Oxygen enrichment mechanisms of condensed phase air in liquid hydrogen environments

Janet Welch, Wayne Rattigan, Janni Vizma, Greg Wray

Presented by Janet Welch

ELVHYS

PROTECTING PEOPLE AND PLACES HSE

- European collaborative research project investigating the safety of liquid hydrogen (LH_2) transfer technologies
- 3-Year project
- 8 European Partners

HSE Health & Safety Executive
Ulster University
DLR
NTNU Norwegian University of Science and Technology
KIT Karlsruher Institut für Technologie
Air Liquide
ALMA MATER STUDIORUM UNIVERSITÀ DI BOLOGNA

Co-funded by the European Union
Clean Hydrogen Partnership
UK Research and Innovation

Introduction

- The hazard of oxygen enrichment of a hydrogen atmosphere is well known.
- Experimental evidence of an oxygen enriched environment leading to an explosion was seen at the HSE in 2014 and was presented at ICHS 2021.*

Condensed air following liquid hydrogen release

Comparison between fireball caused by (a) the initial flash fire and (b) the secondary explosion.

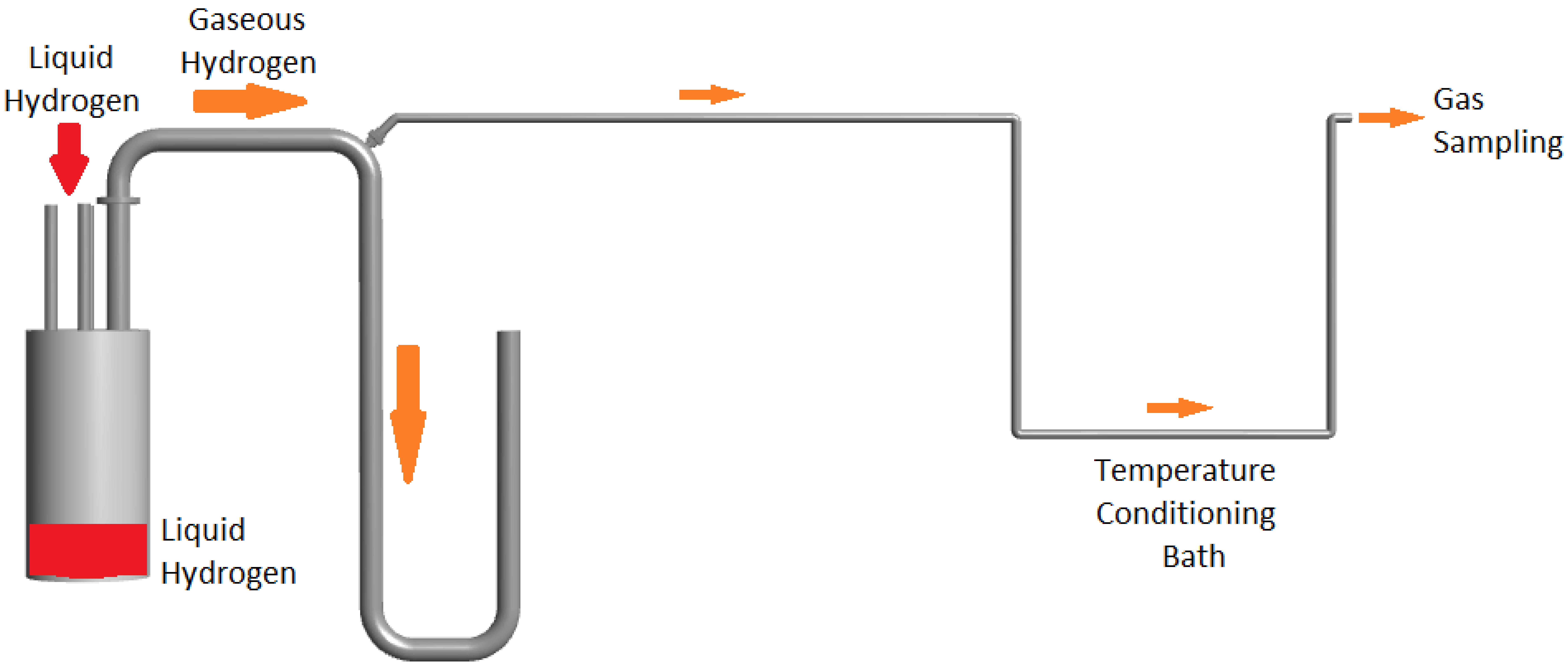
* Atkinson G. (2021) Condensed phase explosions involving liquid hydrogen. International Association on Hydrogen Safety: International Conference on Hydrogen Safety.

