Pressure Relief of Liquids Containing Suspended Solids

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HSE GREAT LAKES SYNGENTA

(RR 085, £25, ISBN 0 7176 2699 7,
see http://hse.gov.uk/flist/august.htm -pdf file available)

Background

- **Much research on relief system design of chemical reactors**
  - ***DIERS***
- **Guidance produced**
  - ***CCPS Guidelines***
  - ***HSE Workbook***
- **No theoretical work and little experimental validation for systems containing suspended solids**

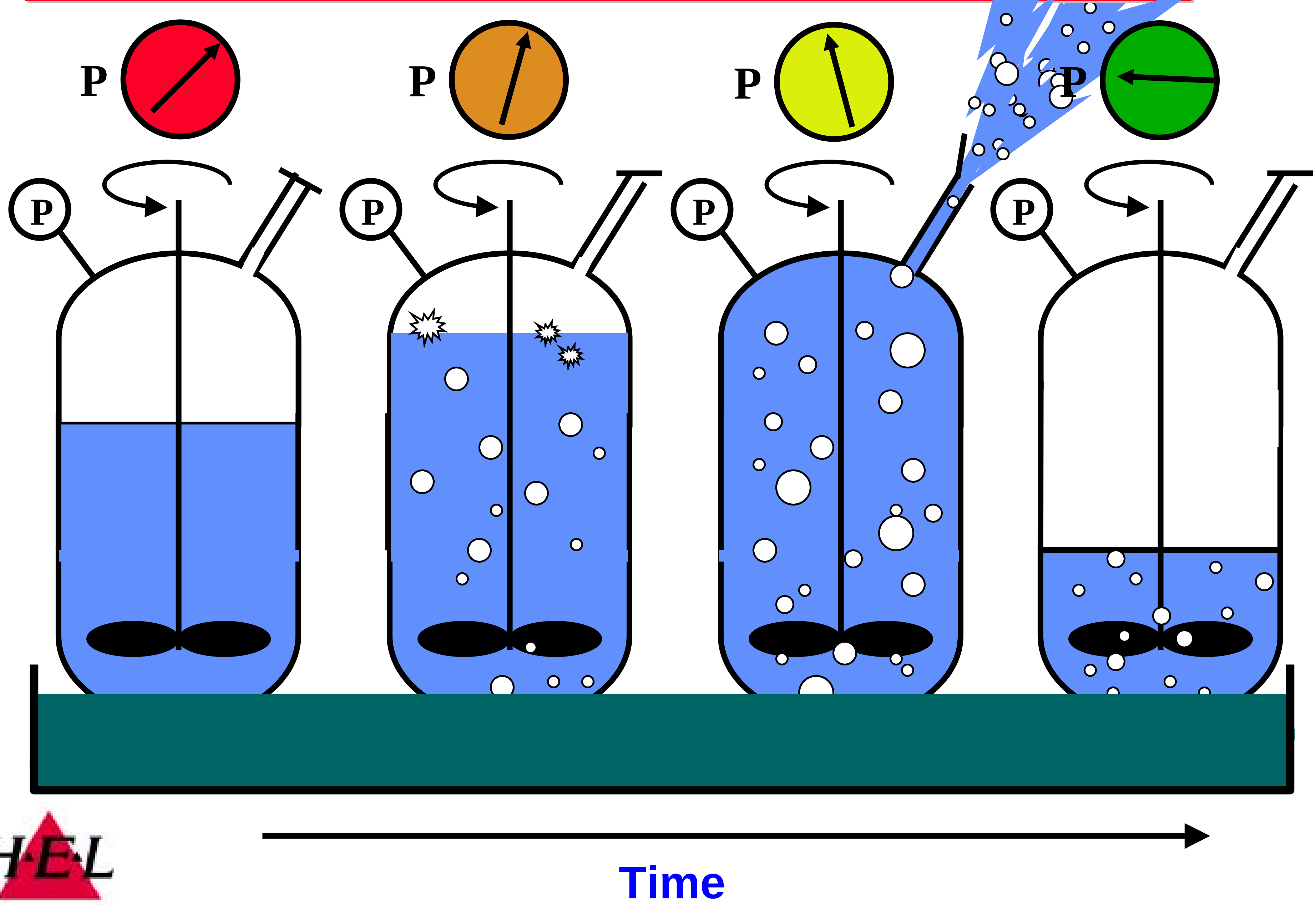
In the UK a runaway reaction incident is reported to the HSE approximately every 3 weeks.

A well organised reactor room like this can quickly be destroyed, and people and the environment harmed, in an overpressurisation bursts the weakest part of the reactor system

Where do solids occur?

- **Reactants**
  - *E.g. in resin reactions*
- **Catalysts**
  - *E.g. hydrogenation reactions*
- **Products/ by-products**
  - *E.g. suspension polymers, crystalline products*
- **Intermediates?**

2 PHASE VENTING: liquid/vapour or gas



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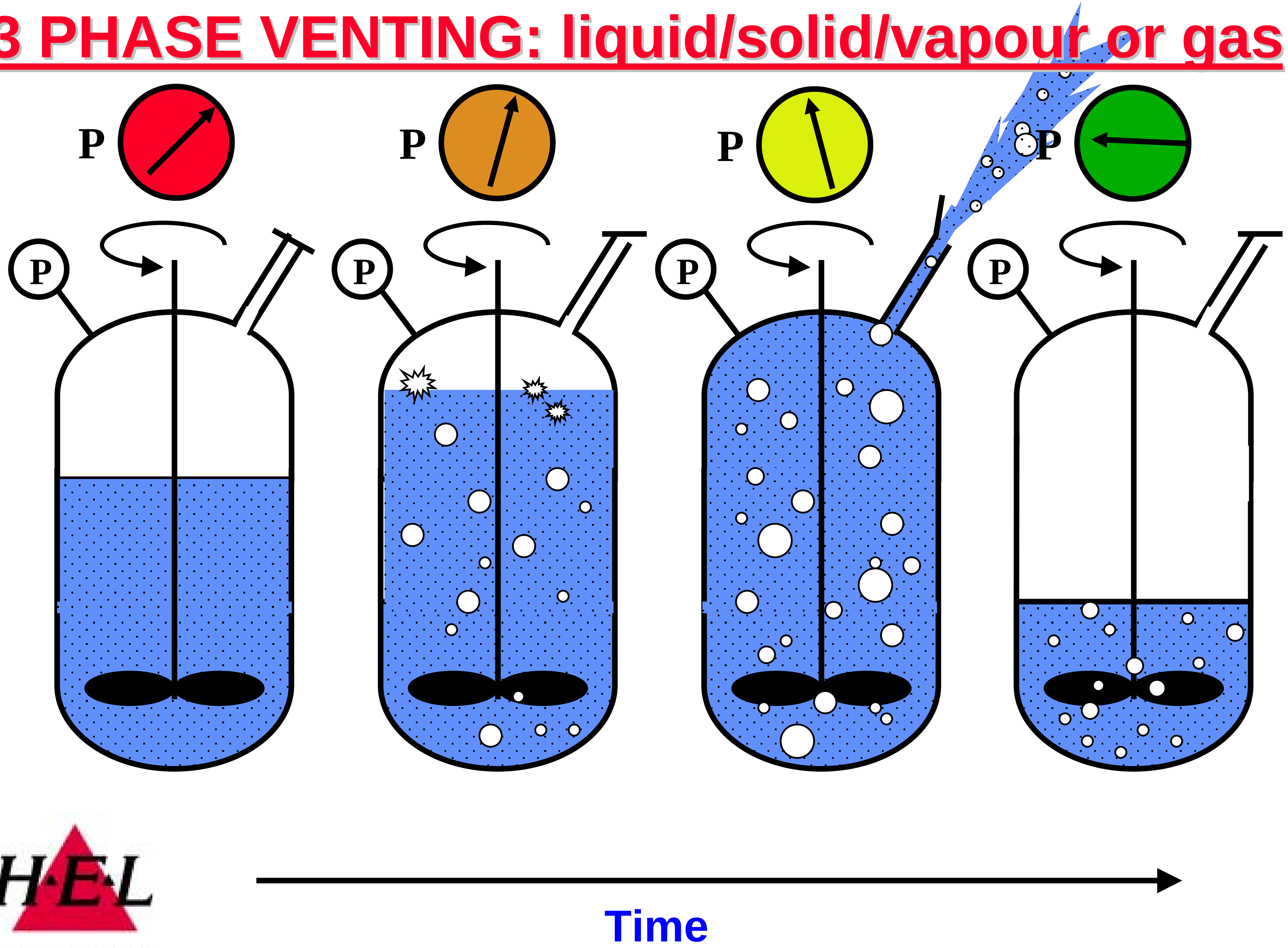
3 PHASE VENTING: liquid/solid/vapour or gas



