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Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

Sub-Committee of Experts on the Transport of Dangerous Goods

Sixtieth session
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Item 2 (b) of the provisional agenda
Explosives and related matters: improvement of test series 8

Recommendations on Test Series 8: Applicability of Test Series 8 (d)

Submitted by the Institute of Makers of Explosives (IME)[*]

Introduction

1. At the fifty-seventh and fifty-eighth sessions of the Sub-Committee of Experts on the Transport of Dangerous Goods, the Institute of Makers of Explosives submitted informal documents INF.13 (57th session) and INF.8 (58th session) that proposed ammonium nitrate emulsions (ANEs) that satisfy the acceptance criteria of the 8(e) CanmetCERL Minimum Burning Pressure (MBP) test[1] should not be subjected to the 8(d) Vented Pipe test.

2. Currently, if ANEs are to be transported in bulk in portable tanks, they must also be subjected to the 8(d) test as one way of determining suitability for containment in tanks as an oxidizing substance. Such containment is integral to the primary method of ANEs transport. As described in informal document INF.13 (57th session), the 8(d) Vented Pipe test is, in effect, a larger scale 8(c) Koenen test and the same limitations of the Koenen test for those ANEs described in informal document INF.13 (57th session) are also encountered during the 8(d) test. This claim is supported by experimental data in informal document INF.13 (57th session) which show that ANEs that result in false positives in the 8(c) test will also do so in the 8(d) test.

3. This document provides additional numerical modelling results, covering transport of ANEs in stainless steel as well as aluminum portable tanks (including tank rupture). The work supports the findings published in informal document INF.8 (58th session) showing the heat, momentum and mass transport phenomena that take place within a tank containing an ANE that is subject to an external fire. Compared to the informal document INF.8 (58th session) baseline, the model was refined to include kinetics of decomposition of ANE and the formation of a crust during a fire scenario. The modelling is based on heat and fluid flow determined experimentally from truck tire and diesel fuel scenarios. Results from these

[*] A/75/6 (Sect.20), para. 20.51
[1] Hereafter referred to as 8(e) Minimum Burning Pressure test or 8(e) MBP test

refinements further support observations in the field and provide a scientific basis for excluding the requirement of the 8(d) test for ANEs that pass the 8(e) test

4. All figures referred to in this document may be found in the annex hereto.

Background

5. Certain ANEs that are candidates for classification as UN 3375, have shown to give false positives in the 8(c) Koenen test and this led to the inclusion of the 8(e) Minimum Burning Pressure (MBP) test into Test Series 8. To be acceptable for classification as UN 3375 under this new test scheme, the following conditions must be met: a reaction time in the 8(c) test longer than 60 seconds and a water content of the candidate ANE greater than 14 %. ANEs that are subject to the 8(e) test must register an MBP equal to or greater than 5.6 MPa to be accepted under UN 3375.

6. The fact that classification of the ANEs subjected to the 8(e) test will not be governed by the 8(c) test, yet requires for bulk transport the 8(d) test, creates an issue for these substances since the likelihood of failing (i.e., yielding false positives) the 8(d) test is almost a certainty, as demonstrated in informal document INF.13 (57th session).

Discussion

7. ANEs have been transported in bulk since the 1980s. There have been several fires during transport and to date none of these fires has led to an explosion involving the ANE. The properties of the ANE, especially emulsions – a high water content, low thermal diffusivity, and high MBP – are contributing factors to the observation that ANEs have not resulted in explosions under these circumstances.

8. The tanker material of construction is either stainless steel or aluminum. Scandinavia mandated the use of aluminum following a large-scale test (informal document INF.20 (21st session)) in which it was shown that the aluminum melted and released the ANE since the flame temperature, typically 900-1000 ºC, is higher than the melting point of aluminum, which is 660 ºC (see Figure 1 in the annex). Furthermore, since the ANE is a poor thermal conductor due to its low thermal diffusivity, the metal reaches its melting point easily. If the substance contained had a high thermal conductivity, e.g., water, the heat would be transferred into the substance and the effect would be that of a metal pan on a stove where the container stays intact. In Australia on 12 March 2018, an ANE transporter with tanks constructed from aluminum was involved in a truck fire and the expected failure of the containing metal was seen (Figure 2).

9. The complexity of instrumenting an experiment that would yield the required information would be resource prohibitive. Therefore, a numerical model was chosen to investigate the fundamental physics of this problem. The tanker fire scenario with steel or aluminum being the material of construction was modelled using COMSOL Multiphysics®[2] with the following fill configurations: 100 %, 90 % representing a realistic case, and 10 % representing a case where the product is returned to the plant without full emptying of the tanker. The corresponding numerical model is based upon fundamental equations of mass, momentum, and heat transfer; and measured physical parameters or correlations widely accepted within the literature. A transient heat flux boundary condition with a peak value of 24 kW/m^2 was applied, in accordance with data from the paper published by Ingason and Hammarström[3]. This flux profile is appropriate because it is the most realistic heat flux from tire fires published. The tanker was modelled as two-dimensional with a symmetry line as shown in Figure 3. Figure 4 shows the ANE tanker filled to 90 % (10 % ullage) with the temperature and velocity profiles of the ANE and the air in the headspace after 60 minutes of heating. Heat penetrates approximately 8 cm of the emulsion matrix. Figures 5, 6 and 7

[2] COMSOL Multiphysics® (see https://comsol.com/products) is a multiphysics numerical simulation software package for finite element analysis and simulation of coupled systems of partial differential equations for electrical, mechanical, fluid, acoustics, and chemical applications.

[3] Ingason, H., *Fire Technology SP Report* (2014)

show the temperature profiles within the tank as a function of time as well as fill level for the transient heat flux of 24 kW/m^2. Ullage has little effect on heat transfer penetration in the emulsion phase within the tank. This is due to two factors, the thermal diffusivity is small, and the fluid is viscous which inhibits convection in the emulsion phase. However, the gas phase convection leads to lowering of the temperature near the air interface as the time increases. The temperature in all cases is well below the reaction activation temperature of 331 ºC (Oxley, et al[4]) indicating reactions did not occur. The reactions modelled in this study include not only the decomposition of the nitrate salts, and the recombination of gas phase species, but also the burning of the oil phase. The calculated fraction of conversion (or decomposition) in the 10 % ullage case as an example, is vanishingly small and is shown as a function of time in Figure 8 of the annex.

10. A transport fire with ANE that occurred in July 2018 in the United States of America (USA) showed that, once the fire had died down, the ANE was able to be pumped out of the tanker where the tank material was stainless steel (Figure 9). The formation of a crust was observed at the base of the tanker. Although the thickness of the crust was not measured in the actual transport fire event, the anecdotal information was that it was a 'thin crust'. The crust material is primarily solid ammonium nitrate (and possibly fuel residue) that is formed when the water in the discontinuous AN solution phase evaporates while the ANE is in contact with the heated surface. Kinetics for crust formation were determined experimentally and included in the numerical model. The temperature exceeds the vaporization point of water (105 °C) after 41 minutes as shown in Figure 10. The vaporization temperature included in the model is elevated due to the high concentration of dissolved salts. The modelling shows that the crust formed in stainless steel tanks is in the order of millimetres. (Figures 11 and 12). As shown in Figure 12, the transient formation of the crust thickness can be predicted by a thermal diffusion length scale.

$$L_{therm\ diff} = \sqrt{D_T \Delta t}$$

Where $L_{therm\ diff}$ (m) is the thermal diffusion length scale, D_T is the thermal diffusivity (m^2/s), and Δt is the change in time (s). Note that the growth in crust thickness closely matches this length scale. The fact that the bulk of the ANE was pumpable is a result of the ANE's low thermal diffusivity and has been borne out from the modelling work in this study. Before crust formation (< 41 min) heat penetration into the bulk is dominated by thermal diffusion. Beyond 41 min exposure to fire the depth of heat transfer is dominated by the formation of the crust. The scale of thermal effects can be predicted by a single physical property, the thermal diffusivity. Is this to mean only the ANE or that of the crust as well?