Introduction

- Theoretical studies and practical work have shown it is possible for liquid hydrogen to condense oxygen from the air and create an oxygen enriched liquid/ solid phase.
- The mechanisms and likelihood of this occurring when atmospheric air (21 vol% oxygen) encounters a liquid hydrogen spill has not previously been experimentally studied.
- This presentation describes work carried out by the UK Health and Safety Executive, Science Division, to study the mechanisms by which oxygen enrichment can occur and the likelihood of this occurring in a liquid hydrogen spill scenario.

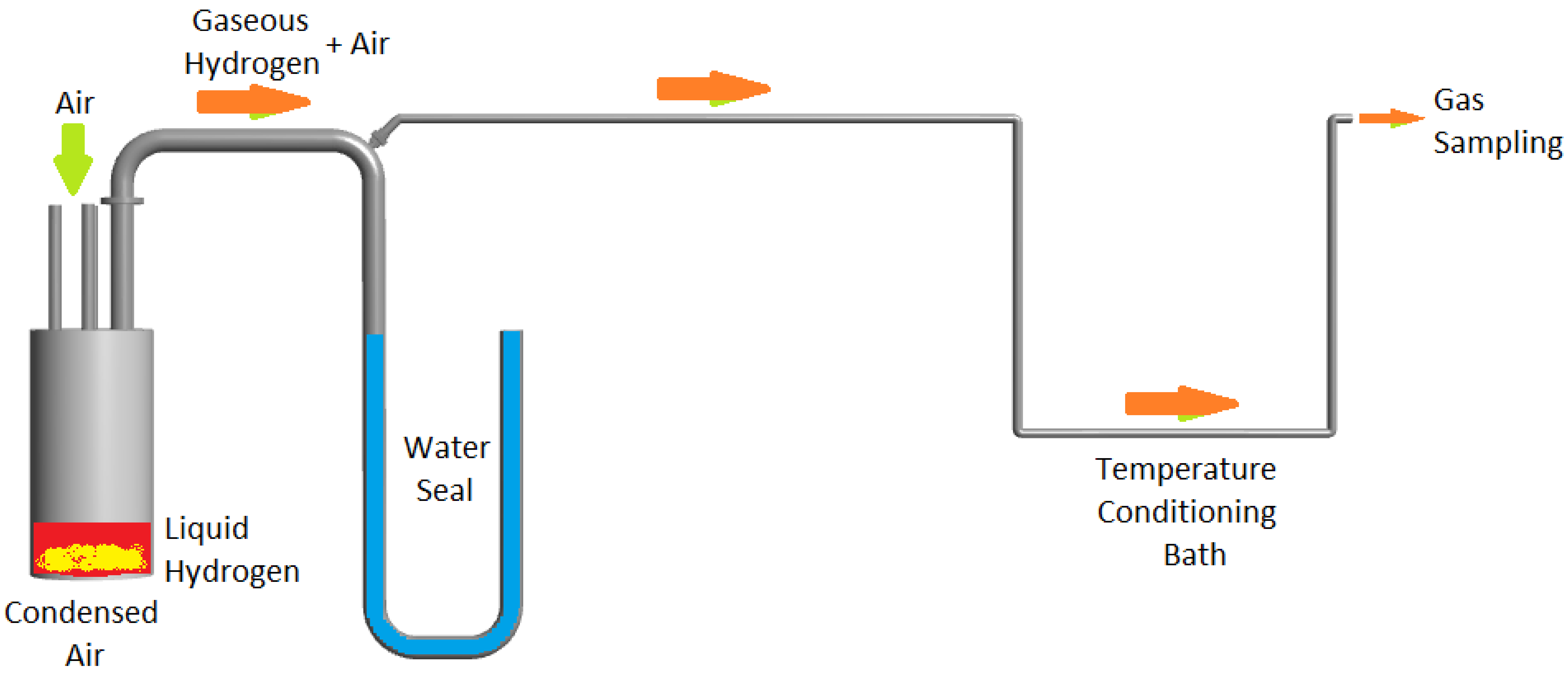
Experimental Methodology – Stage One

- Container surrounded by foam which is temperature conditioned by multiple hydrogen fills to reduce the hydrogen evaporation rate before the final fill to level.