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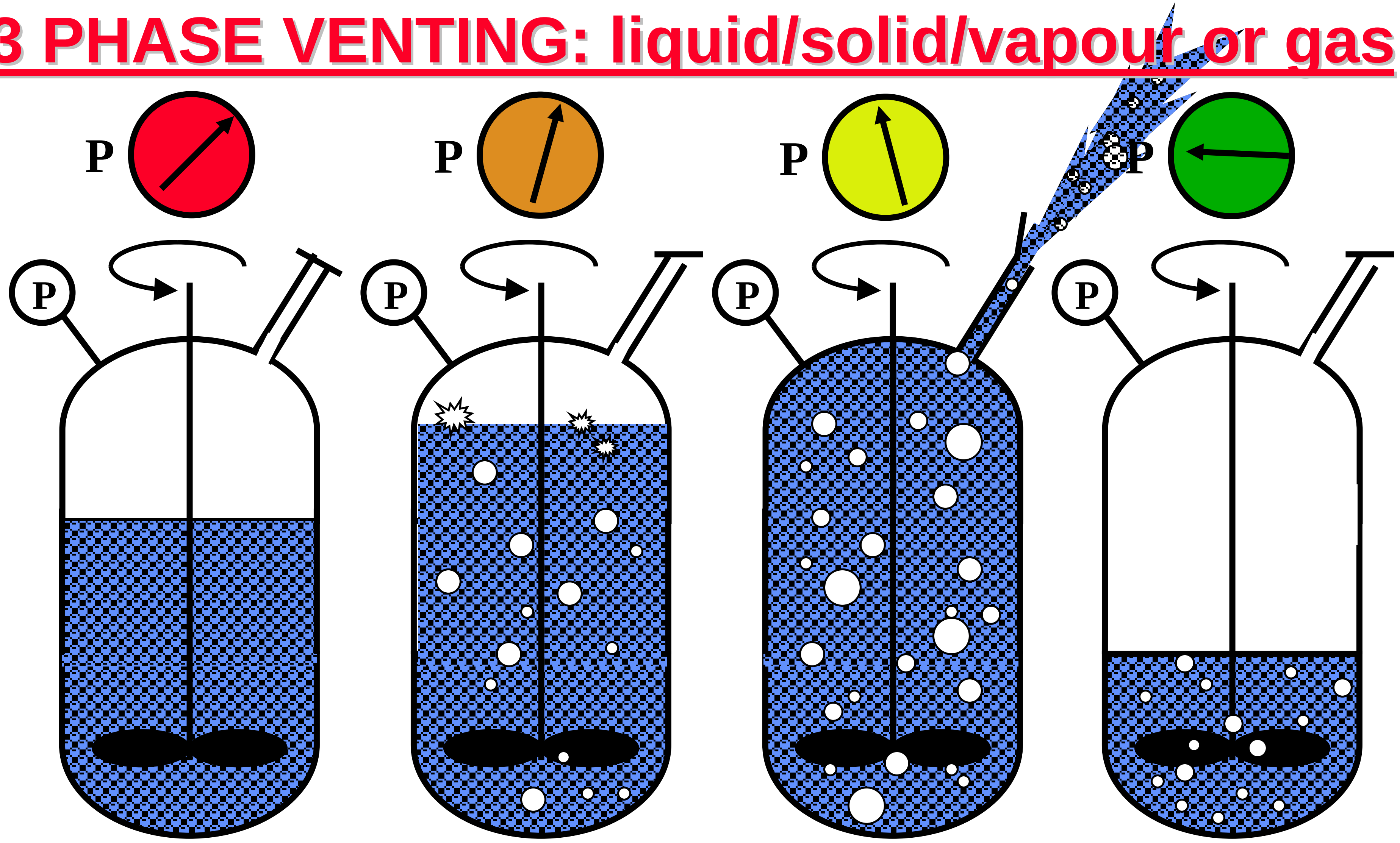

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3 PHASE VENTING: liquid/solid/vapour or gas

- TO WHAT EXTENT DOES THE SUSPENDED SOLID ALTER THE VENTING RATE AS COMPARED WITH 2 PHASE VENTING?

- CAN YOU IN SOME CIRCUMSTANCES USE THE DIERS 2 PHASE EQUATIONS TO SIZE A VENT FOR A 3 PHASE FLOW?

- IF SO, WHAT ARE THESE CIRCUMSTANCES AND HOW DO YOU DO IT?

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3 PHASE VENTING: liquid/solid/vapour or gas

PRIMARILY A HYDRODYNAMIC PROBLEM? THEREFORE INITIALLY STUDY NON-REACTING SYSTEMS

SUPERHEATED WATER OR WATER/GLYCEROL

ADDED SOLIDS OF DIFFERENT DENSITIES THAT WERE BOTH LESS THAN, AND GREATER THAN, THAT OF THE LIQUID

SOLIDS WERE GLASS, APPROXIMATELY SPHERICAL, (SOLID AND HOLLOW) OF RELATIVELY NARROW SIEVE CUTS

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3 PHASE VENTING: liquid/solid/vapour or gas

Much initial experimental work to:

- **Create reproducible experimental procedures**
- **Get rid of initial dissolved gases**
- **Check whether vapour-liquid equilibrium conditions are closely approached during heat up and blowdown**
- **Ensure thermocouples give representative readings, e.g. of vapour temperature. Need to insulate thermocouples from headplate**
- **Ensure dynamics of instrumentation and software do not intrude – not true for balance readings**

3 PHASE VENTING: liquid/solid/vapour or gas

VARIABLES (FACTORS)

1. Fill level
2. Relief pressure
3. Nozzle diameter
4. Particle diameter
5. Particle density
6. Liquid density
7. Stirring intensity
8. Liquid viscosity
9. Particle concentration
10. Presence of surfactant
11. Reaction

THE PRESSURE RELIEF VENTING PROCESS

RESPONSES

- Blowdown times to P_f
- Blowdown times to T_f
- The overpressure
- Liquid carry over
- Solid carry over
- Rates of depressurisation

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Statistical design of experiments
2 level factorial design (full or fractional)

