UN/SCETDG/58/INF.8

**Committee of Experts on the Transport of Dangerous Goods
and on the Globally Harmonized System of Classification
and Labelling of Chemicals** **3 June 2021**

Sub-Committee of Experts on the Transport of Dangerous Goods

Fifty-eighth session
Geneva, 28 June-2 July 2021
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)

Transmitted by the Institute of Makers of Explosives (IME)

Introduction

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

2. If ANEs are to be transported in bulk in portable tanks, they must also be subjected to the 8(d) test to determine suitability for containment, 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 57/INF.13 are also encountered during the 8(d) test. This claim is supported by experimental data in 57/INF.13 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 paper provides additional supporting information using numerical modeling that shows the heat and mass transport phenomena that take place within a tank containing an ANE that is subject to an external fire. The modeling is based on heat/fluid flow determined experimentally from truck tire and diesel fuel scenarios. Results from the modeling support observations in the field.

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 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 failure of the ANE to explode under these circumstances.

8. The tanker material of construction is either stainless steel or aluminium. Scandinavia mandated the use of aluminium following a large-scale test (see informal document INF.20 (21st session)) in which it was shown that the aluminium melted and released the ANE since the flame temperature, typically 900-1000 ºC, is higher than the melting point of aluminium, which is 660 ºC (Figure 1). 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 March 12, 2018, an ANE transporter with tanks constructed from aluminium was involved in a truck fire and the expected failure of the containing metal was seen (Figure 2).

9. The tanker fire scenario with steel being the material of construction was modeled using COMSOL Multiphysics®[1] 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. 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[2]. The tanker was modeled two-dimensional with a symmetry plane as shown in Figure 3. Figure 4 shows the tanker filled to 90 % (10 % ullage) with ANE with the temperature and velocity profiles of the ANE and the air in the headspace after 60 minutes of heating. Figures 5 to 7 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. The primary observations are that the bulk temperature is unchanged and with increasing ullage the convective effects, both in the ANE and the air contribute to lowering the temperature as the time increases. The temperature in all cases is well below the reaction activation temperature of 331 ºC (Oxley, et al.[3]) indicating reactions did not occur. The calculated rate of reaction is less than numerical error and is not shown in the figures referred to above.

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 steel (Figure 8). The formation of a crust was observed at the base of the tanker. The crust material is primarily solid ammonium nitrate (and possibly fuel residue) that is formed when the water gets evaporated while the ANE is in contact with the heated surface. 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 modeling work in this study.

11. The numerical simulations above with COMSOL Multiphysics® did not account for the crust formation described in paragraph 10 above. The model was enhanced to include this phenomenon and a more conservative heat flux of 80 kW/m^2 also used. Results of the new runs are shown in Figures 9 to 11. 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 ~0.1 m of arc length. This observation is due to the equivalent thermal diffusion length scales (which solely depend upon physical properties) between the two simulations. The crust buildup is shown in Figure 10, where there is an increase in the

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[1] 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.

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

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

volume fraction with time, as would be expected, with growth at 20 minutes ~0.04 m increasing to ~0.07 m at 60 minutes. Although the crust was not measured in actual transport fire event, the anecdotal information was that it was a ‘thin crust’. The model was run with the lower heat flux of 24 kW/m^2 to determine the extent of crust formation with this lower heat flux. The results are given in Figure 11 where, after 60 minutes, ~0.02 m of crust is formed. These models, with the two different heat fluxes, demonstrate that there will be crust formation, with the higher heat flux forming a thicker crust. These results reflect the phenomenon seen in transport fires in steel tanks, the most recent being the event in the USA (Figure 8).

12. The modeling work clearly shows the behavior of an ANE in a tank when 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 modeling 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 an explosion of the bulk of the ANE resulting from transport fires as described. The tank would either fail, 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 be subjected to the 8(d) test and can be considered suitable for containment in portable tanks as oxidizing substances based on their MBPs that far exceed the pressures that 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 indicated by blue underscored 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 18.7.1.1 of the MTC as follows (new text indicated by blue underscored 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 18.8.1.1 of the MTC as follows (new text indicated by blue underscored 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."

