at state A when $\rho_{\text{fill}} > \rho_c$, $\rho_{\text{fill}} = \rho_c$, or $\rho_{\text{fill}} < \rho_c$.

When $\rho_{\text{fill}} > \rho_c$, say $\rho_{\text{fill}} = 900$ kg/m^3, heating the water initially at state **A** follows the vapor-pressure curve of water until state **B** is reached, where the liquid water completely fills the system due to thermal expansion of the liquid water, a condition termed *liquid full*. Further heating beyond state **B** will no longer follow the vapor-pressure curve but will follow the 900 kg/m^3-isochore (constant density ρ_{fill} line) in the liquid region, as shown in Fig. 2. In the liquid region, a slight increase in temperature results in a significant increase in pressure along the isochore, therefore, a liquid full condition can lead to extreme overpressure when heated.

When $\rho_{\text{fill}} = \rho_c = 322$ kg/m^3, heating the water initially at state **A** in the system follows the vapor-pressure curve of water and remains two phases (liquid and vapor) until the critical point of water is reached.

When $\rho_{\text{fill}} < \rho_c$, say $\rho_{\text{fill}} = 50$ kg/m^3, heating the water initially at state **A** again follows the vapor-pressure curve of water, where liquid water and water vapor coexist, until all the liquid water has evaporated into water vapor at state **K**. Further heating beyond state **K** will no longer follow the vapor-pressure curve but follow the 50 kg/m^3-isochore in the vapor region, as illustrated in Fig. 2. In the vapor region, a significant increase in temperature only causes a moderate increase in pressure along the isochore.

4. BLEVE or no BLEVE

Based on the hypothesis proposed by Reid [13], two conditions are required for potential occurrence of BLEVE: (1) the depressurization of the heated liquid must be very rapid and (2) the temperature of the heated liquid must be above its superheat limit at 0.101 MPa. The thermodynamic analysis developed herein provides a method for identifying the states of water under which the second condition is satisfied; however, it cannot provide information for the first condition on how rapid depressurization of the liquid water to its limit of superheat that leads to rapid phase transition from liquid to vapor when the system is breached. Figure 1 is re-plotted as Fig. 3 for $\rho_{\text{fill}} > \rho_c$, Fig. 4 for $\rho_{\text{fill}} = \rho_c$, and Fig. 5 for $\rho_{\text{fill}} < \rho_c$ with additional illustrations and annotations to explain how the second condition could be met.