11. Numerical simulations at a more conservative heat flux of 80 kW/m^2 were also carried out. Note that this is over two times higher than that recommended by Ingason and Hammarström.[2] The higher heat flux produces a much higher temperature close to the heated surface, as expected, and this temperature is well above the decomposition temperature of the ANE. The temperature within the bulk ANE however is unchanged due to the low thermal diffusivity of the substance. The distance within the tanker where the temperature drops to that of the bulk is roughly equal to the case where the heat flux was 24 kW/m^2, namely at approximately 5 cm of the tank radius (Figure 13). This observation is due to the equivalent thermal diffusion length scales (which solely depend upon physical properties) between the two simulations (see Figure 4 for 24 kW/m^2 scenario). Both models, with the two heat fluxes, demonstrate that there will be crust formation. In the 80 kW/m^2 case, the fraction of conversion is substantial. The reactions are constrained and run to completion within the crust phase as shown in Figure 14. The crust reacts before the ANE phase for two reasons. First, in the ANE, the presence of water acts to inhibit the decomposition of ammonium nitrate resulting in a slower rate of reaction.[3] Second, the thermal properties of the ANE/crust isolate the heated section of the ANE/crust to a thin section near the heated tank wall. This constrains the volume of material that can react as shown in the temperature profiles in Figure 15. The rate of reaction becomes rapid and approaches a singularity at 10 minutes as shown in Figure 16. These results reflect the phenomenon seen in transport fires in stainless steel tanks, the most recent being the event in the USA (Figure 9). The addition of melting mechanics of an

[4] Oxley J.C., *Thermochimica Acta*, 153 (1989) 269-286*

aluminum tank to the model shows that the 80 kW/m^2 flux alone is inadequate to cause the phase transition which occurs at 660 ºC. Decomposition reactions of the crust and ANE phase are required to provide the necessary heat to attain this elevated temperature. In the model, a heat flux in excess of 200 kW/m^2 is required to melt the aluminum tank. This is physically impossible with a tire/diesel fire and therefore the contribution from ANE/crust decomposition kinetics are required.

12. The modelling work clearly shows the behavior of an ANE in a stainless steel or aluminum tank that is subjected to an external fire, the phenomena of which have been observed in actual transport incidents where the fire is invariably fueled by the tires. Bulk ANE tankers are not pressure vessels, and their pressure range is typically 0.1 to 0.6 MPa (1 to 6 bar). ANEs that are subjected to the 8(e) test must have an MBP equal to or above 5.6 MPa, which is an order of magnitude higher than the burst pressure of a tanker.

13. The incidents described and the modelling show that the bulk of the ANE remains close to the ambient temperature and hence its MBP will also remain at the original value, i.e., equal to or greater than 5.6 MPa. This means that there will be a very low likelihood of any ignition, should it occur, near the internal heated surface progressing to an explosion of the bulk of the ANE during transport fires. The tank would either fail, by rupture if it is stainless steel or melting if it is aluminum, thus relieving the container and any confinement, or the fire would die out once the fuel has been consumed, leaving the bulk of the ANE intact.

Proposal

14. ANEs that satisfy the acceptance criteria of the 8(e) test should not need to be subjected to the 8(d) test and should be considered suitable for containment in portable tanks as oxidizing substances since their MBPs far exceed the pressures at which portable tanks will fail.

15. Amend footnote [b] of Table 18.1 in section 18.2 of the Manual of Tests and Criteria (MTC) as shown below (new text is indicated in underlined text):

> “[b] *These tests are intended for evaluating the suitability of ANEs for containment in portable tanks as an oxidizing substance. ANEs that satisfy the acceptance criteria of Test 8 (e) need not be subjected to Test 8 (d) as they are already considered suitable for containment in portable tanks as an oxidizing substance*.”

16. Amend the first paragraph of section 18.7.1.1 of the MTC as shown below (new text is indicated in underlined text):

> “This test is not intended for classification but is included in this Manual for evaluating the suitability for containment in portable tanks as an oxidizing substance. ANEs that satisfy the acceptance criteria of Test 8 (e) need not be subjected to Test 8 (d) as they are already considered suitable for containment in portable tanks as an oxidizing substance.”

17. Amend the first paragraph of section 18.7.2.1 of the MTC as shown below (new text is indicated in underlined text):

> “This test is not intended for classification but is included in this Manual for evaluating the suitability of a candidate for "ammonium nitrate emulsion or suspension or gel, intermediate for blasting explosives", to be contained in portable tanks as an oxidizing substance. ANEs that satisfy the acceptance criteria of Test 8 (e) need not be subjected to Test 8 (d) as they are already considered suitable for containment in portable tanks as an oxidizing substance.”

18. Amend section 18.8.1.1 of the MTC as shown below (new text is indicated in underlined text):

> “18.8.1.1 *Introduction*
>
> This test is used to determine the sensitiveness of a candidate ammonium nitrate emulsion or suspension or gel, intermediate for blasting explosive,

to the effect of intense localized thermal ignition under high confinement. This test can be performed in case of a positive ("+") result in Test 8(c) when the time to reaction in this test has exceeded 60 seconds and the substance has a water content greater than 14 %.

This test is also applicable for determining the suitability of ANEs for containment in portable tanks as an oxidizing substance."

19. Amend section 18.8.1.4.1 of the MTC as shown below (new text is indicated in underlined text):

"18.8.1.4.1 The result is considered positive ("+") and the substance should not be classified in Division 5.1 if the MBP is less than 5.6 MPa (800 psig). Substances with MBPs equal to or greater than 5.6 MPa (800 psig) are considered suitable for containment in portable tanks as an oxidizing substance (see 18.8.1.1)."

Annex

Figures referred to in this document

Figure 1. Figures are taken from informal document INF.20 (21st session) showing the aluminum tanker test with ANE, carried out in Kuosanen, 2002

The tank was made of aluminium (5 mm wall thickness) and equipped with four separate compartments. Only one compartment was used (5 m^3) in the test and it was the one above the four double tires, at the end of the tank (see Figure 1-1). The compartment was filled with 6 000 kg (4.3 m^3) of emulsion matrix.

Figure 1-2 shows the burning tanker and Figures 1-3 and 1-4, the tank after the fire.

Figure 1-1: The tank before the fire.

Figure 1-2 The tank during fire. White smoke indicates decomposing emulsion matrix.

Figure 1-3: The tank after the fire (rear view)

Figure 1-4: The tank after the fire (side view).

Figure 2. ANE transport incident on 12 March 2018 in Queensland. (reported in SAFEX Incident Notice IN18-01)