18. Amend 18.8.1.4.1 of the MTC as follows (new text indicated by blue underscored 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 taken from UN/SCETDG/21/INF.20 showing the aluminium 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 1-4: The tank after the fire (rear view)

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

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

Figure 3. Modeling of Tanker showing the Axisymmetric Geometry Used

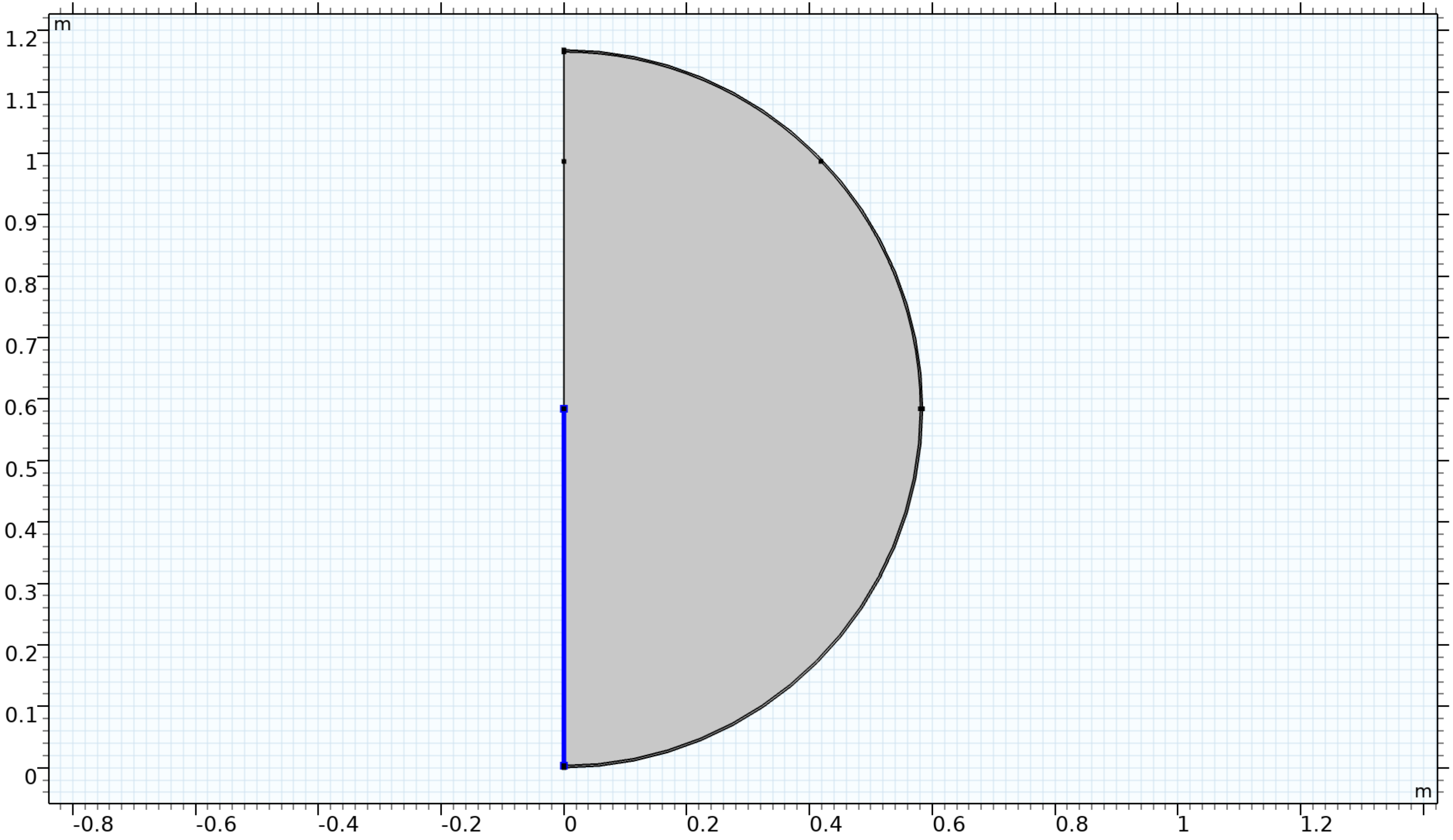

Figure 4: Modeling Output – Temperature and Velocity Profiles for 10 % Ullage Tanker at 60.15 minutes; 24 kW/m^2