Pneumatically actuated ball valve, micro switch and nozzle holder

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3 PHASE VENTING: liquid/solid/vapour or gas

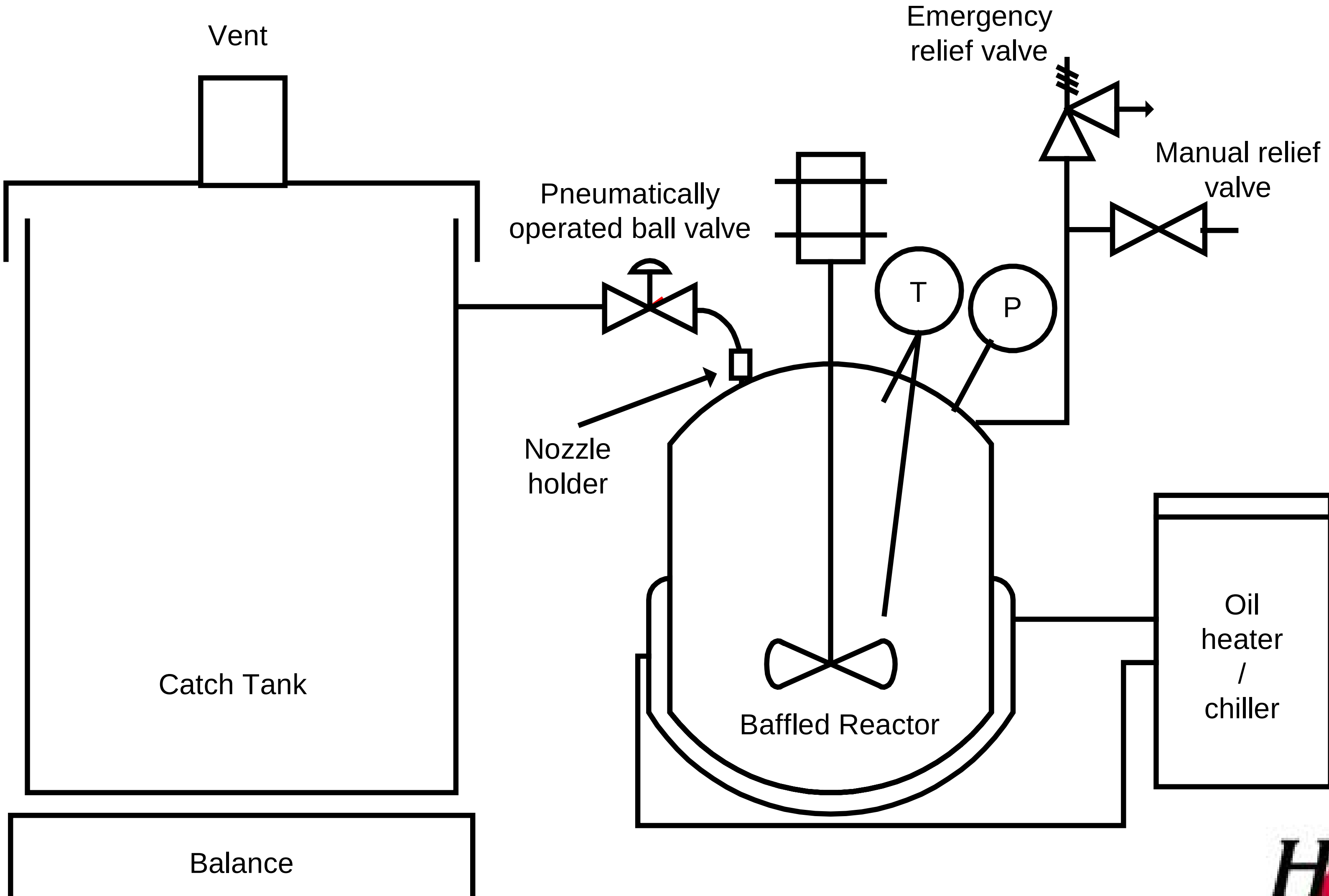

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Figure 17. Pressure profiles for depressurisation of water containing 70-110 µm diameter solids