Figure 3. Modelling of tanker showing the axisymmetric geometry used

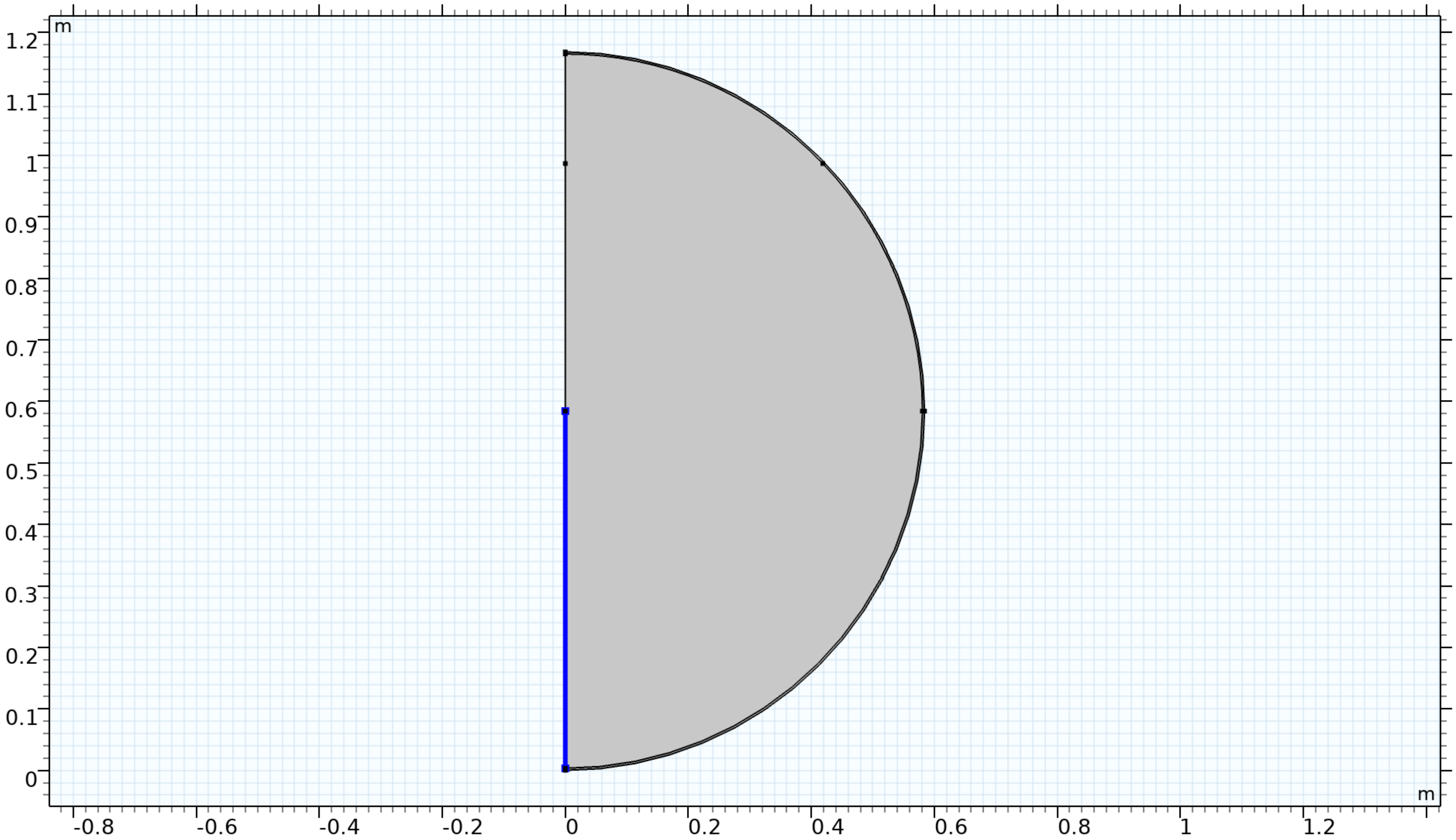

Figure 4: Modelling output – Temperature and velocity profiles for 90 % full tanker (10 % Ullage) at 60 minutes; 24 kW/m^2

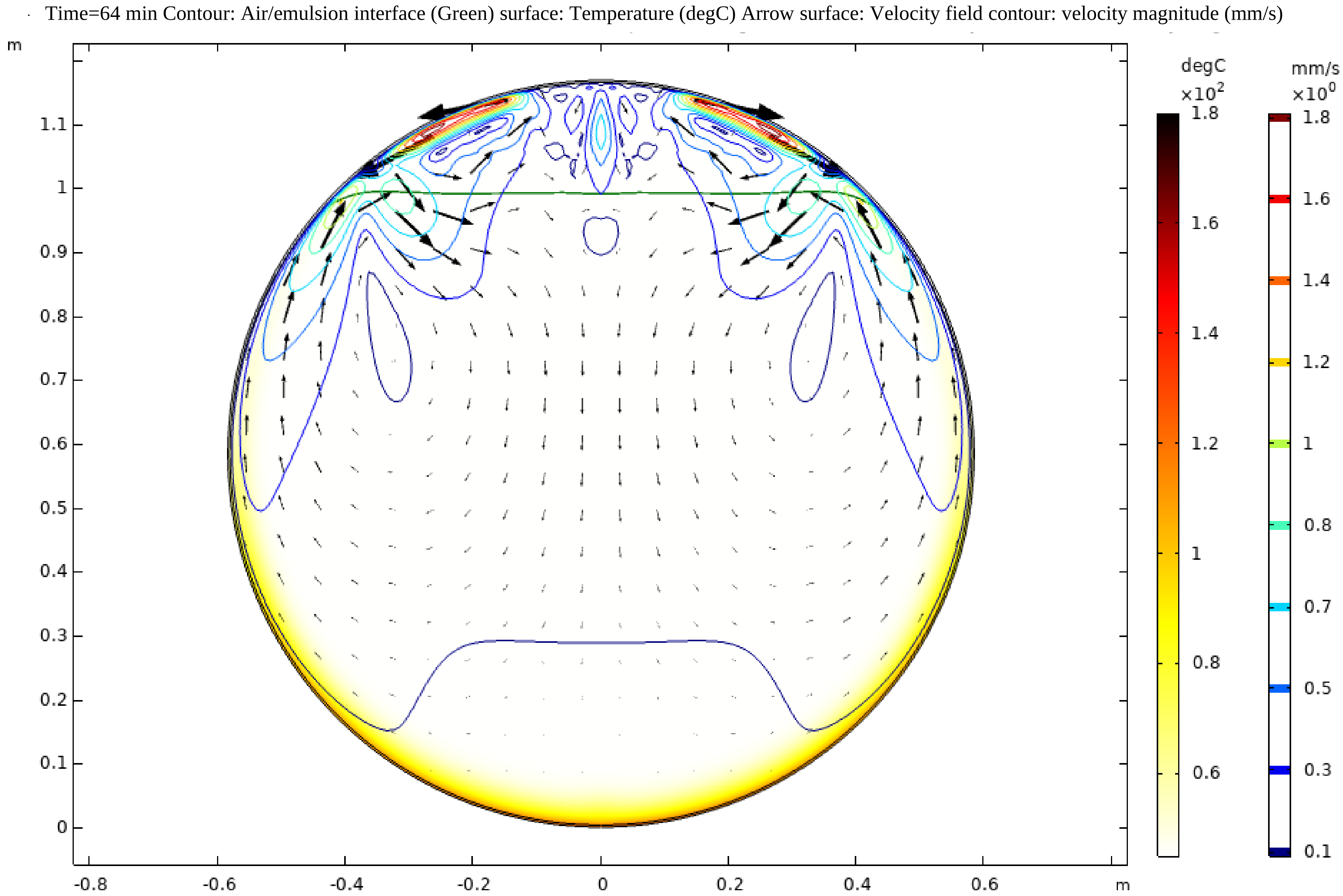

Figure 5: Modelling output – Temperature profile with time for 90 % full tanker (10 % ullage); Heat flux 24 kW/m^2