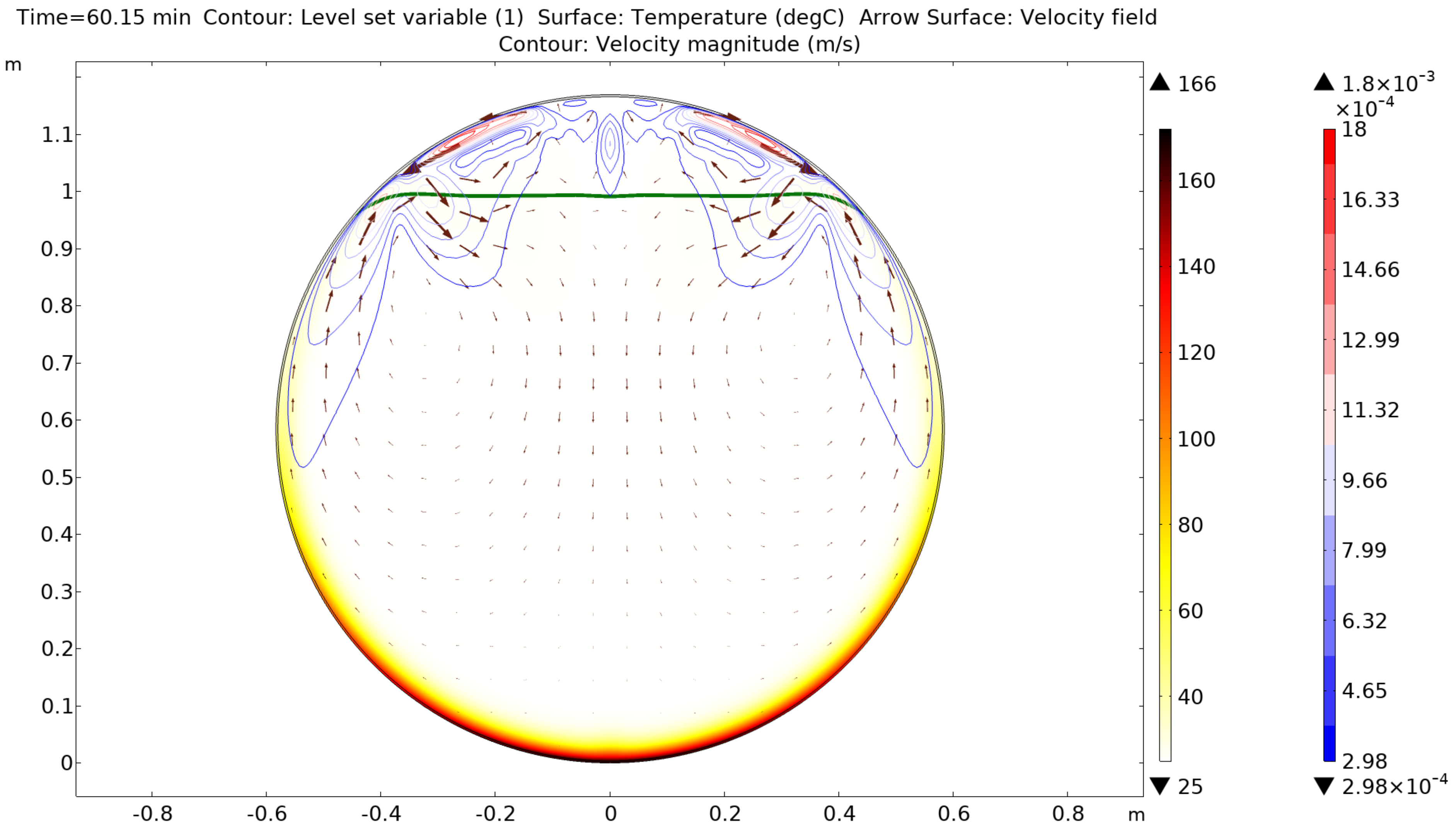

Figure 5: Modeling Output – Temperature Profile with Time for Full Tanker (0 % Ullage); Heat Flux 24 kW/m^2