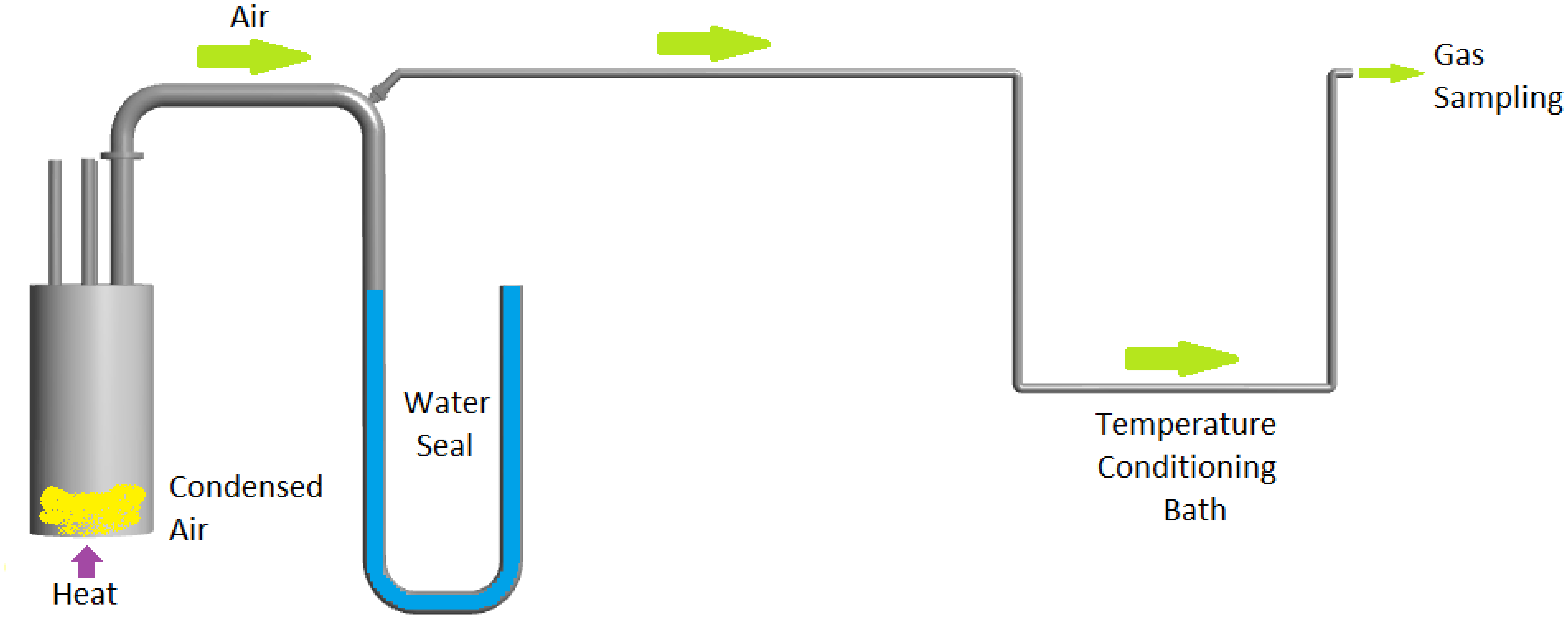
Experimental Methodology – Stage Two

- Ambient bottled air was introduced using a flow controller, the hydrogen takes heat energy from the air, condensing the air while the liquid hydrogen boils.



Experimental Methodology – Stage Three

- Stage Three started once there was no hydrogen detected in the vapour phase.
- The condensed air was heated and boiled off.



Results

- Three tests were undertaken.

Test	1	2	3
Liquid hydrogen fill level (dm^3)	13	27	54
Calculated volume of liquified oxygen (dm^3)	0.6	0.9	1.5
Calculated volume of liquefied nitrogen (dm^3)	3.8	6.0	9.7

- Three distinct periods of oxygen enrichment were observed, to be discussed.
- This presentation discusses the evidence observed for the phase changes associated with the air components and the periods of oxygen enrichment.

ELVHYS

PROTECTING PEOPLE AND PLACES HSE

Liquid Oxygen and Nitrogen form a Eutectic Mixture

- Liquid oxygen and liquid nitrogen are completely miscible with each other and form a eutectic mixture.
- During the air freezing process impure crystals are formed, when nitrogen crystalises up to 20 % of the nitrogen atoms within the crystal structure can be replaced with oxygen atoms.*
- In this work we are only interested in the process of eutectic melting.
- A eutectic solid is a solid mixture of two or more components that melts as a mixture at a temperature below each components pure melting point.