1 litre scale, 5 mm nozzle, 200 rpm stirring

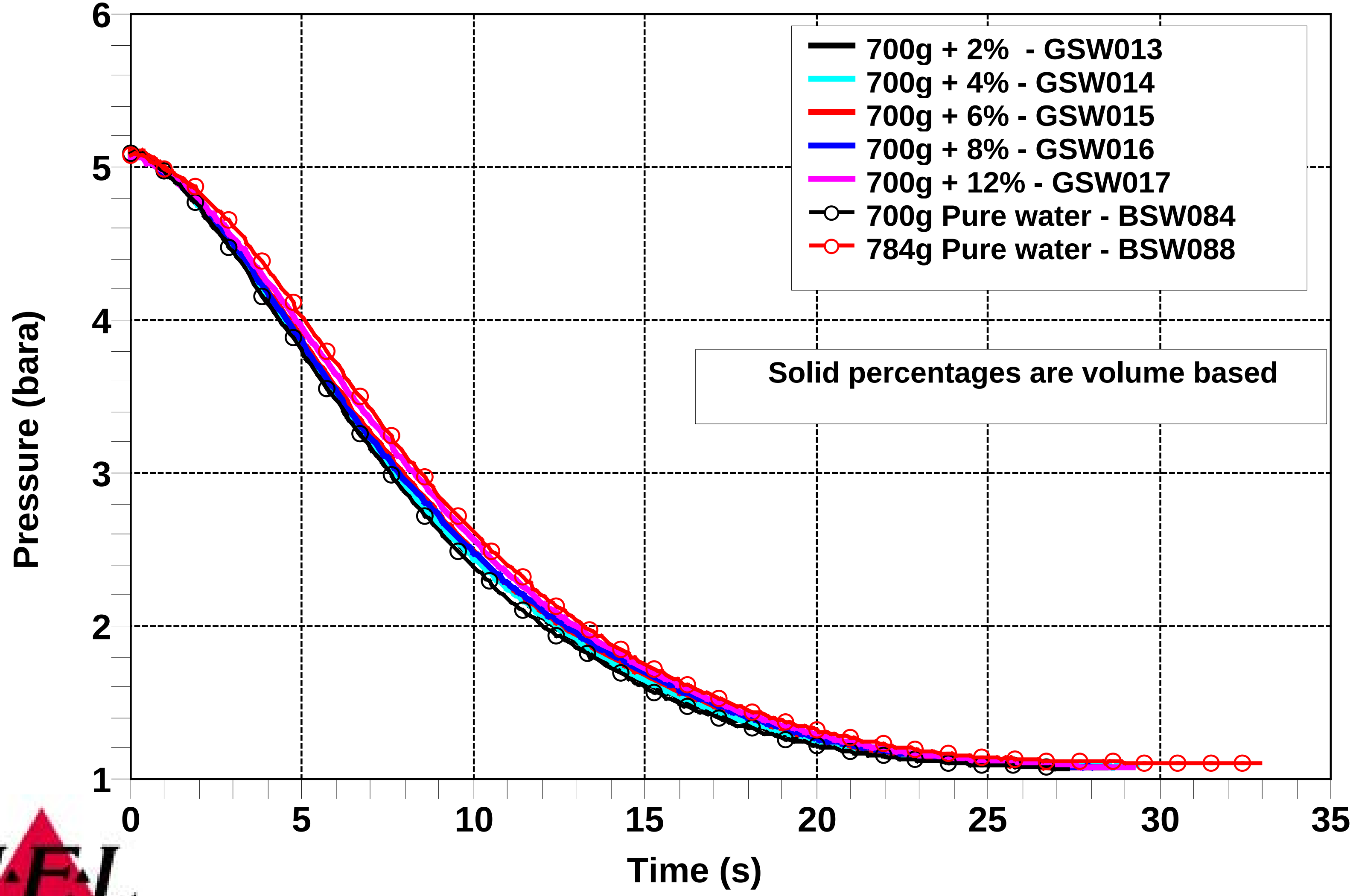

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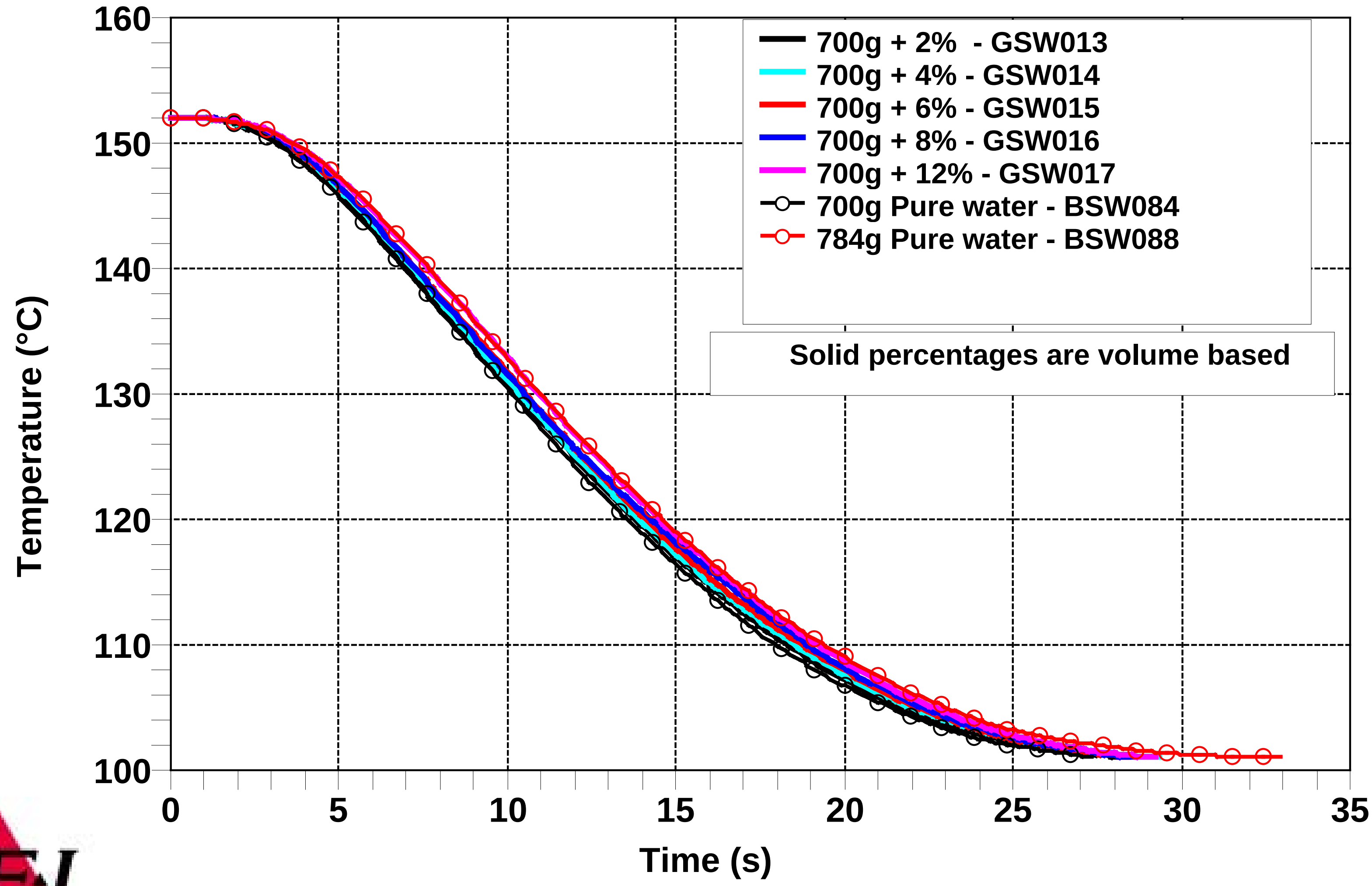
Figure 18. Temperature profiles for depressurisation of water containing 70-110 µm diameter solids

1 litre scale, 5 mm nozzle, 200 rpm stirring



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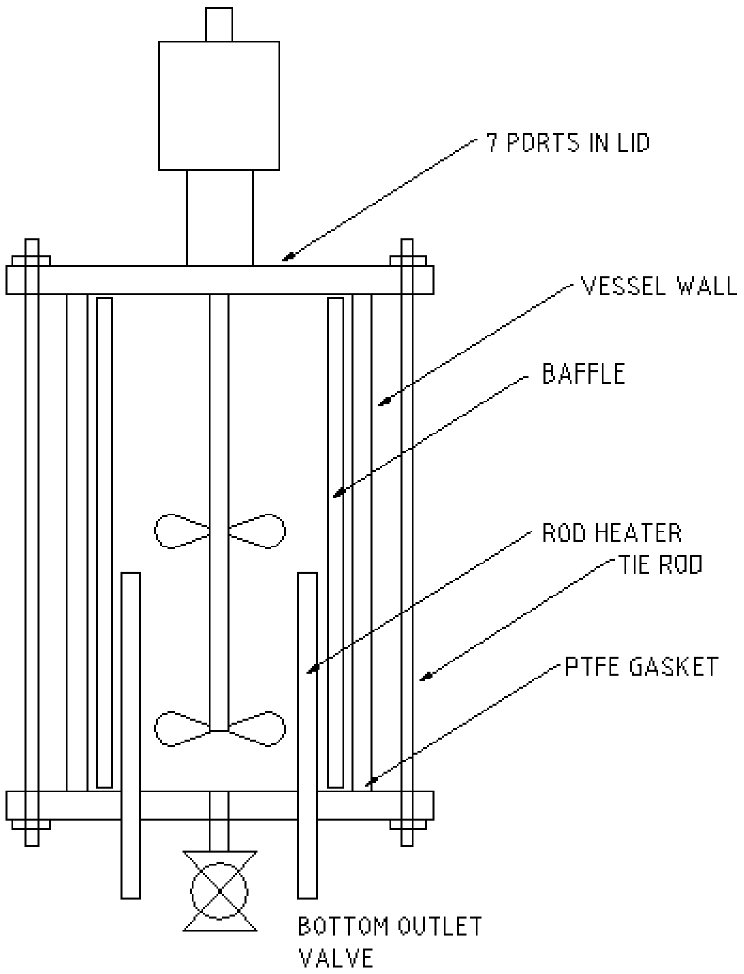
3 PHASE VENTING: liquid/solid/vapour or gas



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HEL, 10 litre, electrically heated, 20 bar reactor

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INITIAL CONCLUSIONS FROM NON-REACTING 1 & 10 LITRE, WATER BASED STUDIES

0.002 < particle to nozzle diameter ratio < 0.169
Solid densities 600 and 2500 kgm^{-3}