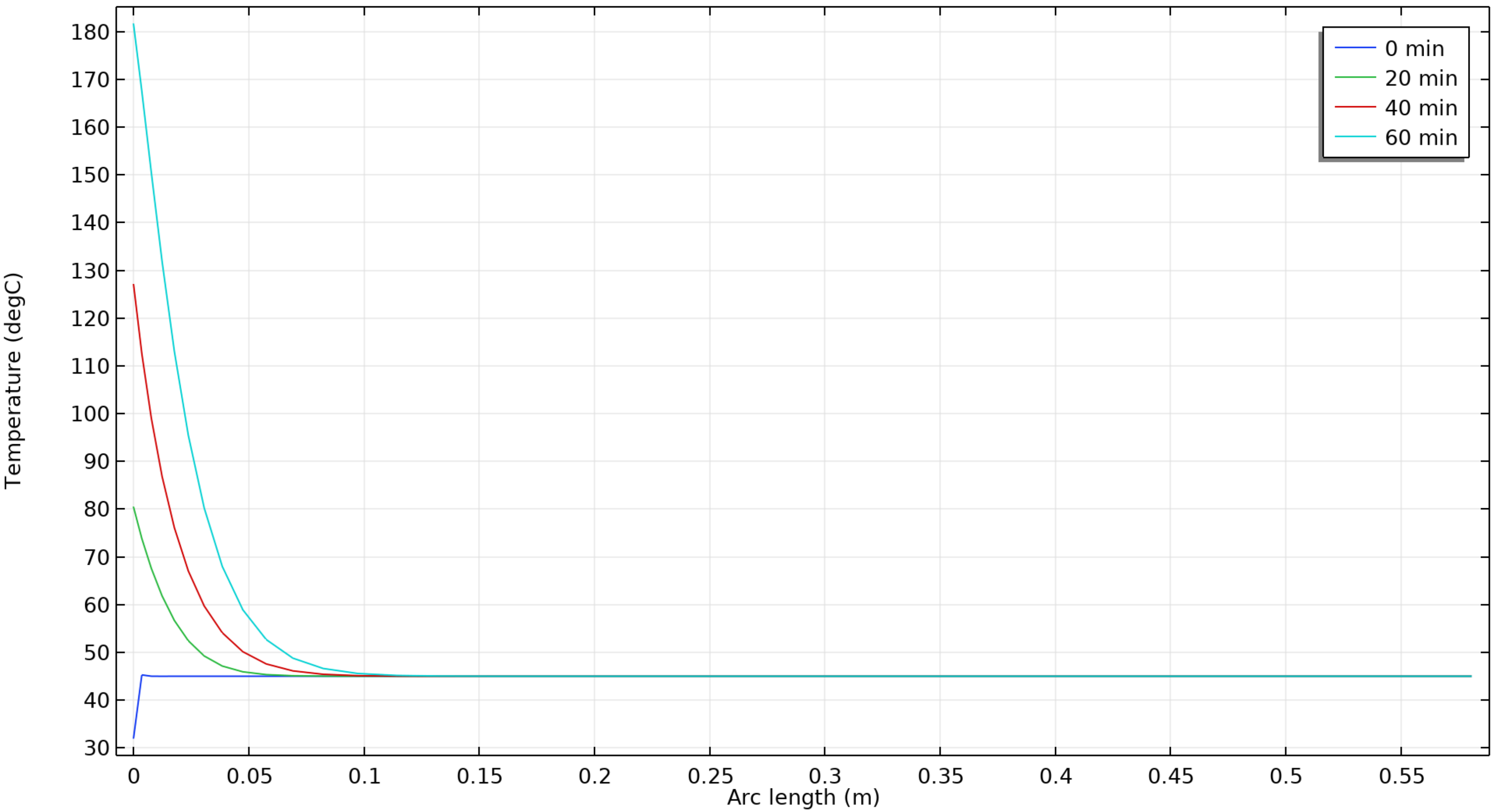

Figure 6: Modeling Output – Temperature Profile with Time for 90 % Full Tanker (10 % Ullage); Heat Flux 24 kW/m^2