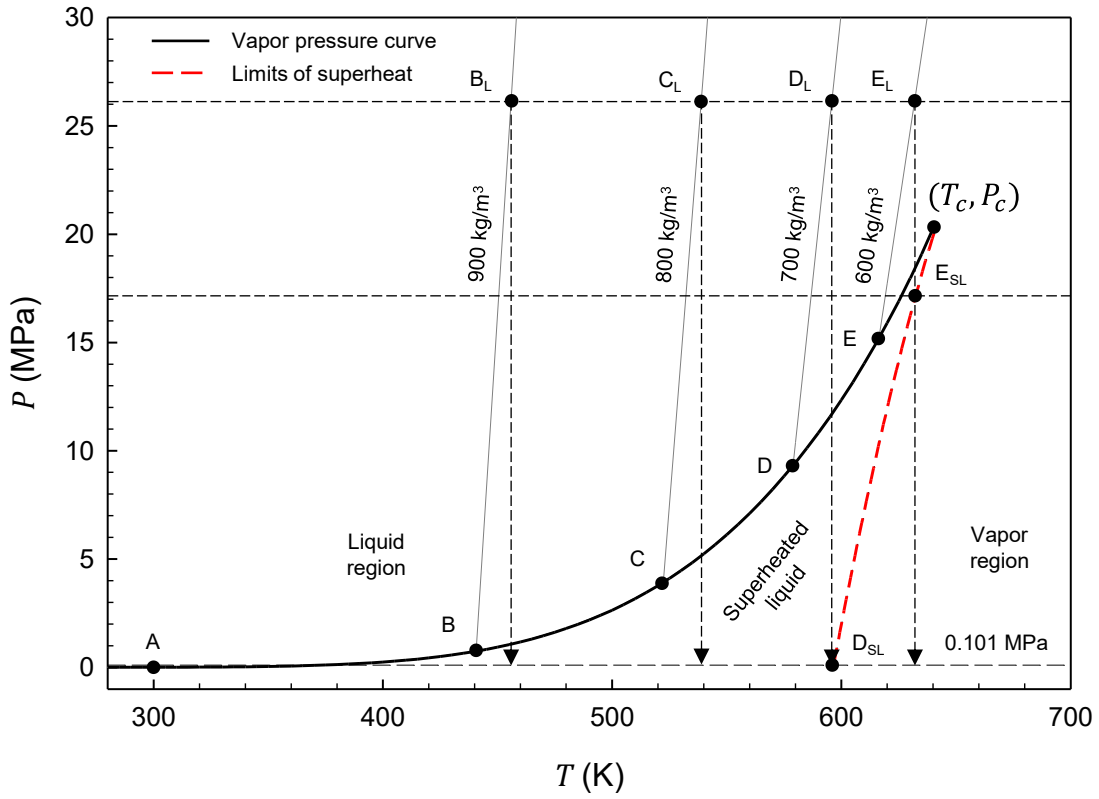

Fig. 3. States in the liquid region where BLEVE would or would not occur when $\rho_{\text{fill}} > \rho_c$.

When $\rho_{\text{fill}} > \rho_c$ (Fig. 3) and $\rho_{\text{fill}} = 900$ kg/m^3, heating water from the initial state **A** to state **B**, first follows the vapor-pressure curve. At state **B**, the closed system will be liquid full. Continuing heating beyond state **B** will no longer follow the vapor-pressure curve; instead, it will follow the 900 kg/m^3-isochore in the liquid region, as discussed in Section 3 above. If depressurization to 0.101 MPa (atmospheric pressure) were to occur at $\mathbf{B_L}$, this thermodynamic process is represented by the vertical dashed arrow originating from state $\mathbf{B_L}$, traversing the superheated liquid region, and terminating at the horizontal constant 0.101 MPa line. The vertical dashed arrow never intersects with the locus of limits of superheat. What this implies is that the water can be superheated, but it never reaches its limit of superheat at 0.101 MPa

under this condition. According to Reid's second condition [13], BLEVE would not occur. Similarly, heating water with $\rho_{\text{fill}} = 800$ kg/m^3 from the initial state **A** to state **C** (liquid full) and then onto $\mathbf{C_L}$ along the 800 kg/m^3-isochore, followed by depressurization from $\mathbf{C_L}$ to 0.101 MPa, would not induce BLEVE.

On the contrary, heating water with $\rho_{\text{fill}} = 700$ kg/m^3 from the initial state **A** to state **D** (liquid full) and then onto $\mathbf{D_L}$ along the 700 kg/m^3-isochore, followed by depressurization from $\mathbf{D_L}$ to 0.101 MPa, would cause BLEVE. Since the dashed arrow, in this case, intersects the locus of limits of superheat at 0.101 MPa, the superheated water reaches its limit of superheat, thus causing a rapid phase transition with a corresponding energy release. Following the same argument, the heating and depressurization processes from the initial state **A** with $\rho_{\text{fill}} = 600$ kg/m^3 to state **E** (liquid full) and then onto $\mathbf{E_L}$ along the 600 kg/m^3-isochore, followed by depressurization to 0.101 MPa, would also cause BLEVE. In this case, the dashed arrow also intersects the locus of limits of superheat during depressurization. Reid [13] postulated that BLEVE intensity was proportional to the pressure difference between the pressure at depressurization and the pressure at the superheat limit temperature. The intensity of BLEVE in the former case ($\rho_{\text{fill}} = 700$ kg/m^3) would be higher than the latter ($\rho_{\text{fill}} = 600$ kg/m^3) since the pressure difference, $P(\mathbf{D_L})$ - $P(\mathbf{D_{SL}})$, is *greater than* the pressure difference, $P(\mathbf{E_L})$ - $P(\mathbf{E_{SL}})$, where $P(\mathbf{D_L})$, $P(\mathbf{D_{SL}})$, $P(\mathbf{E_L})$, and $P(\mathbf{E_{SL}})$ are the pressures at states $\mathbf{D_L}$, $\mathbf{D_{SL}}$, $\mathbf{E_L}$, and $\mathbf{E_{SL}}$ respectively. For illustrative purposes and clarity, the pressure when depressurization occurs is assumed to be the same for $\rho_{\text{fill}} = 900$ kg/m^3, $\rho_{\text{fill}} = 700$ kg/ m^3, and $\rho_{\text{fill}} = 600$ kg/m^3 in Fig. 3, i.e., $P(\mathbf{B_L}) = P(\mathbf{C_L}) = P(\mathbf{D_L}) = P(\mathbf{E_L})$.