- Temperature and pressure profiles are very reproducible
- Solid/liquid carryover in replicate tests shows more variation, particularly on the small scale. For this reason work mainly on the 10 litre scale
- Solids (even up to 30 % v/v) have little influence on the temperature and pressure profiles during venting
- There is some limited evidence that solids may help nucleation, homogeneous flow, and promote carryover
- Liquid is discharged preferentially to solid, irrespective of the density ratio

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REACTION TESTS ON THE 10 LITRE SCALE

- **Reaction must be fast and promote 2 or 3 phase flow during venting**
- **Preference for minimising the handling of flammable vapours**
- **Cost of reagents and disposal (30 experiments)**
- **Industrial relevance**

Water and acetic anhydride eventually chosen. Several runaway incidents with this system in both reactors and storage tanks (See Leigh and Krzeminsky for details of tank rupture with 1 fatality and 20 injuries)

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Figure 3. Temperature and pressure versus time from PHI-TEC test (phi = 1.06)

Water and acetic anhydride (mole ratio 1.5)

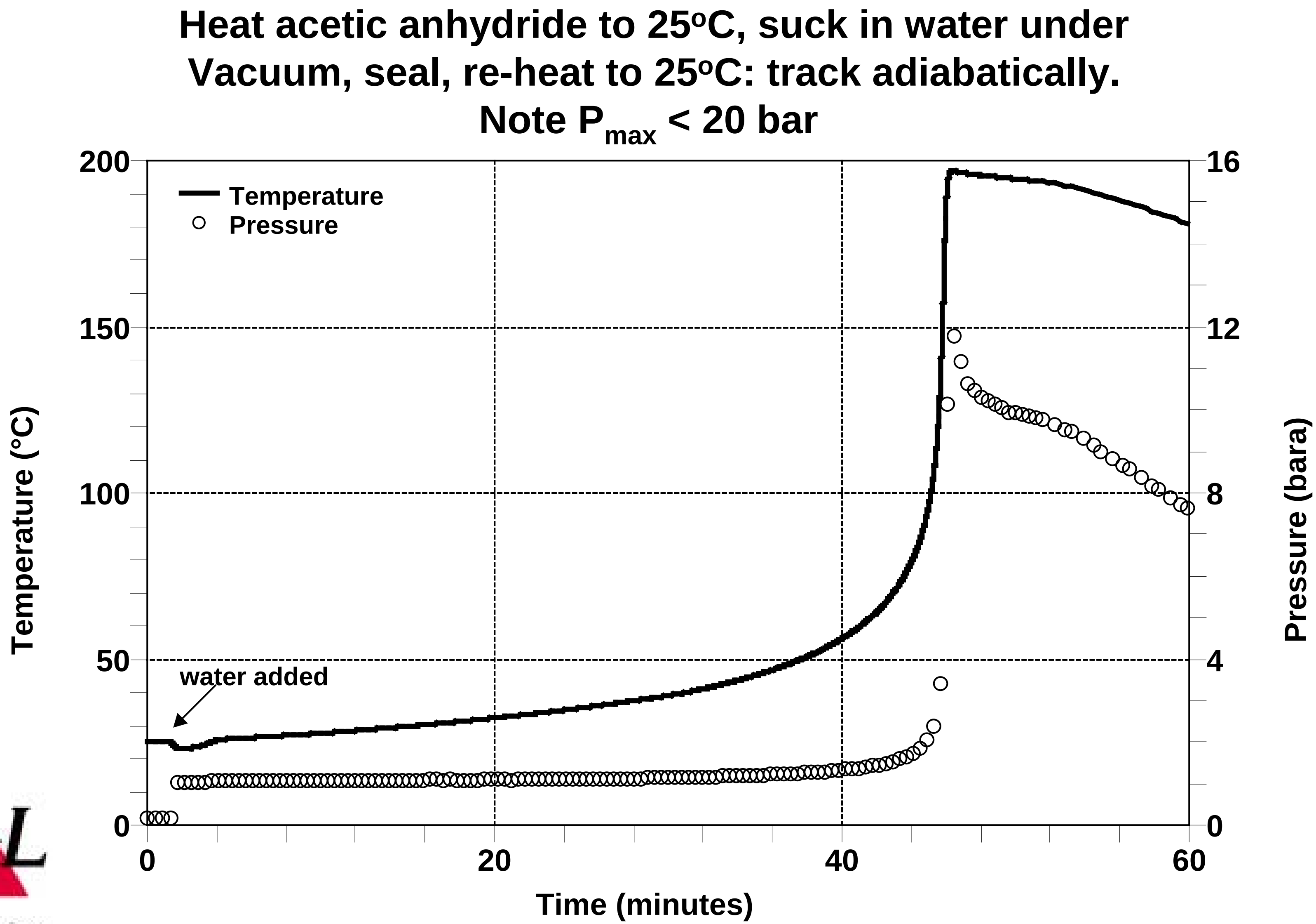

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Figure 4. Self heat rate against temperature, from PHI-TEC test (phi = 1.06)

Water and acetic anhydride (mole ratio 1.5)