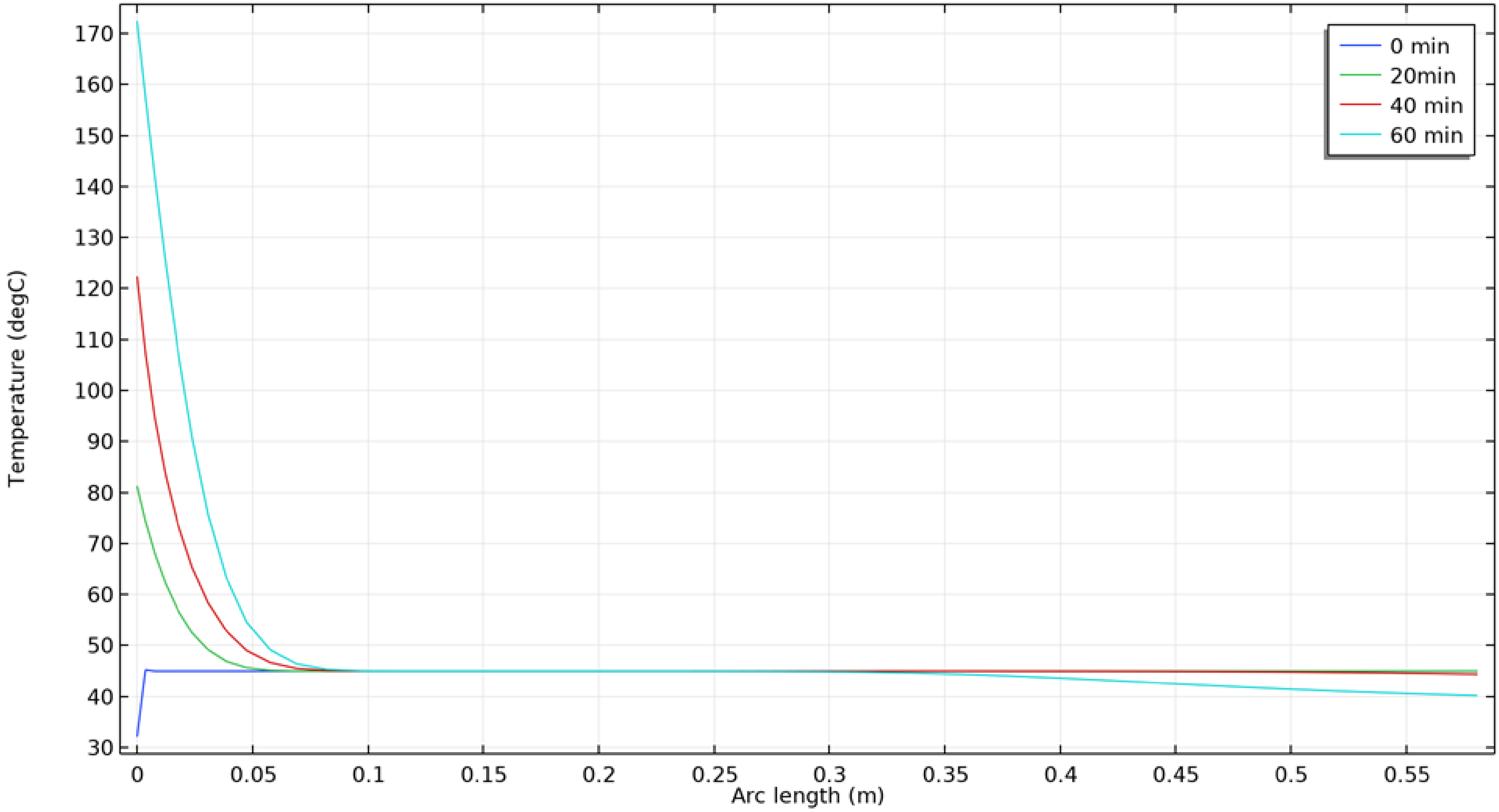

Figure 7: Modeling Output – Temperature Profile with Time Tanker with 10 % Heel (90 % Ullage); Heat Flux 24 kW/m^2