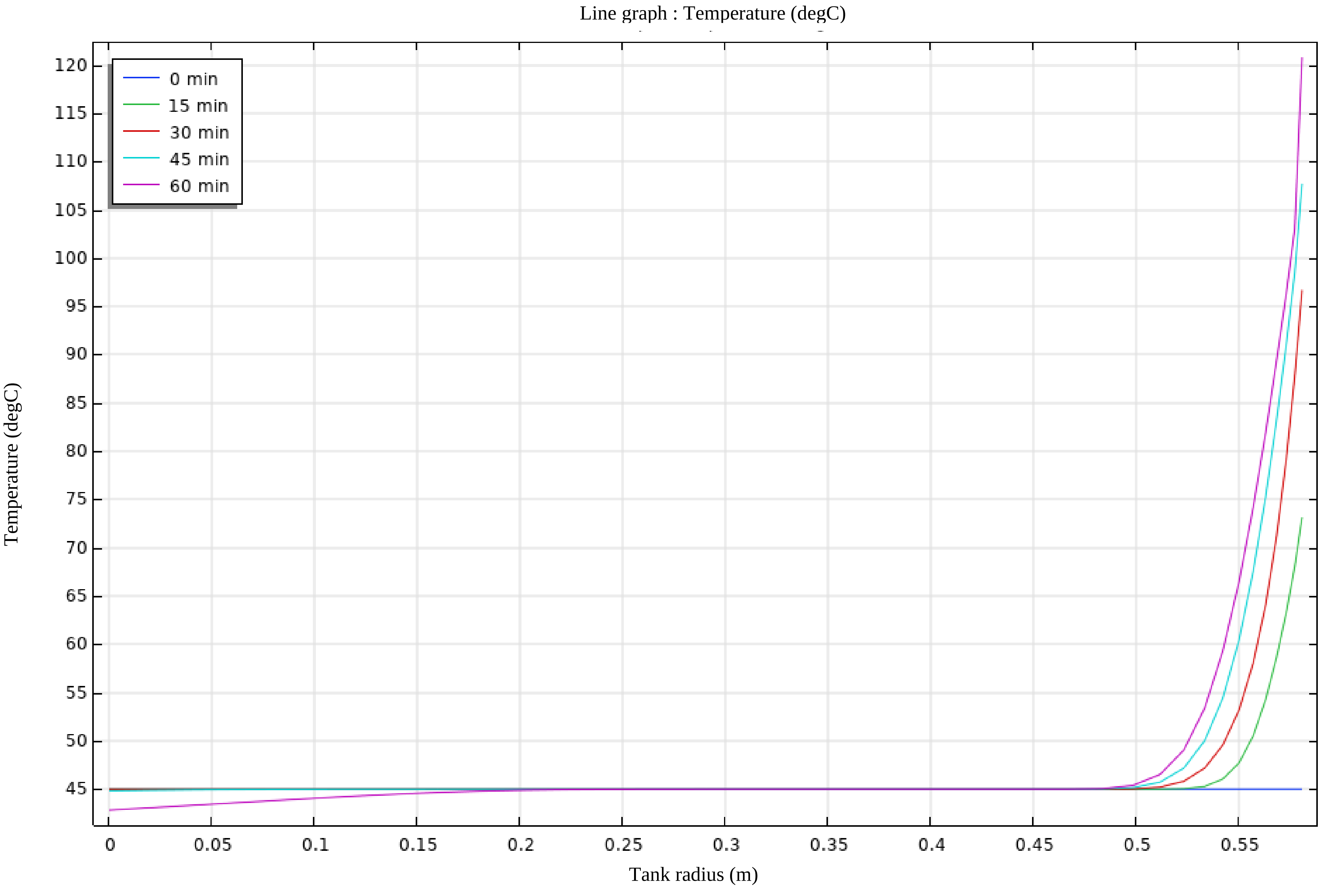

Figure 6: Modelling output – Temperature profile with time for 100 % full tanker (0 % ullage); Heat flux 24 kW/m^2

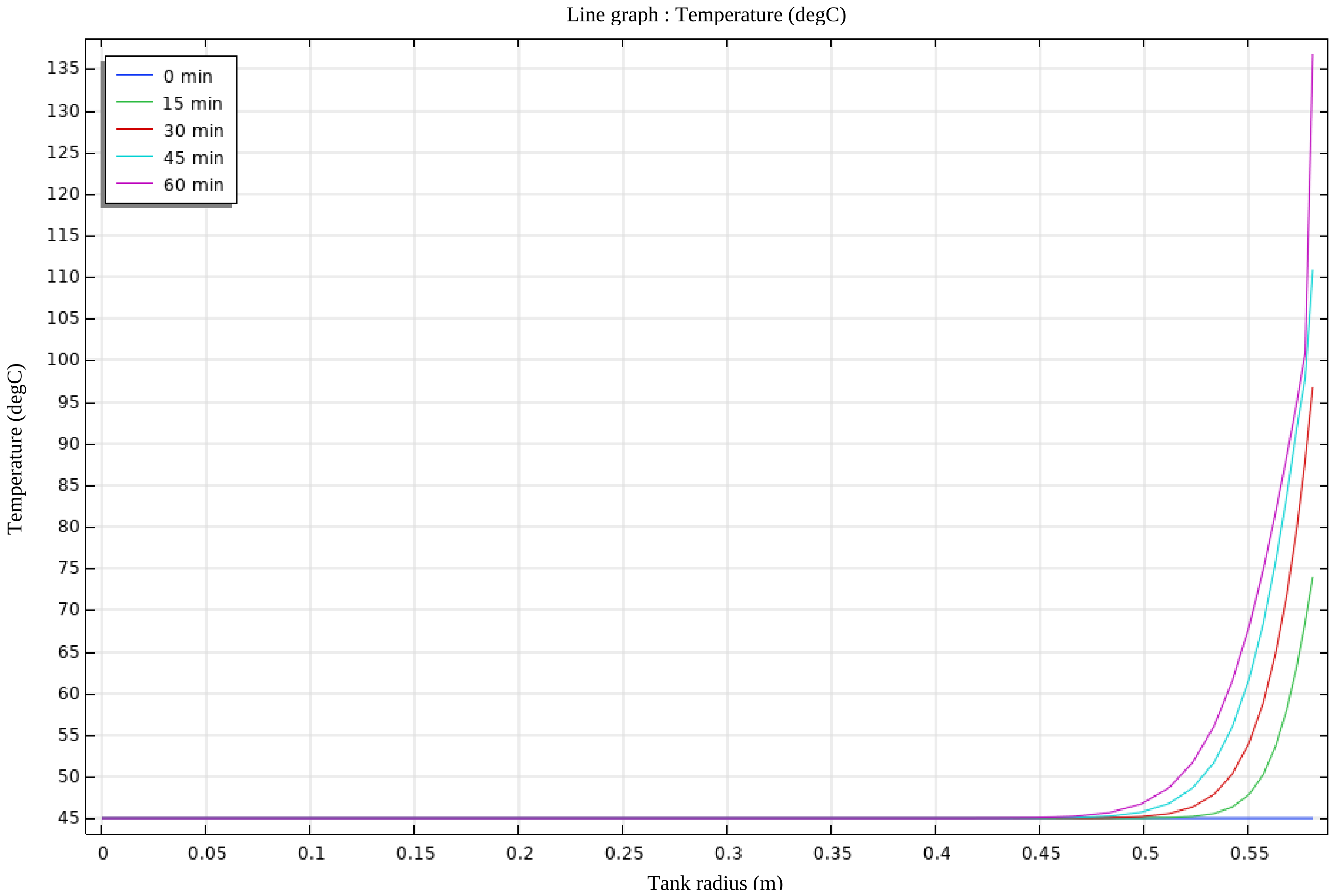

Figure 7: Modelling output – Temperature profile with time for 10 % full tanker (90 % ullage); Heat flux 24 kW/m^2