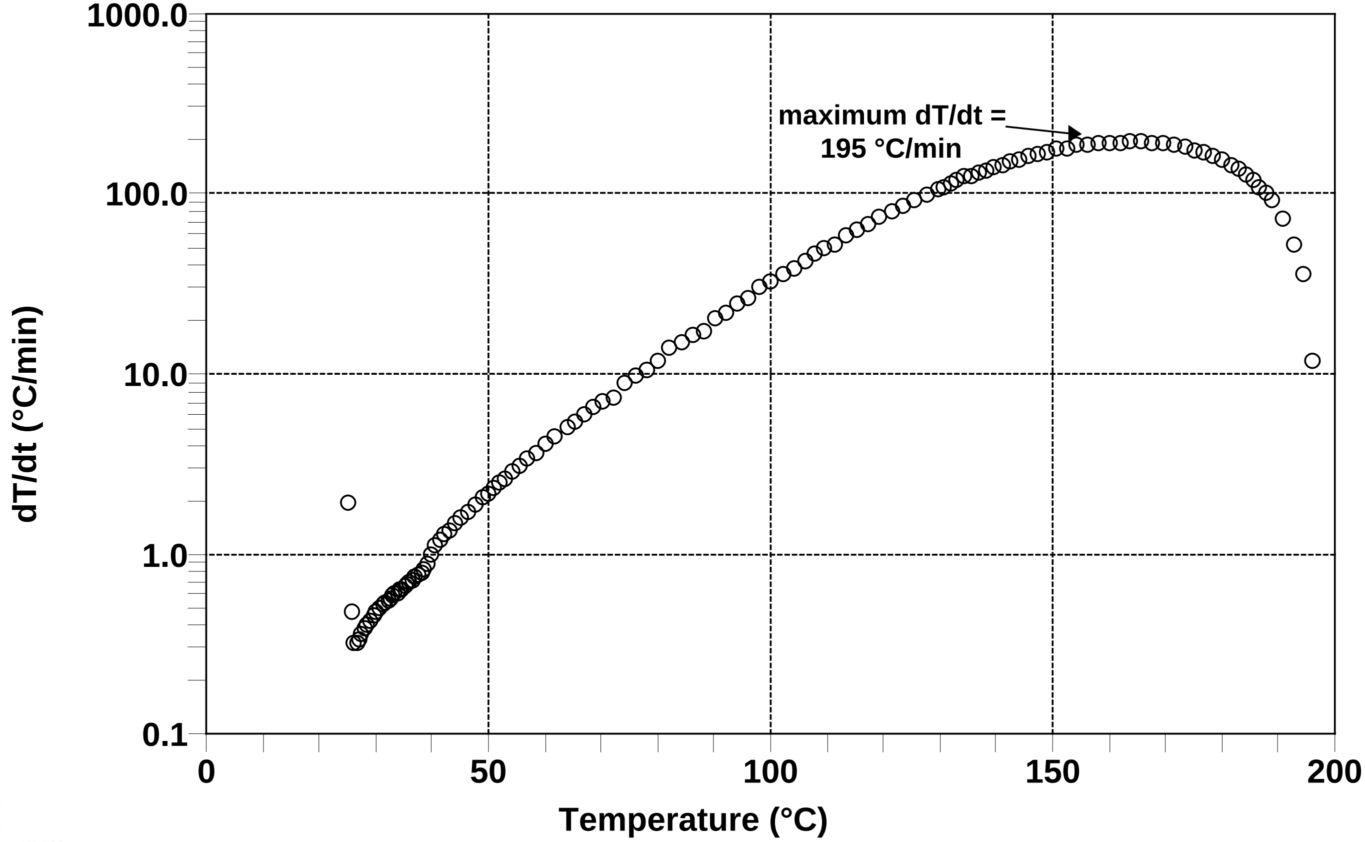

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Figure 7. Temperature and pressure versus time from PHI-TEC test (phi = 1.05)

Water and acetic anhydride (mole ratio 1.5) with electrical heating to 80°C as planned to be used with the 10 litre vessel

Reaction now seriously fast but maximum pressure still < 20 barg

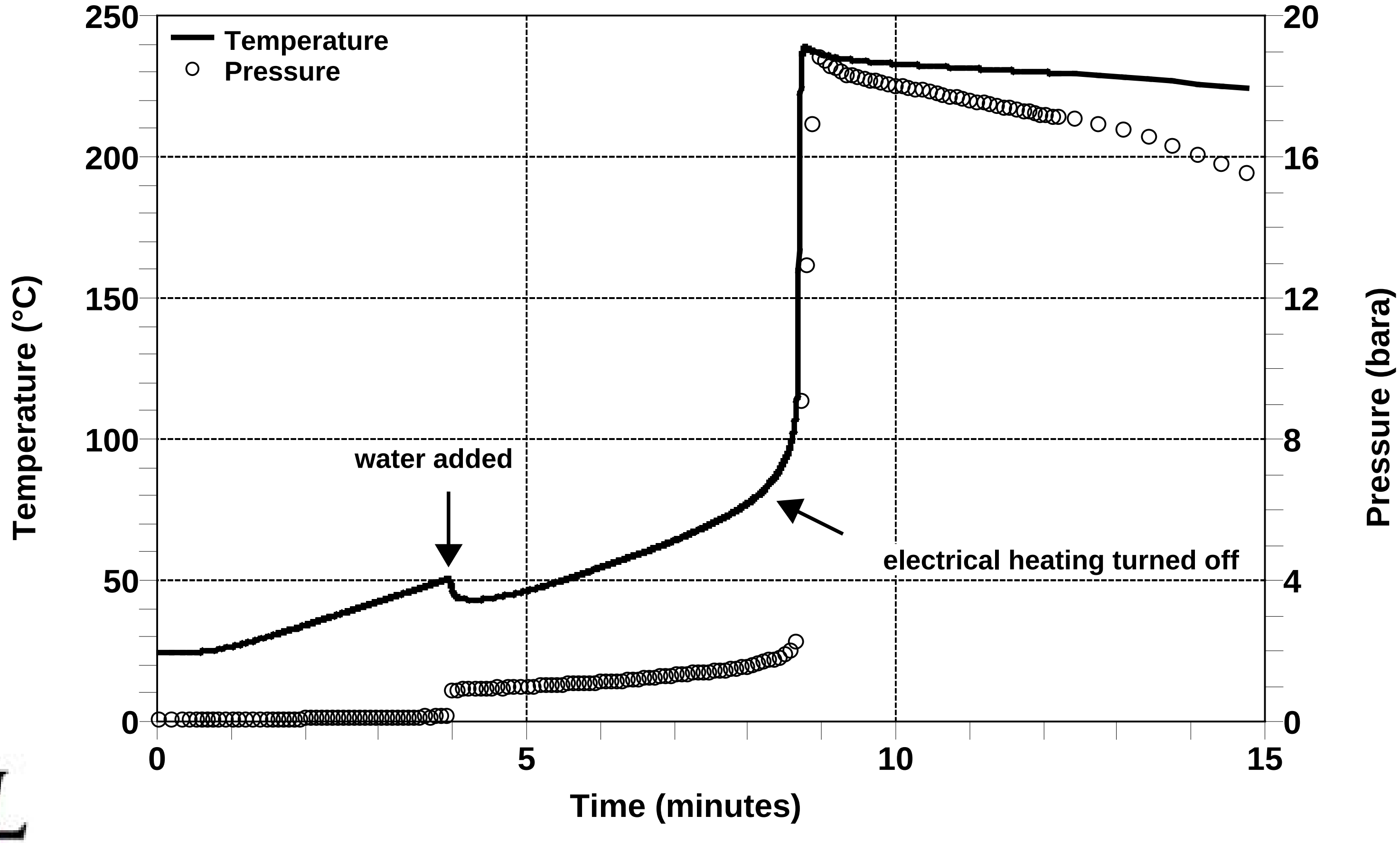

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Figure 8. Self heat rate against temperature, from PHI-TEC test (phi=1.05)

Water and acetic anhydride (mole ratio 1.5) with electrical heating to 80°C as used with the 10 litre vessel