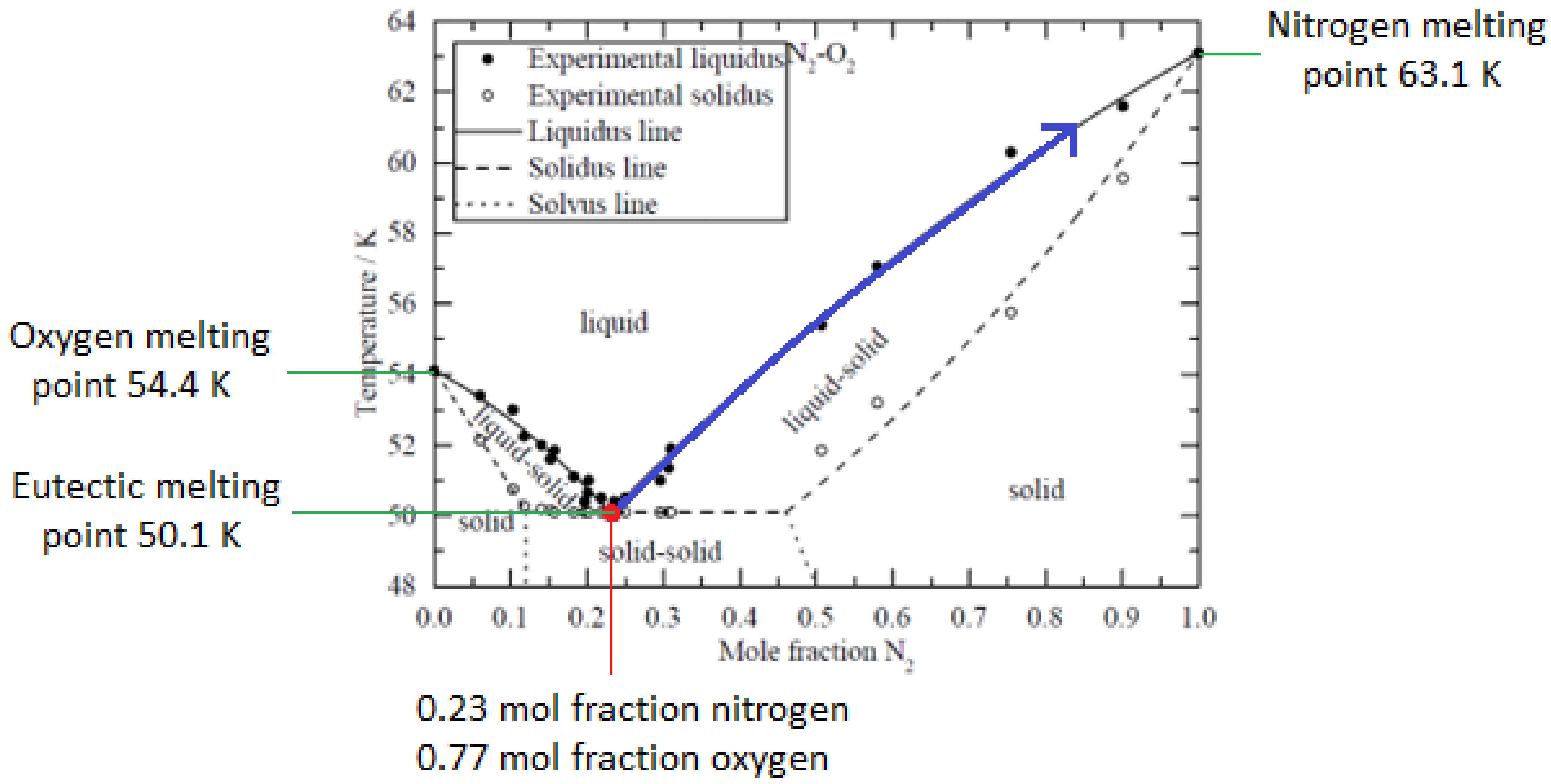
* Sihachakr D., Loubeyre P. (2004) *O_2 / N_2 mixtures under pressure: A structural study of the binary phase diagram at 295 K*. Physical Review B. 70(13):134105

ELVHYS

PROTECTING PEOPLE AND PLACES HSE

Explaining Eutectic Melting using the Oxygen and Nitrogen Binary Phase Diagram

- As the oxygen starts to melt it dissolves some of the solid nitrogen into the liquid phase. This impure liquid has a lower boiling point, the eutectic melting point (red dot).
- The mixture melts at the eutectic point until all the minor component, oxygen, has melted.
- As the remaining solids melt the melting point increases along the liquidus line (blue arrow).