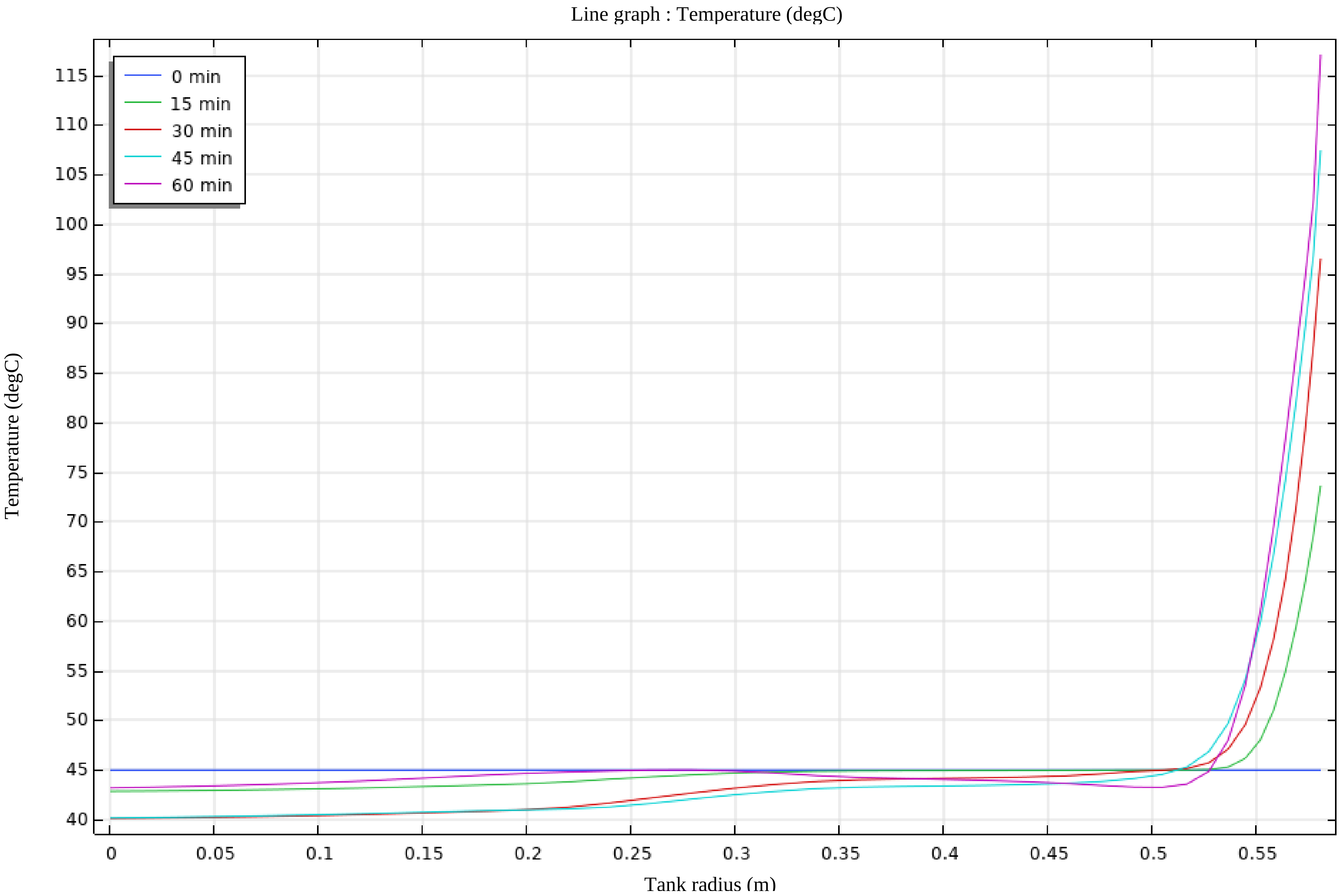

Figure 8: Modelling output – Volume fraction of ANE converted (10 % Ullage); Constant heat flux 24 kW/m²

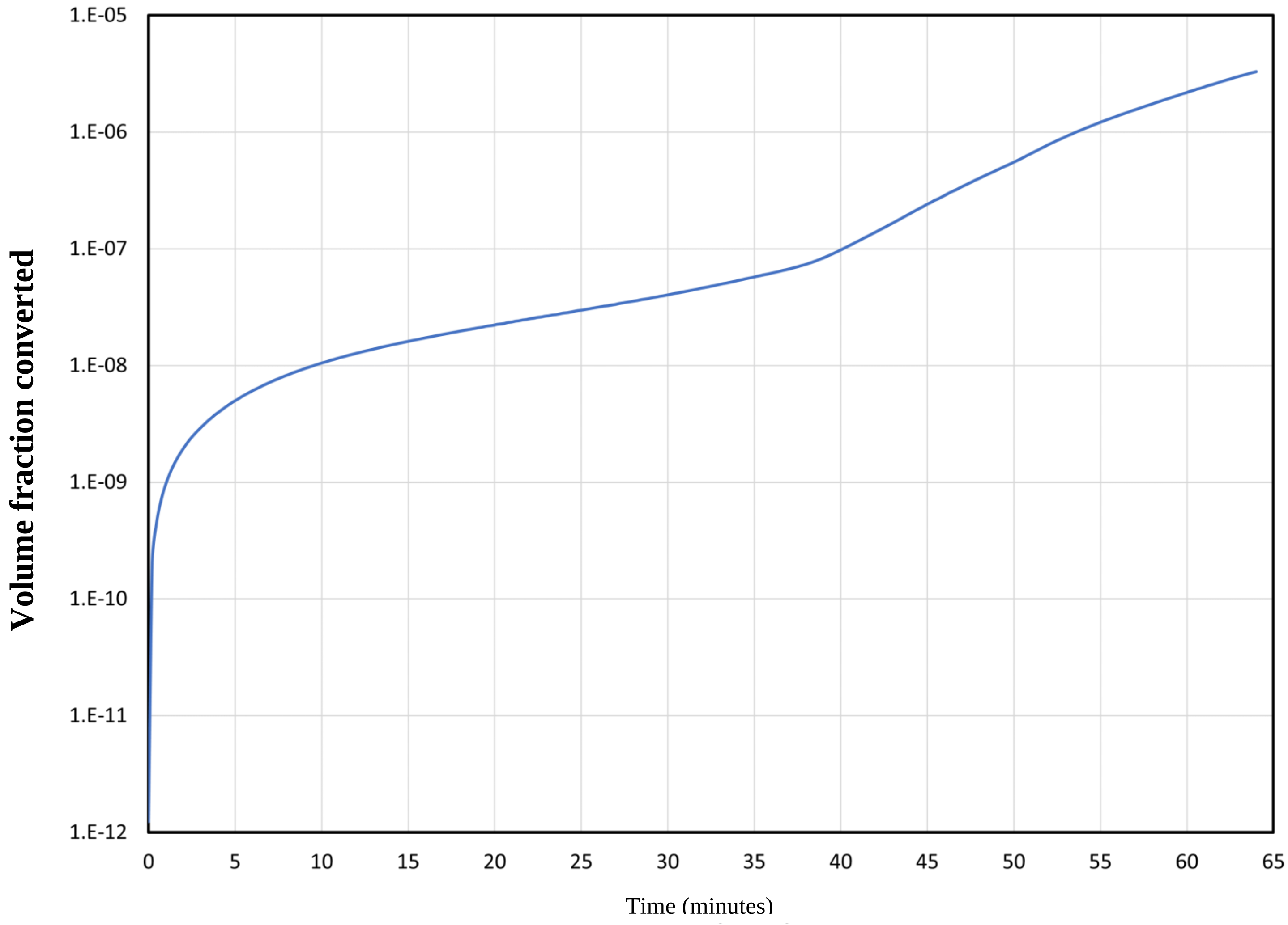

Figure 9: Transport Fire Incident, South Carolina, USA, July 12, 2018

Figure 10: Modelling output – Temperature profile in the near vaporization for 90 % full tanker (10 % ullage); Heat flux 24 kW/m^2