Approximately 21 times faster than without electrical heating

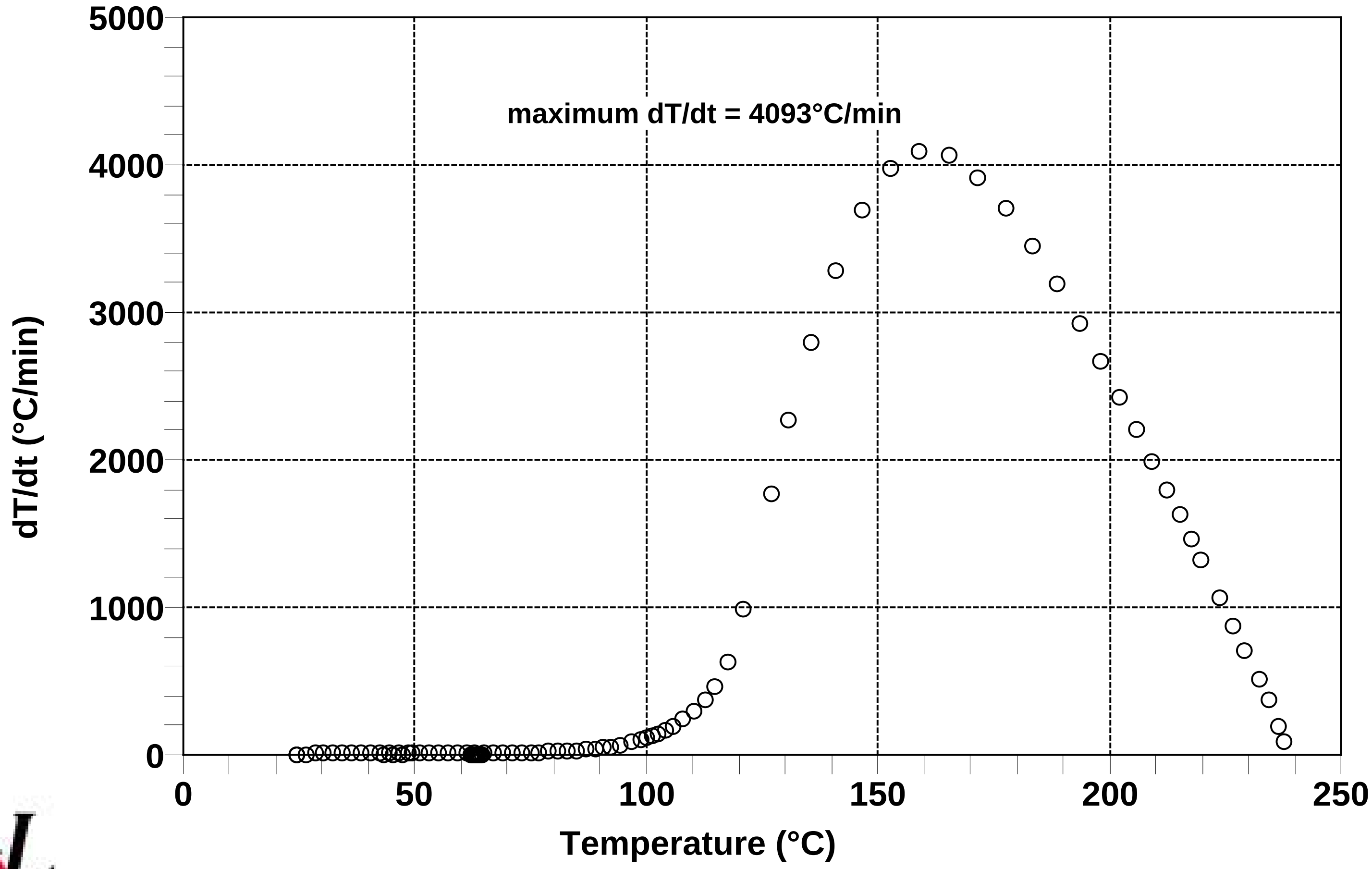

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Figure 8. Pressure profile for venting of reacting system tests at centrepoint

10 litre scale, 6210 ml charge (5750 ml reactants + 8 % by volume glass), water and acetic anhydride (mole ratio 1.5) 9 mm nozzle, 200 rpm stirring

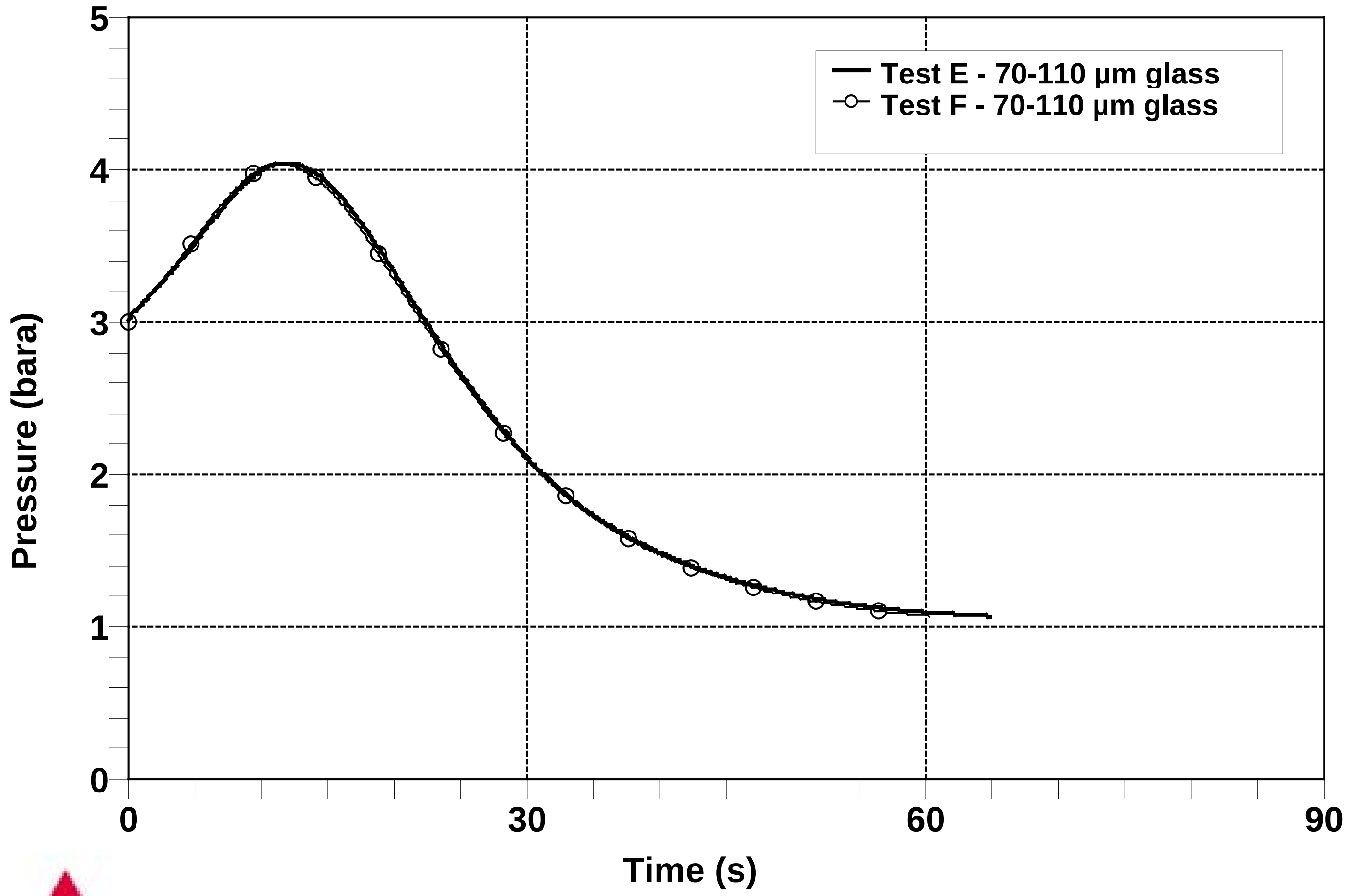

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Figure 9. Temperature profile for venting of reacting system tests at centrepoint

10 litre scale, 6210 ml charge (5750 ml reactants + 8 % by volume glass), water and acetic anhydride (mole ratio 1.5) 9 mm nozzle, 200 rpm stirring