Annotated binary phase diagram from Kochenburger T.M., Oellrich L.R. (2015) *Evaluation of a two-stage mixed refrigerant cascade for HTS cooling below 60 K*. Phys. Procedia, 67:227–232.

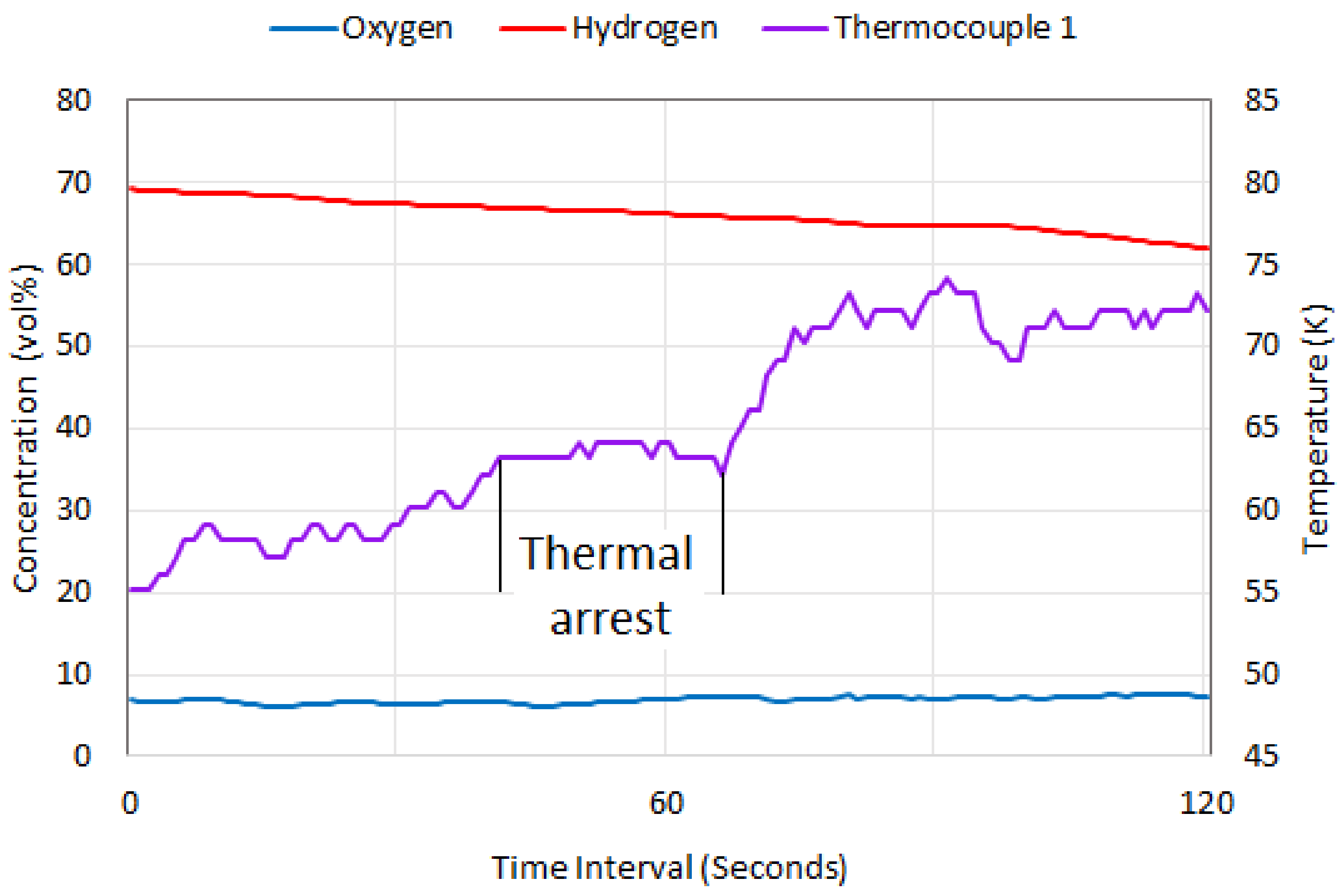
PROTECTING PEOPLE AND PLACES HSE

ELVHYS

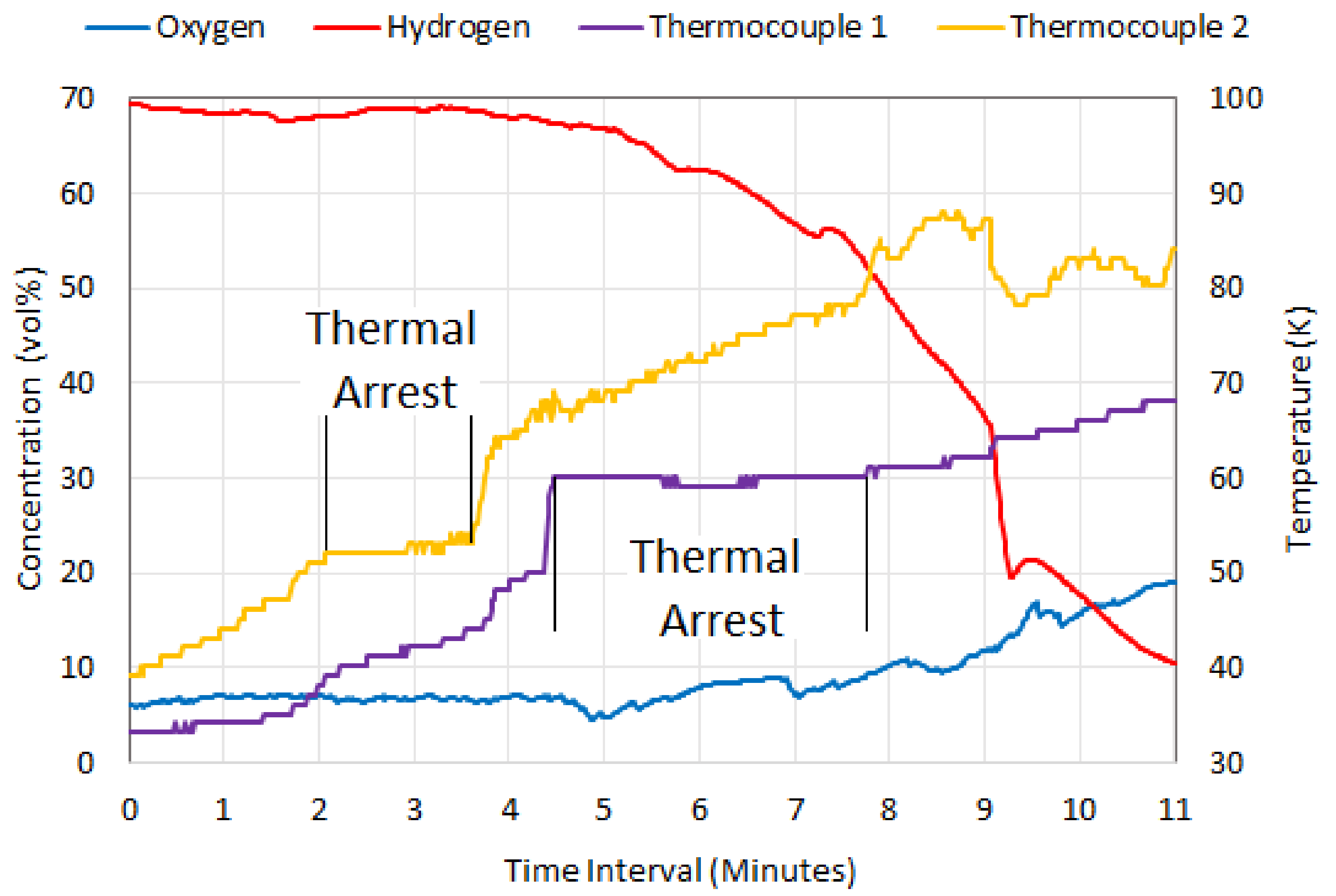
Evidence of Eutectic Melting Observed at the End of Stage Two

- At the end of stage two as the last of the liquid hydrogen boils-off the temperature(s) at the bottom of the container start to rise.
- ‘Warm’ air is still being introduced at the top of the container.
- There is still hydrogen present in the container vapour space.