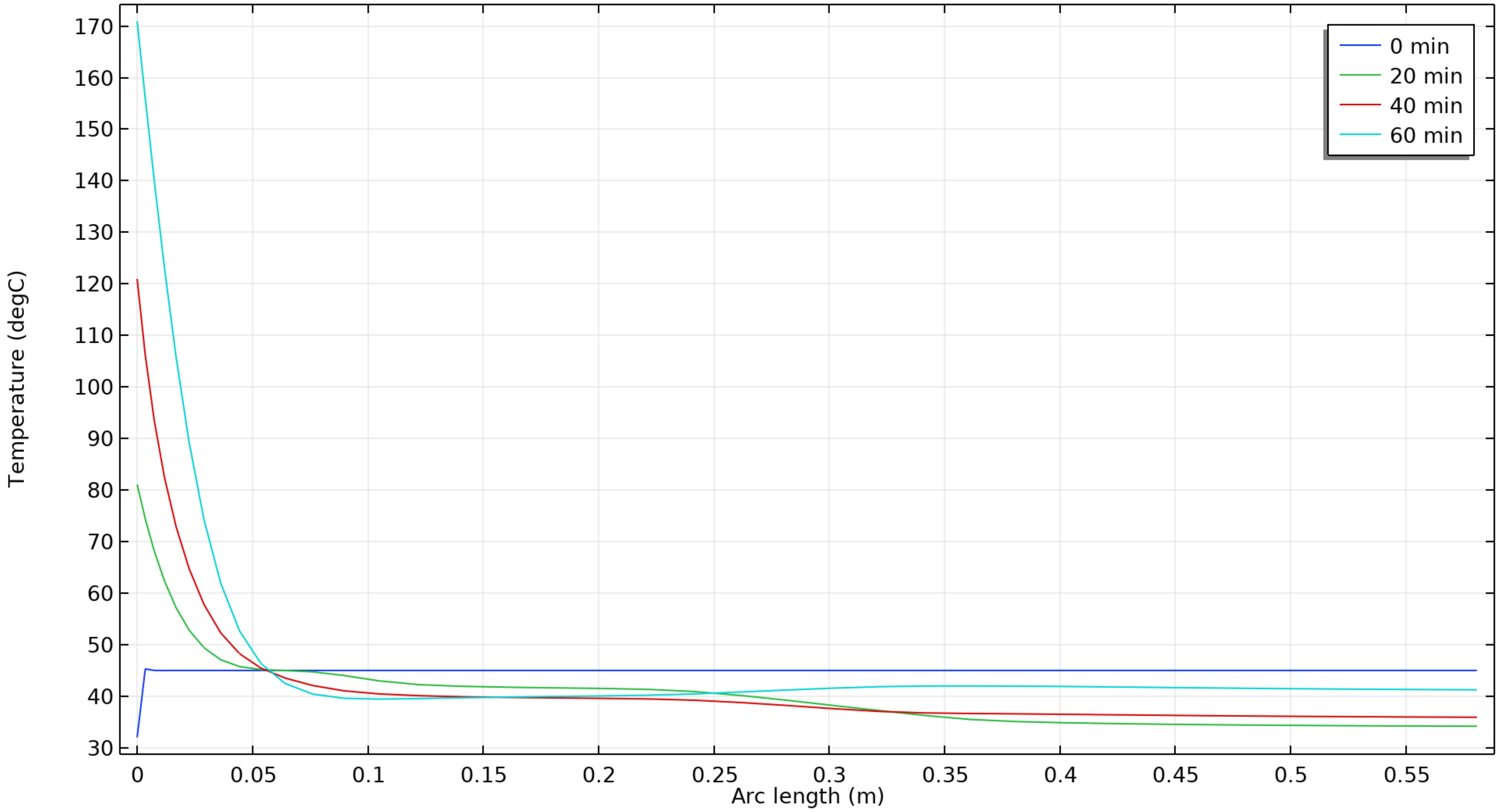

Figure 8: Transport Fire Incident, South Carolina, USA, July 12, 2018

- Tractor pulling tanker trailer blew its front tire
- Driver lost control of vehicle crossing median striking three other vehicles en route.
- Cab caught on fire while crossing median.