When $\rho_{\text{fill}} = \rho_c$ (Fig. 4), heating water from the initial state **A** to any state (**F**, **G**, or **H**) now follows the vapor-pressure curve until the critical point is reached, as discussed in Section 3 above. If depressurization to 0.101 MPa occurs at state **F**, shown by the vertical dashed arrow originating from state **F**, BLEVE would not occur because the dashed arrow never intersects the locus of limits of superheat. If depressurization occurs at state **G** instead, shown by the vertical dashed arrow originating from state **G**, BLEVE would occur because the dashed arrow intersects the locus of limits of superheat at 0.101 MPa. If depressurization occurs at state **H**, shown by the vertical dashed arrow originating from state **H**, BLEVE would also occur because the dashed arrow intersects the locus of limits of superheat before reaching 0.101 MPa. The BLEVE intensity is weaker in the latter case because the pressure difference, $P(\mathbf{H})$ - $P(\mathbf{H_{SL}})$ is *less than* the pressure difference, $P(\mathbf{G})$ - $P(\mathbf{G_{SL}})$, where $P(\mathbf{G})$, $P(\mathbf{G_{SL}})$, $P(\mathbf{H})$, and $P(\mathbf{H_{SL}})$ are the pressures at states **G**, $\mathbf{G_{SL}}$, **H**, and $\mathbf{H_{SL}}$ respectively.

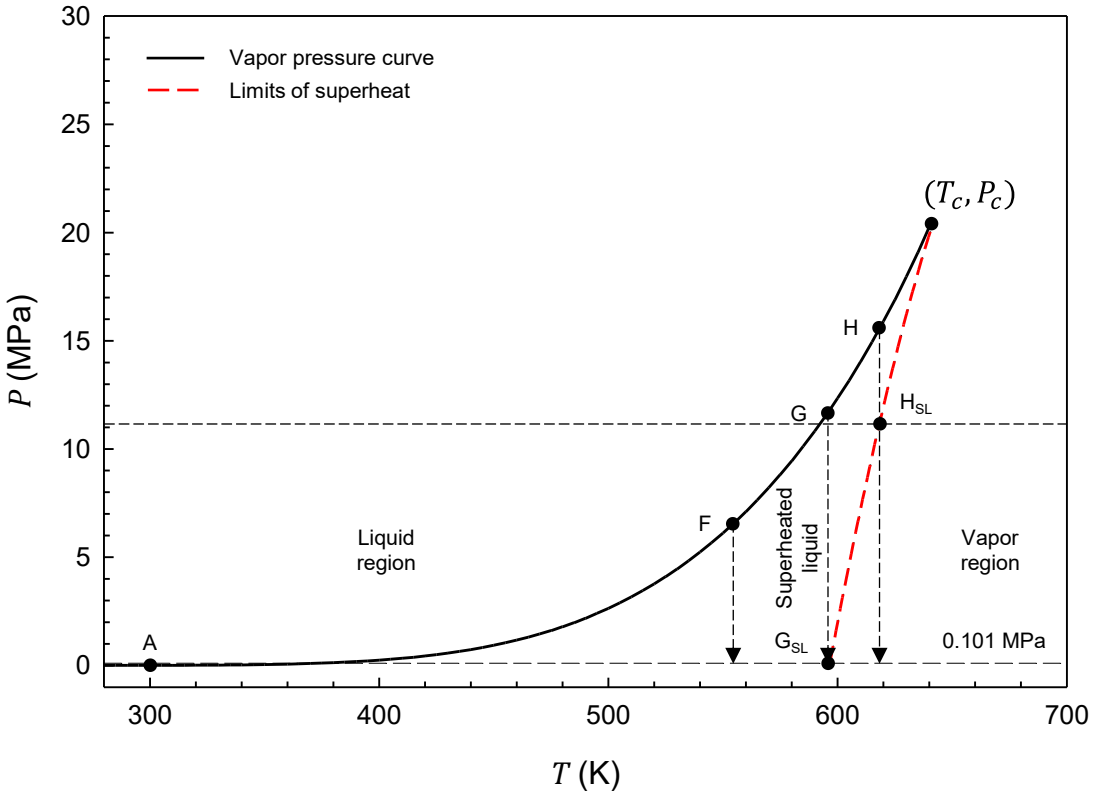

Fig. 4. States along the vapor-pressure curve where BLEVE would or would not occur when $\rho_{fill} = \rho_c$.