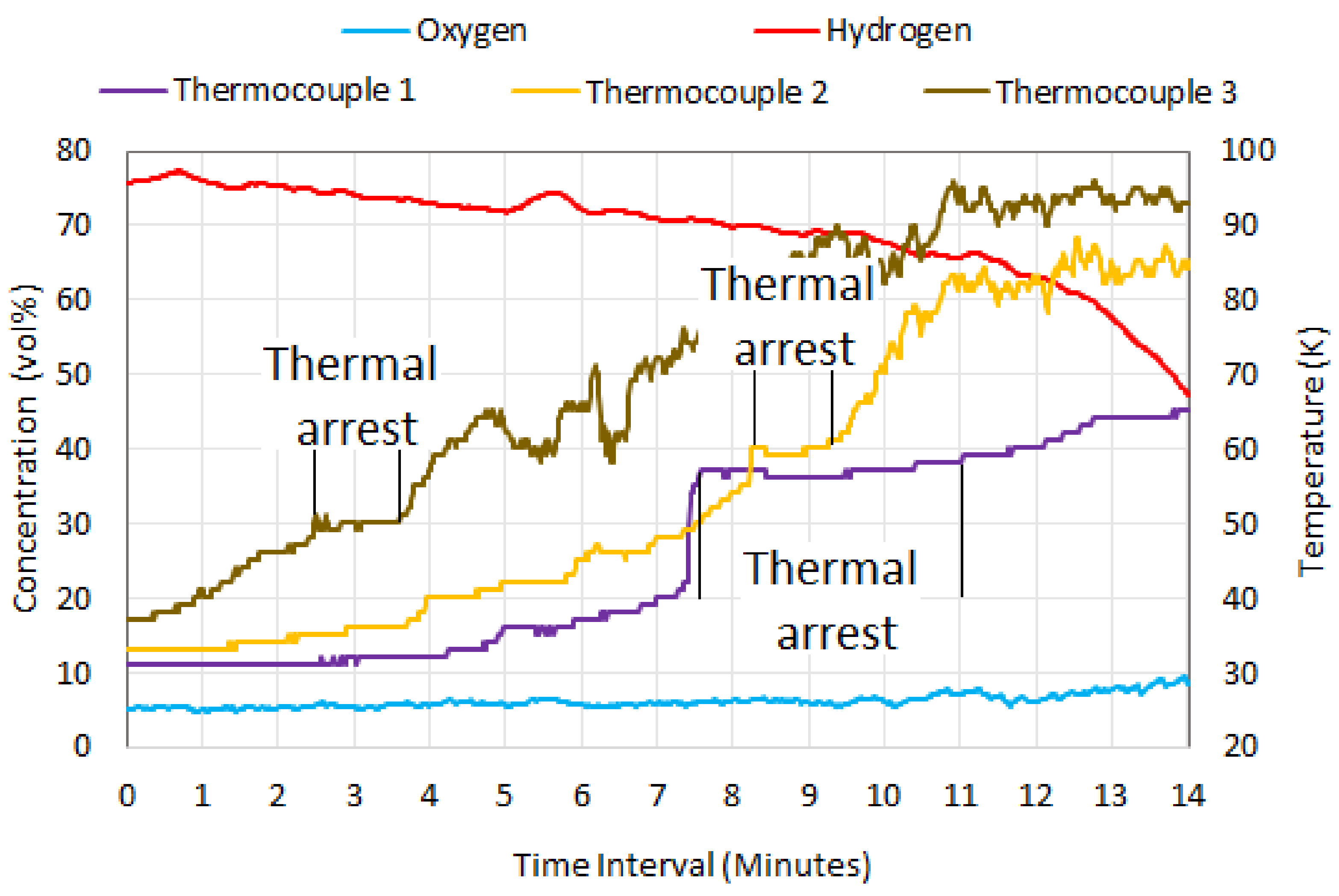
Test 1



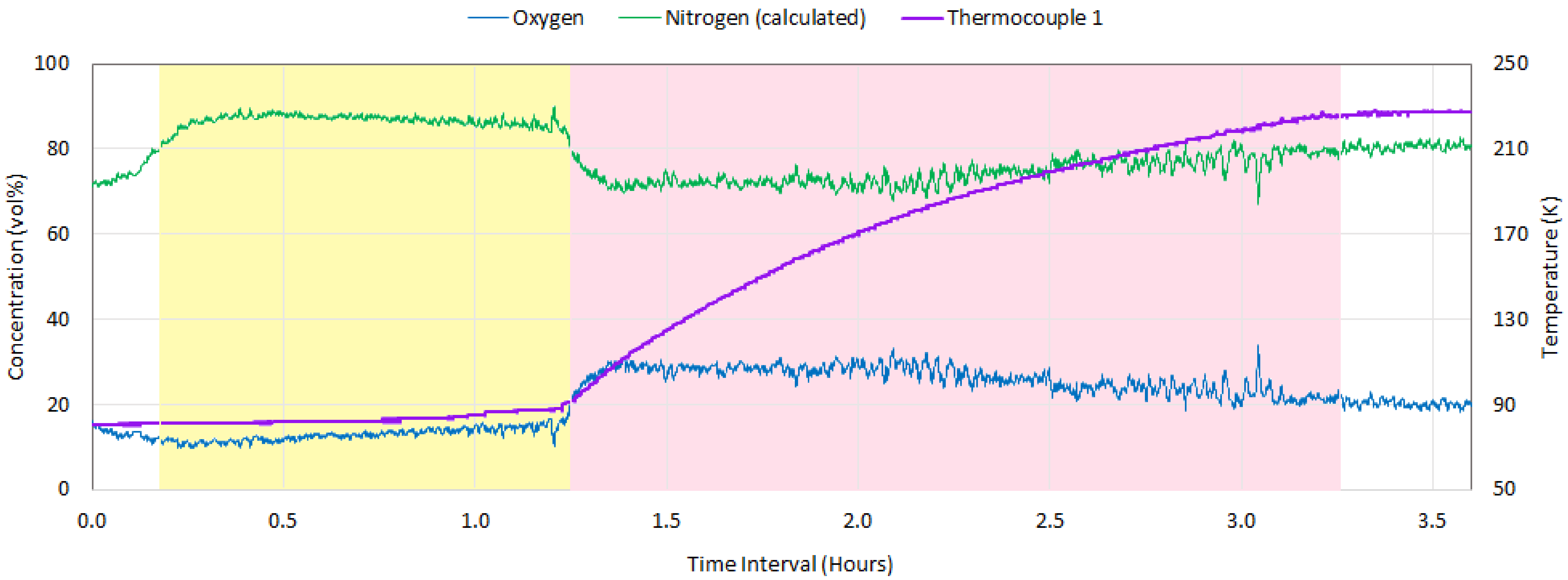
Test 2



Test 3



Test 1 - Evidence of Oxygen Enrichment of the Liquid and Vapour Air Phase during Stage Three.



- The last trace of hydrogen in vapour phase was observed just before the yellow box.
- Yellow box = Vapour phase oxygen deficient, liquid phase becomes oxygen enriched.
- The liquid phase is calculated to be at peak oxygen enrichment level at the yellow/pink boundary.
- Pink box = Vapour phase oxygen enriched with the level of enrichment dropping over time.

Conclusions

- Evidence for a complicated solid to vapour phase change system for solid air products has been observed in these tests. The system is characterised by 5 main periods.
  1. Pure eutectic melting of an oxygen and nitrogen mixture, resulting in an oxygen enriched liquid phase.
  2. Melting of the remaining solid nitrogen, diluting the oxygen enriched liquid phase.
  3. Boil-off from nitrogen, resulting in an oxygen enriched liquid phase.
  4. The oxygen enriched liquid phase boil-off, resulting in a period where both the liquid and vapour phase are oxygen enriched.
  5. The liquid phase ceases to be oxygen enriched, but the vapour phase continues to be oxygen enriched until it is dispersed from the liquid surface.

Conclusions