- Minor injuries to driver and struck vehicles’ occupants.
- Residents evacuated to 1-mile radius.
- ANE transferred to another tanker once fire was put out.
- ANE had 18.26% water

Figure 9: Modeling Output – Temperature Profile with Time; Tanker 90 % Full (10 % Ullage); Heat Flux 80 kW/m^2

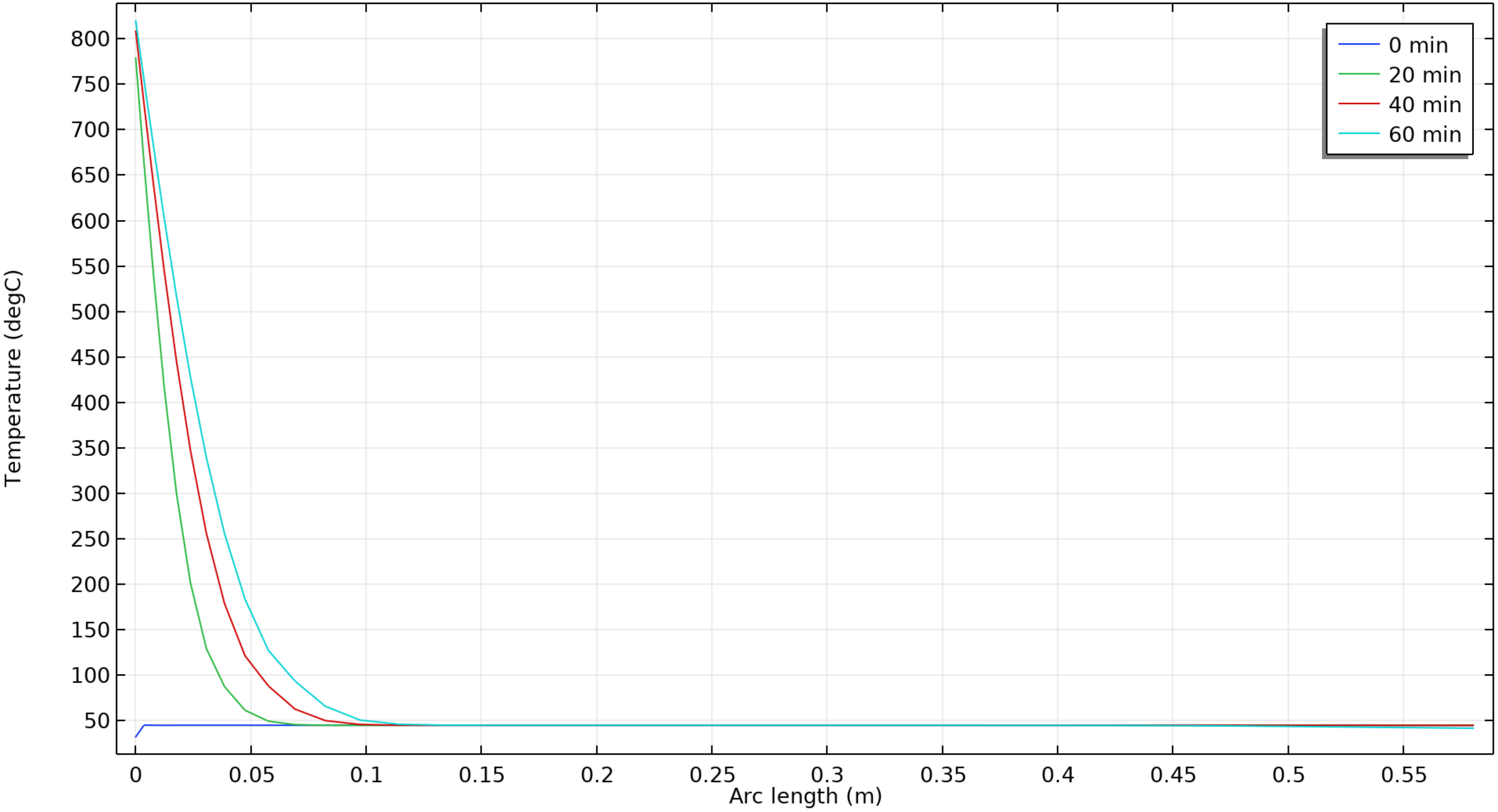

Figure 10. Modeling Output – Volume Fraction of crust with Time; Tanker 90 % Full (10 % Ullage); Heat Flux 80 kW/m^2