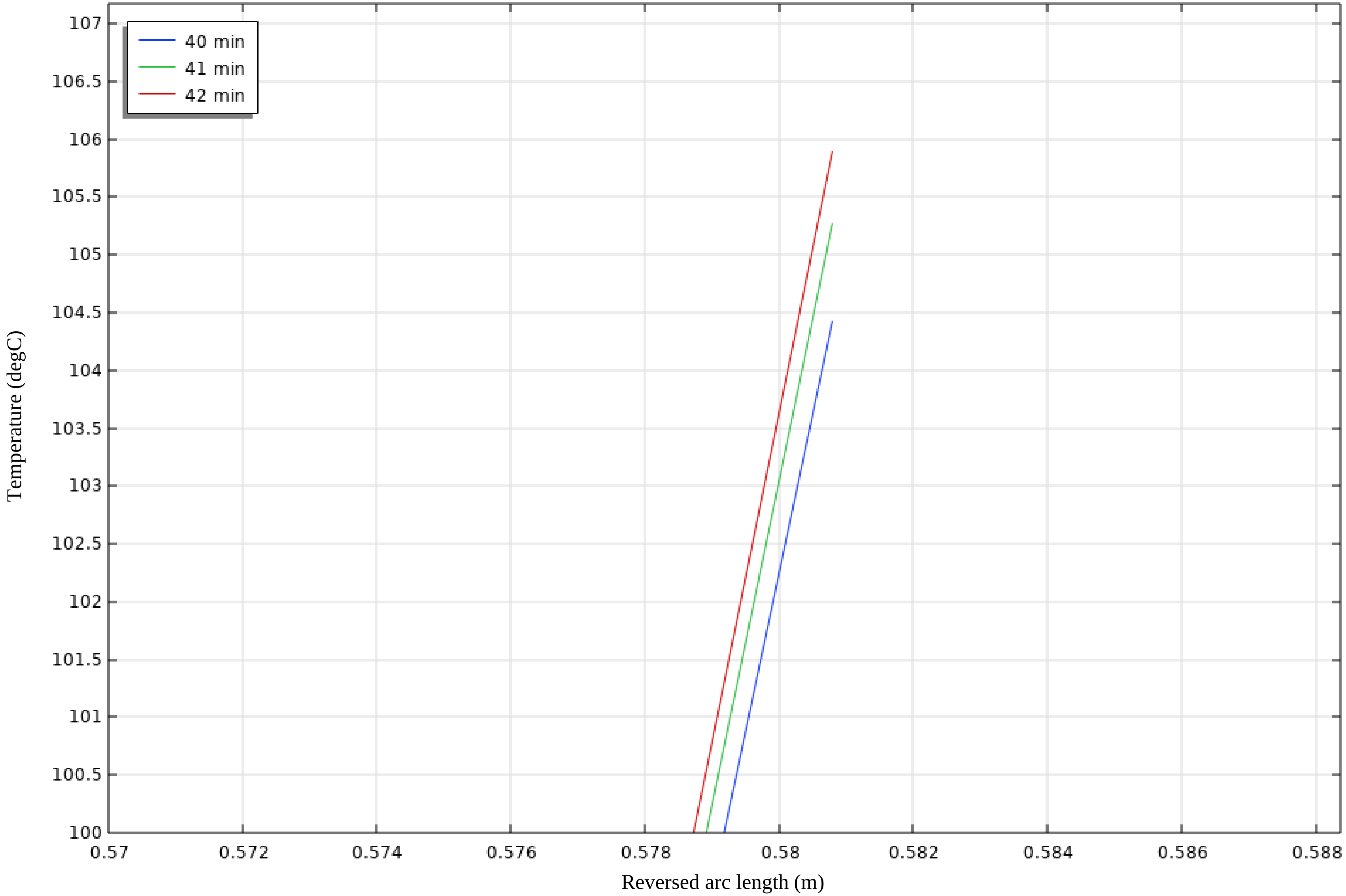

Figure 11: Modelling output – Crust phase and velocity vectors for 90 % full tanker (10 % ullage); Heat flux 24 kW/m^2

Time=64 min Contour : Air/emulsion interface (Green) (1) surface : Crust volume fraction (Magenta) Arrow surface : Velocity field contour ; Vaporization position, (Blue)

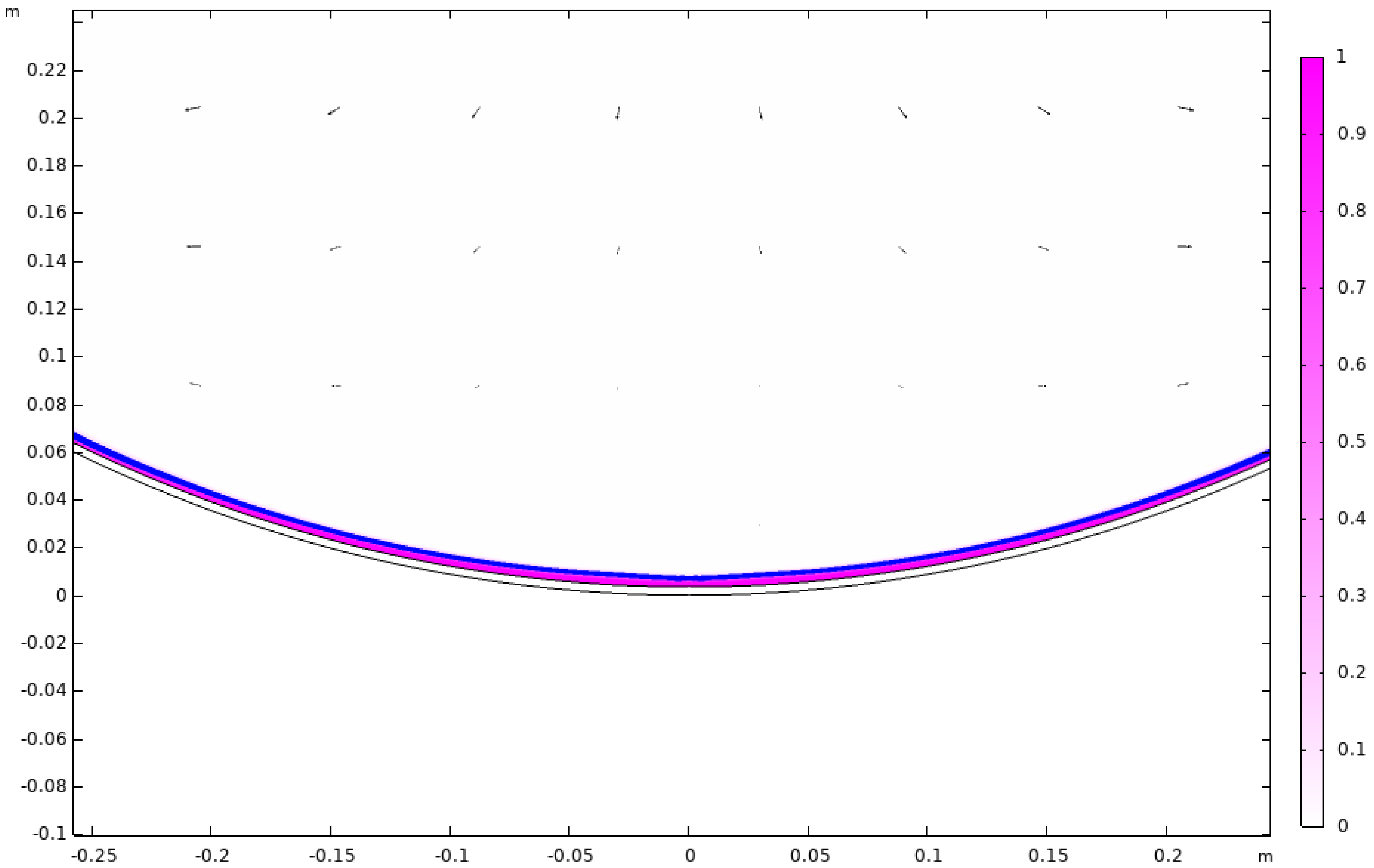

Figure 12: Modelling output – Crust thickness evolution with time (10 % ullage); Heat flux 24 kW/m^2