- The hazard of an oxygen enriched condensed air phase being present in an environment where there has been a liquid hydrogen spill has been shown to be credible, and an ensuing condensed phase explosion should an adequate ignition source be present.
  - First, there is the potential for a condensed phase explosion to occur shortly after the spill has ceased, when both hydrogen vapours and an oxygen enriched liquid phase may be present.
  - Second, when liquid nitrogen evaporates it leaves an oxygen enriched condensed air phase.
  - Finally, an oxygen enriched vapour was present from a prolonged period of time after the initial spill.

PROTECTING PEOPLE AND PLACES

Acknowledgements

- European project partners funded by the European Union
- HSE contribution co-funded by UKRI, Lloyds Research Foundation and HSE

ELVHYS project No. 101101381 is supported by the Clean Hydrogen Partnership and its members. UK participants in Horizon Europe Project ELVHYS are supported by UKRI grant numbers 10063519 (University of Ulster) and 10070592 (Health and Safety Executive).

PROTECTING PEOPLE AND PLACES HSE

ELVHYS

[ELVHYS EU project - Hydrogen Safety, Liquid Hydrogen Transfer](https://elvhys.eu/home)

https://elvhys.eu/home

Thank you. Questions?

Janet.Welch@hse.gov.uk

- **Disclaimer**: the contents of this presentation, including any opinions and/or conclusions expressed, are those of the authors alone and do not necessarily reflect HSE policy
- To review HSE areas of research interest, search here: https://ari.org.uk/