When $\rho_{\text{fill}} < \rho_c$ (Fig. 5), BLEVE would never occur. Heating water with $\rho_{\text{fill}} = 25$ kg/m^3 from the initial state **A** to state **J**, first follows the vapor-pressure curve. At state **J**, all the liquid water has evaporated, and further heating will follow the 25 kg/m^3-ioschore in the vapor region. If depressurization happens somewhere along this isochore, there will be no liquid water to be superheated. Similarly, heating water with $\rho_{\text{fill}} = 50$ kg/m^3 from the initial state **A** to state **K** (no liquid water) and then along the 50 kg/m^3-isochore followed by depressurization results in no BLEVE.

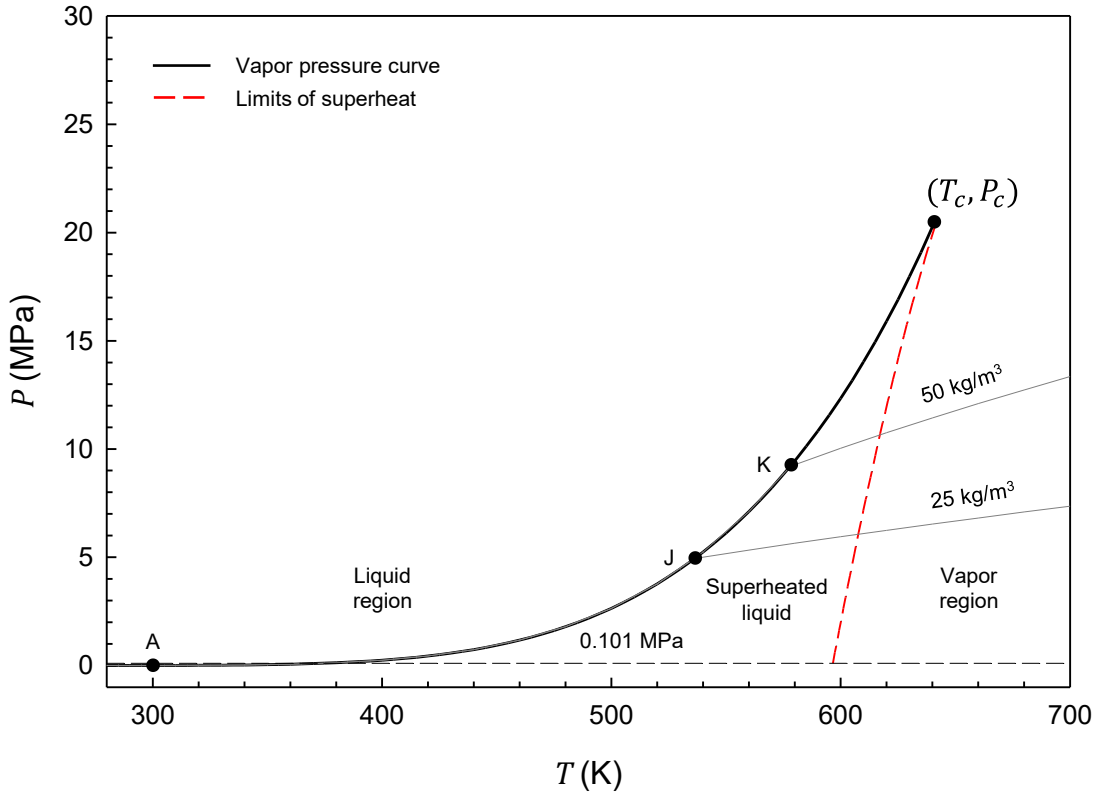

Fig. 5. States in the vapor region where BLEVE would not occur when $\rho_{fill} < \rho_c$.

Based on what has been discussed, the P–T region where BLEVE is likely to occur can be identified and is shown in Fig .6. This region (hatched area) includes a portion of the liquid region and a portion of the vapor-pressure curve but excludes the vapor region since a liquid state is needed for the liquid to be superheated. Therefore, the condition, either $\rho_{\mathrm{fill}} = \rho_c$ or $\rho_{\mathrm{fill}} > \rho_c$, is required for BLEVE. The hatched region has a very narrow temperature range from 597 K to the critical point of water (641.7 K). For a given pressure at depressurization, the range of isochores within the hatched area is narrow, implying that only certain ρ_{fill} would result in BLEVE. Hence, the thermodynamic conditions that favor the occurrence of BLEVE are limited.