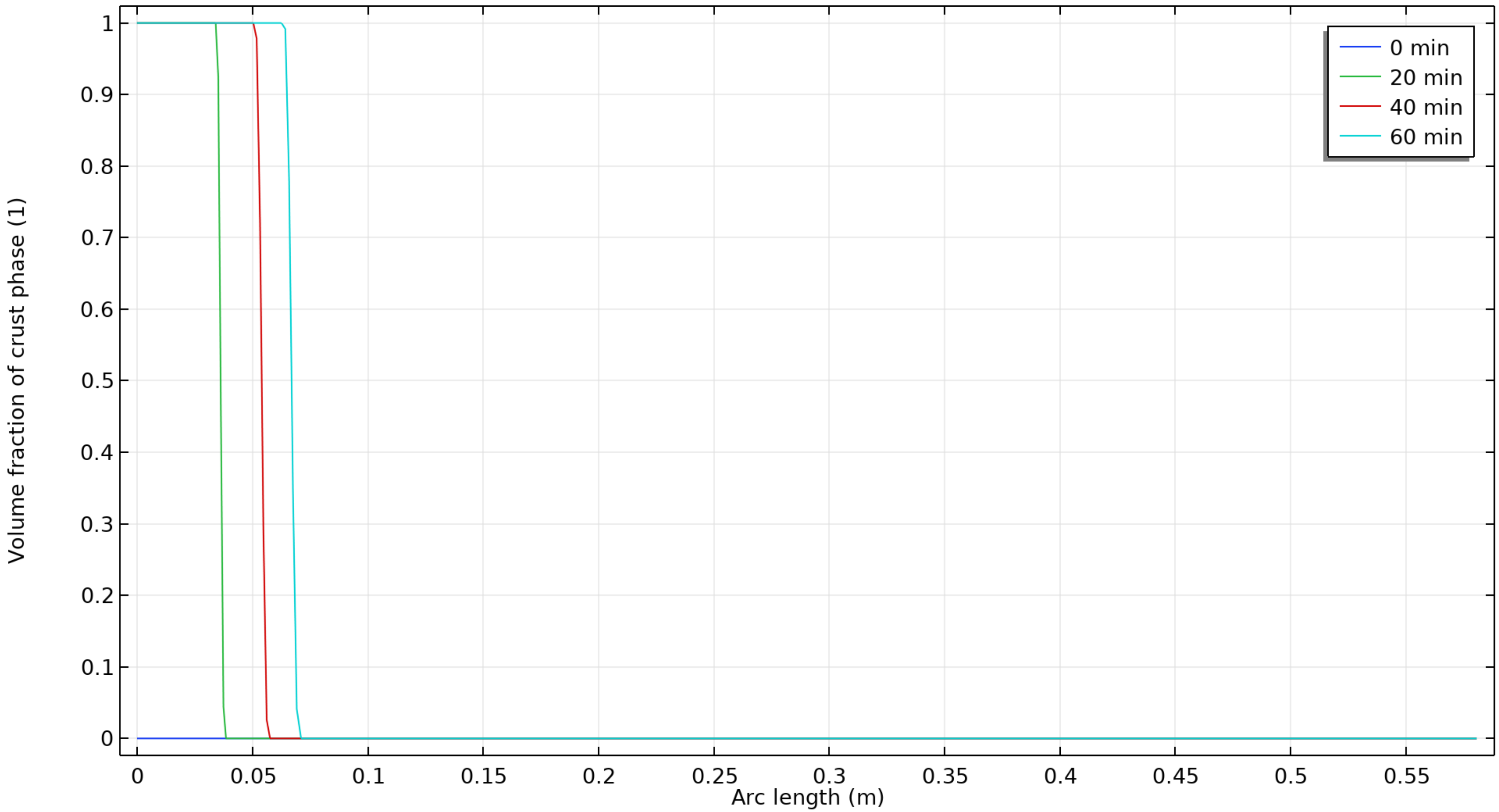

Figure 11. Modeling Output – Volume Fraction of crust with Time; Tanker 90 % Full (10 % Ullage); Heat Flux 24 kW/m^2