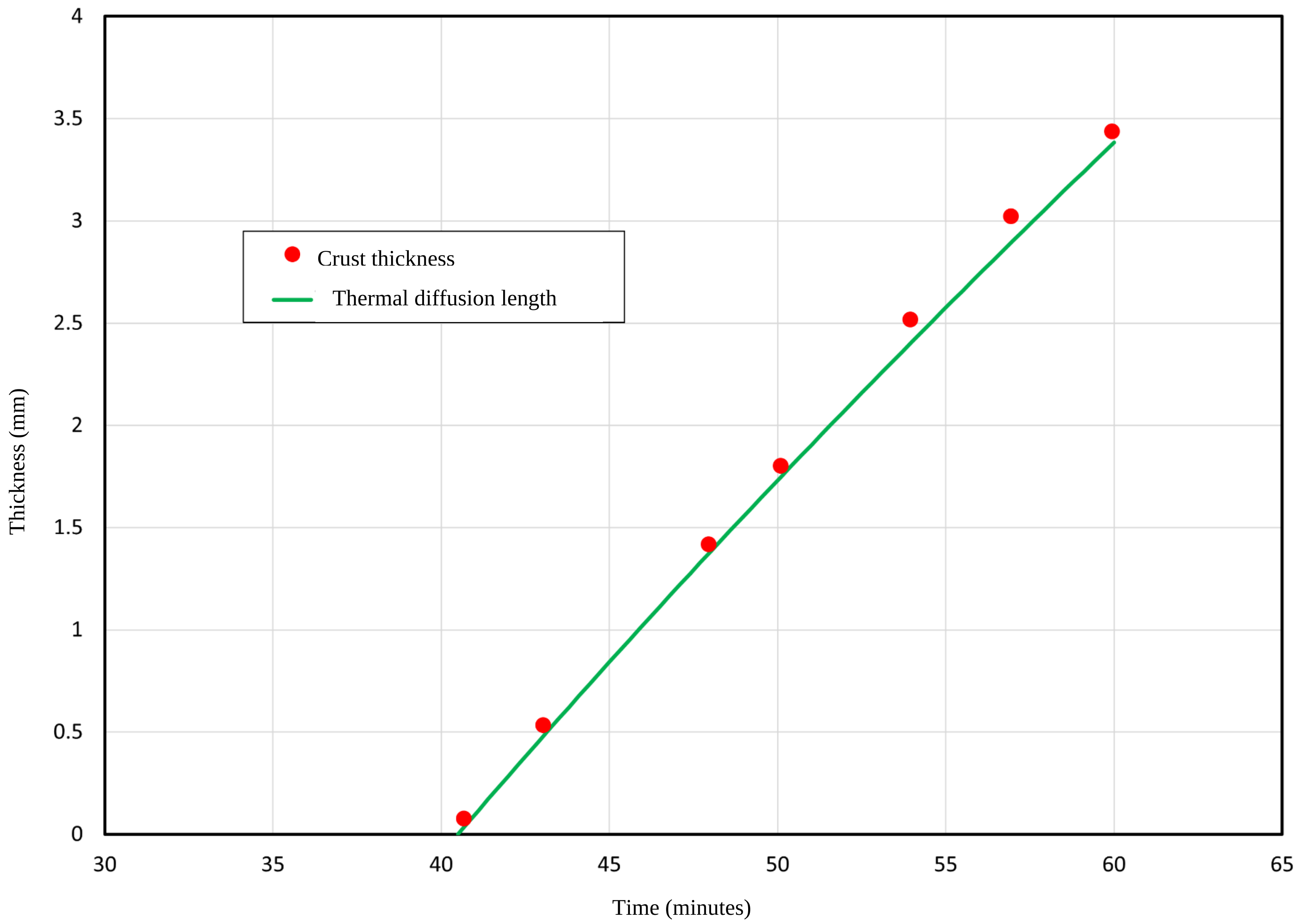

Figure 13: Modelling output – Temperature and velocity profiles for 10 % ullage tanker at 6.9 minutes; 80 kW/m^2

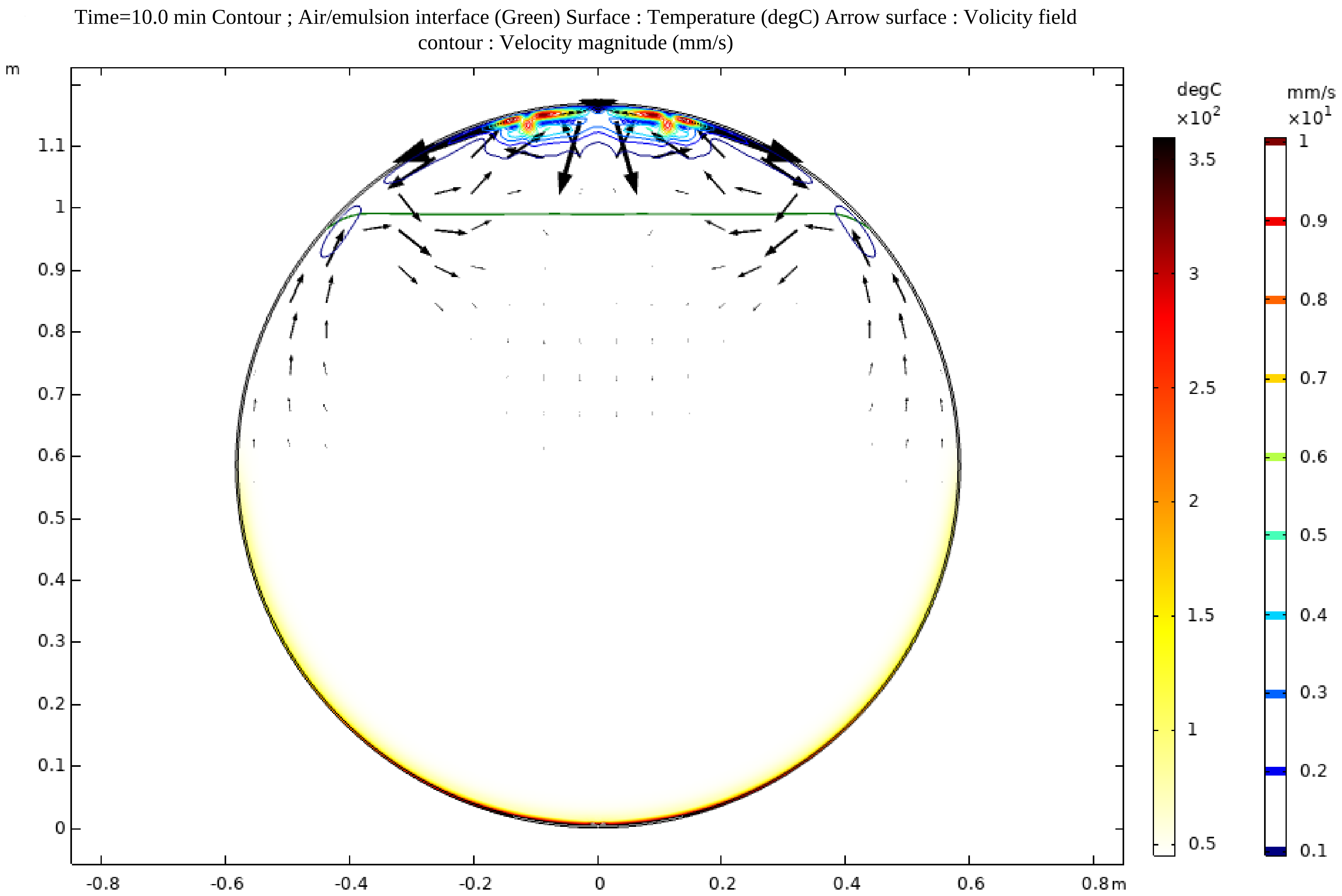

Figure 14: Modelling output – Volume fraction and position of converted ANE (10 % ullage); Constant heat flux 80 kW/m^2