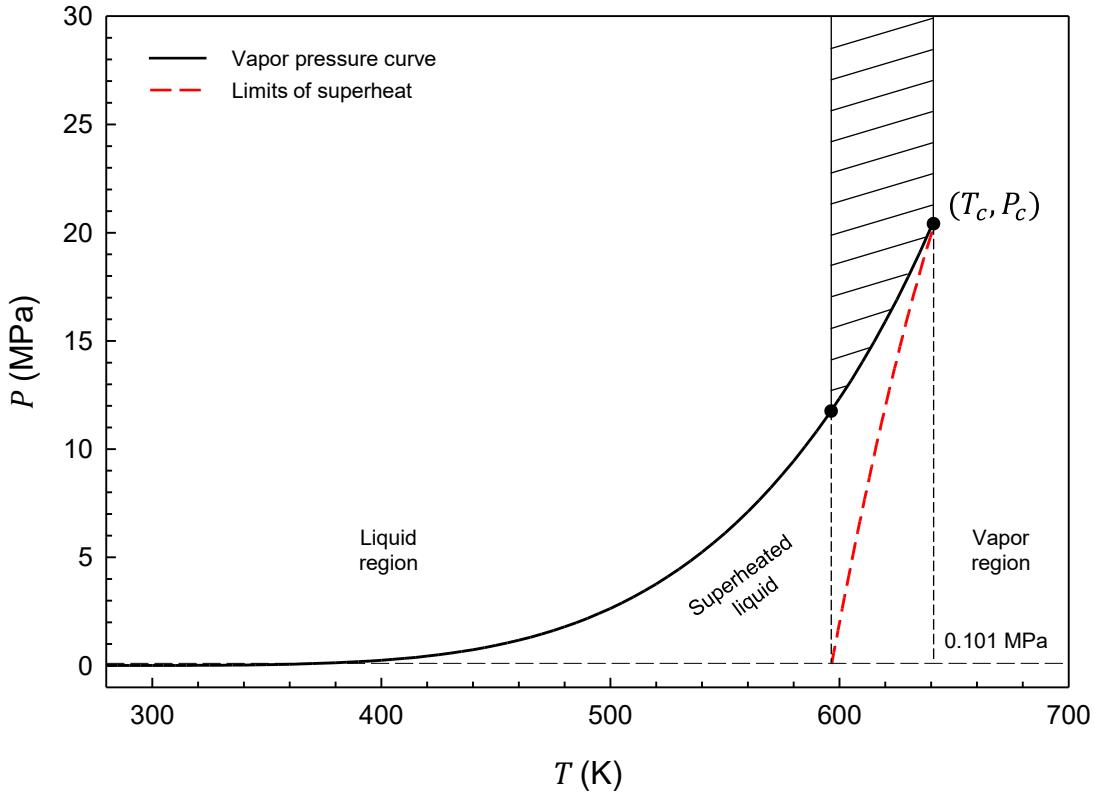

Fig. 6. *P–T* region (hatched area) of water where BLEVE would potentially occur.

A review of literature indicates that fire-induced spalling in concrete generally occurs at exposed concrete surface temperatures between 250 °C (523 K) and 420 °C (693 K) [1,2,20,21]. Depending on the exposure time to high temperatures and the dimensions and the constituents of the concrete, it is likely that temperature range that favors BLEVE could be attained within the concrete [8] (Ichikawa, 2000). The observation of moisture clog in certain region within the heated concrete [1–7] and measured pressures within concrete pores exceeded the saturated vapor pressure of water [20] could be construed as an indication of $\rho_{\text{fill}} > \rho_c$ condition. Therefore, the thermodynamic conditions that are conducive to BLEVE could hypothetically be achieved.

5. Conclusions

The BLEVE hypothesis on fire-induced spalling of concrete was examined using superheated liquid theory. The Peng-Robinson EOS was used to calculate the thermodynamic limits of superheat of water, which was needed to assess BLEVE. Water trapped within a heated interior region of concrete was used as an idealized closed system to examine the thermodynamic behavior of water that subsequently would lead to potential occurrence of BLEVE. The condition that the interior region of concrete was either completely (liquid full) or partially (liquid and vapor) filled with liquid water was necessary for BLEVE. BLEVE would not occur if only water vapor was present in the system. The thermodynamic conditions that favored BLEVE were identified and delineated in the P–T phase diagram of water and were shown to be highly constrained to narrow ranges of temperature and amount of water trapped in the region. Literature review on concrete spalling indicates that the thermodynamic conditions identified in this study that favor BLEVE could be hypothetically attained inside the concrete when exposed to fires.

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