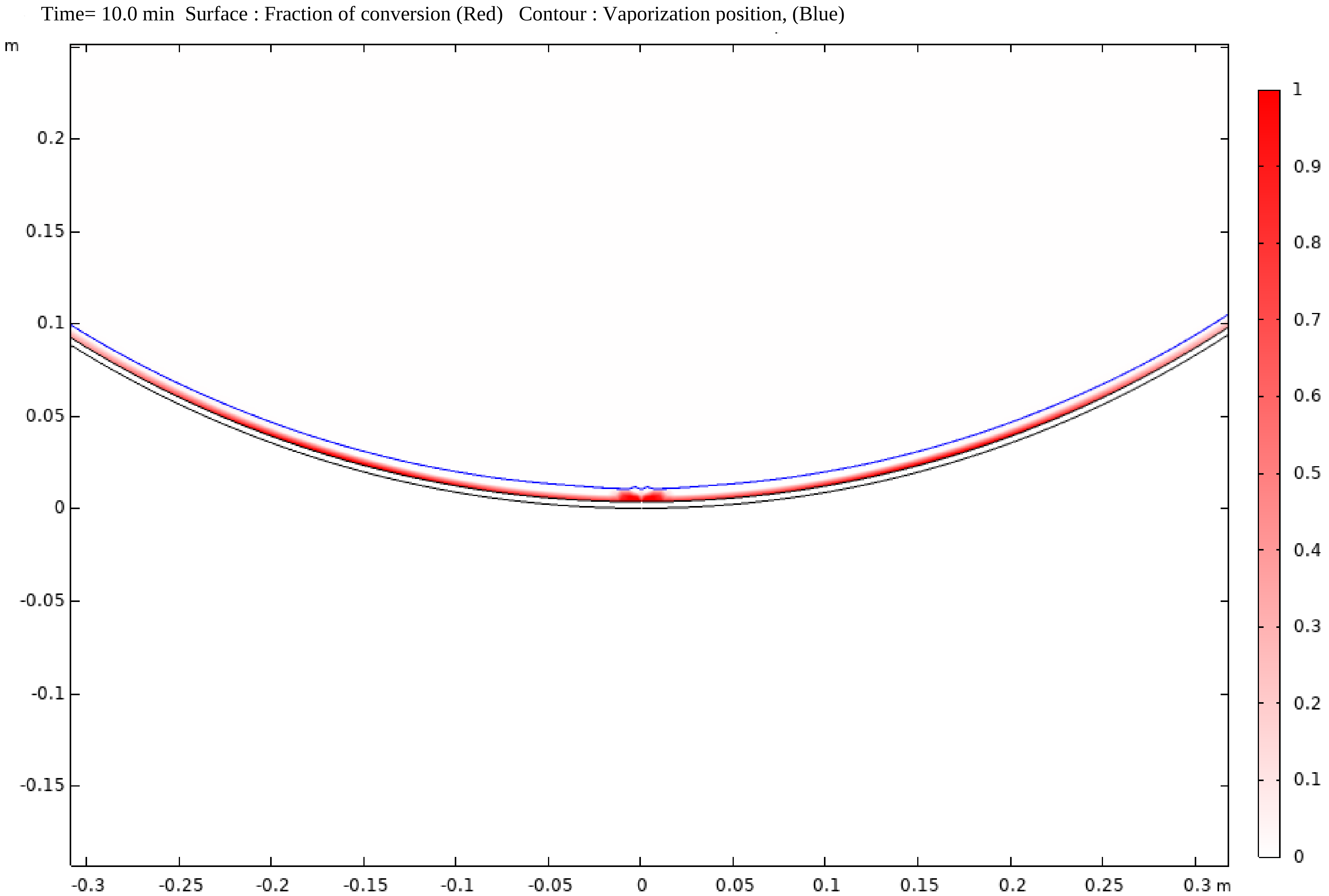

Figure 15: Modelling output – Temperature profile with time for 90 % full tanker (10 % ullage); Heat flux 80 W/m[2]

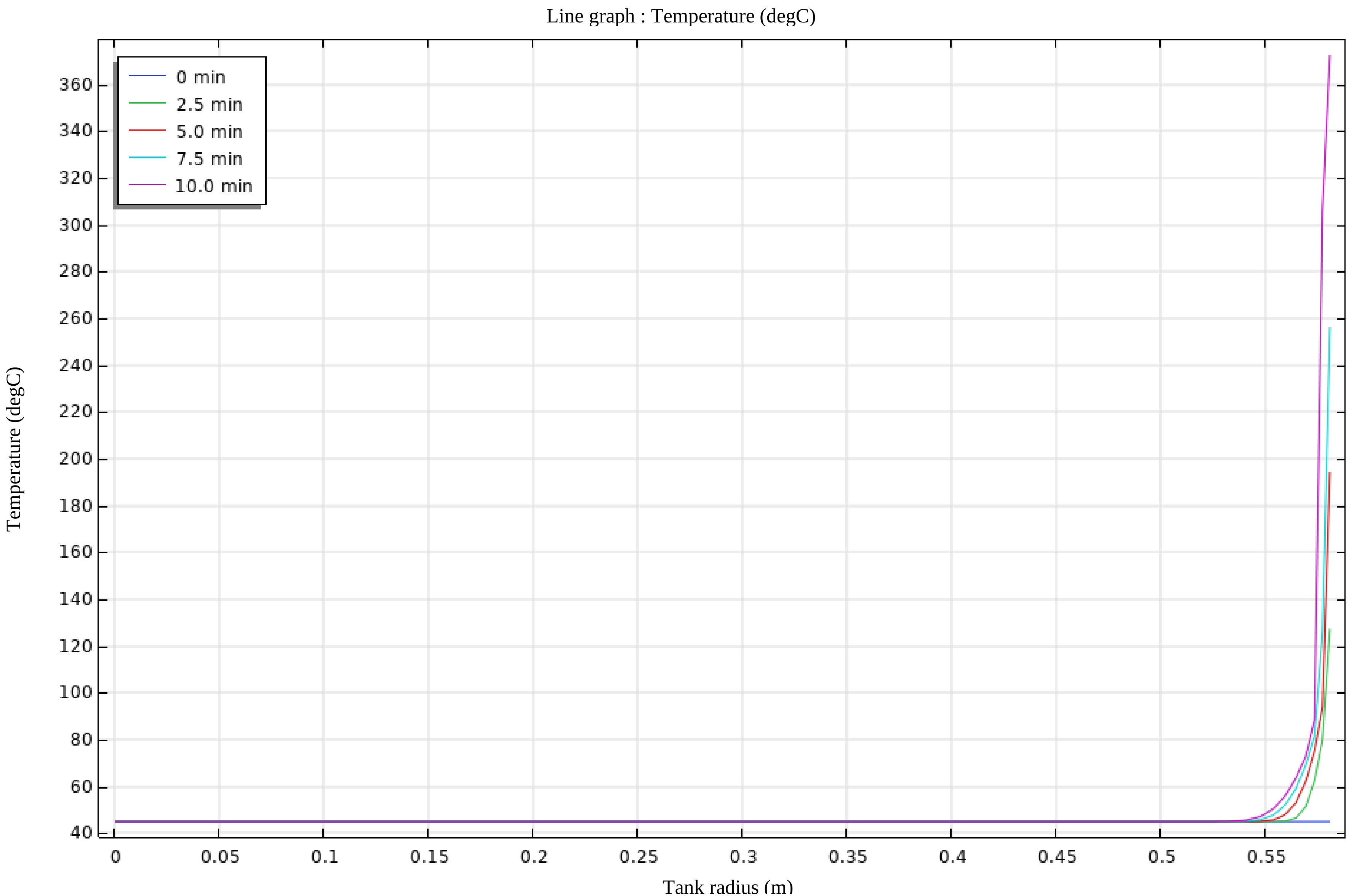

Figure 16: Modelling output – Reaction rate (10 % ullage); Constant heat flux 80 kW/m²