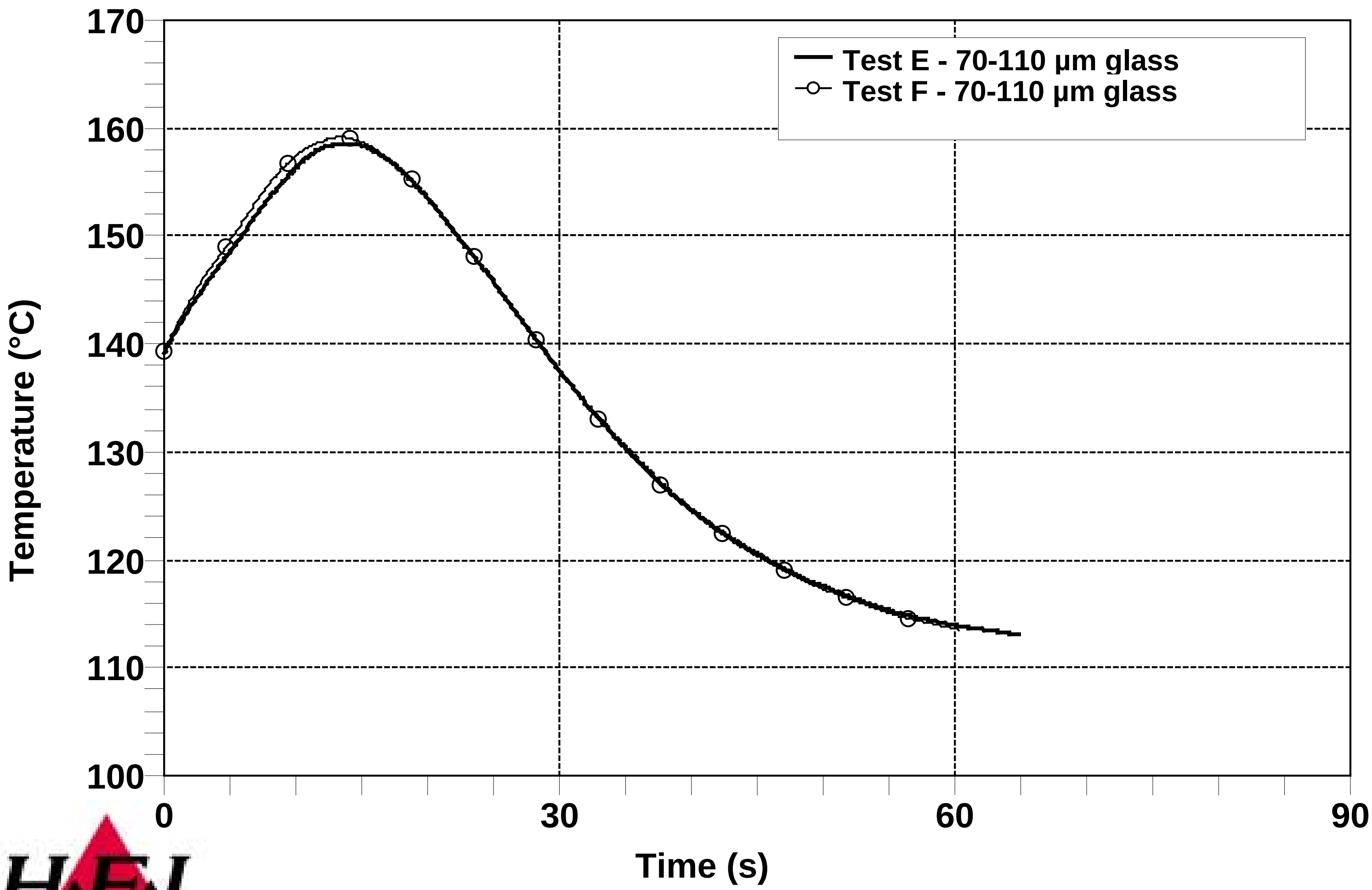

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Figure 10. Heat rate profiles for reacting system tests at centrepoint

10 litre scale, 6210 ml charge (5750 ml reactants + 8 % by volume glass), water and acetic anhydride (mole ratio 1.5) 9 mm nozzle, 200 rpm stirring

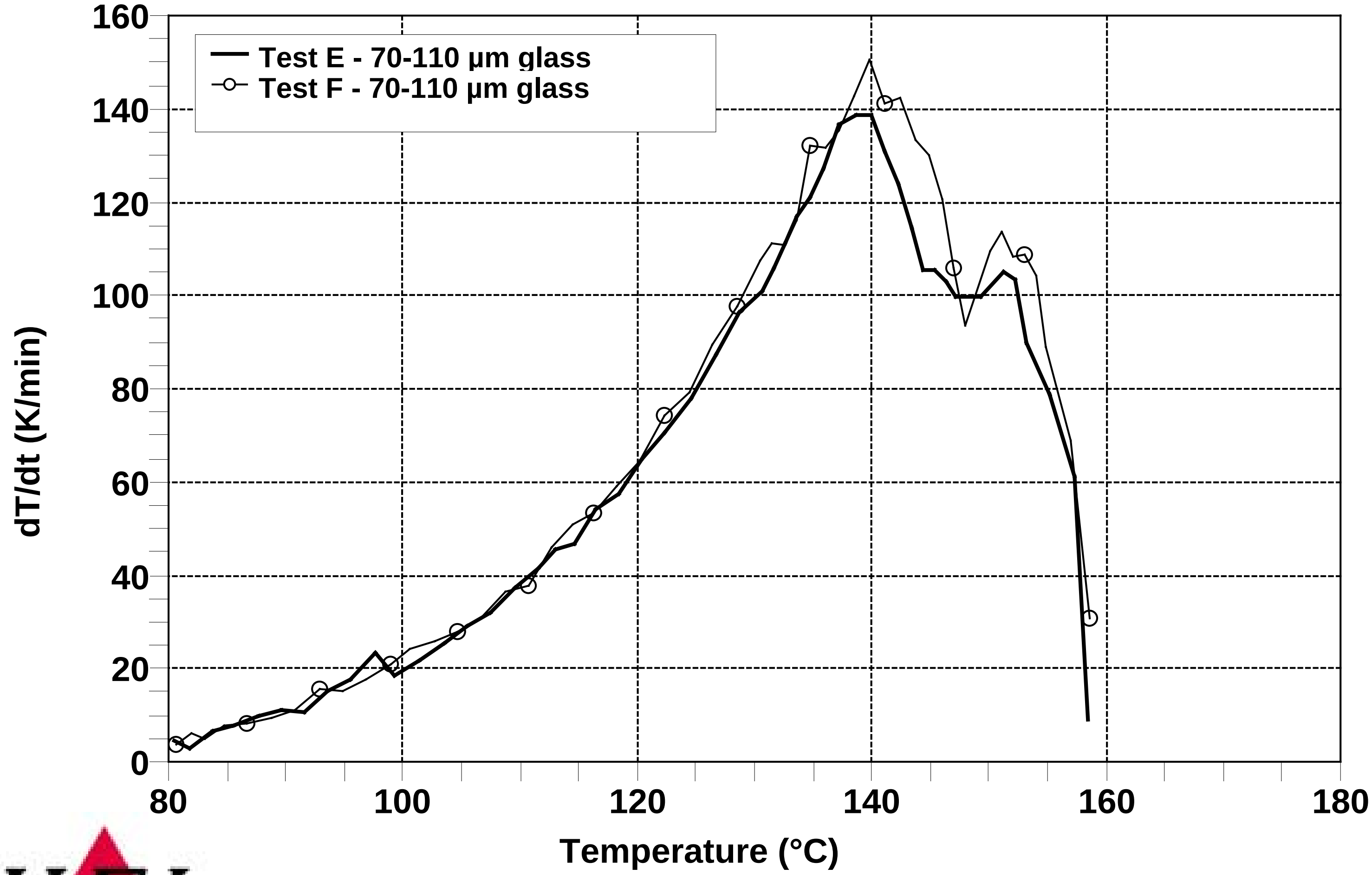

Figure 2. Pressure profile for venting of reacting system tests at low fill level

10 litre scale, 5750 ml charge (5000 ml reactants + 15% by volume glass), water and acetic anhydride (mole ratio 1.5) 9 mm nozzle, 200 rpm stirring.

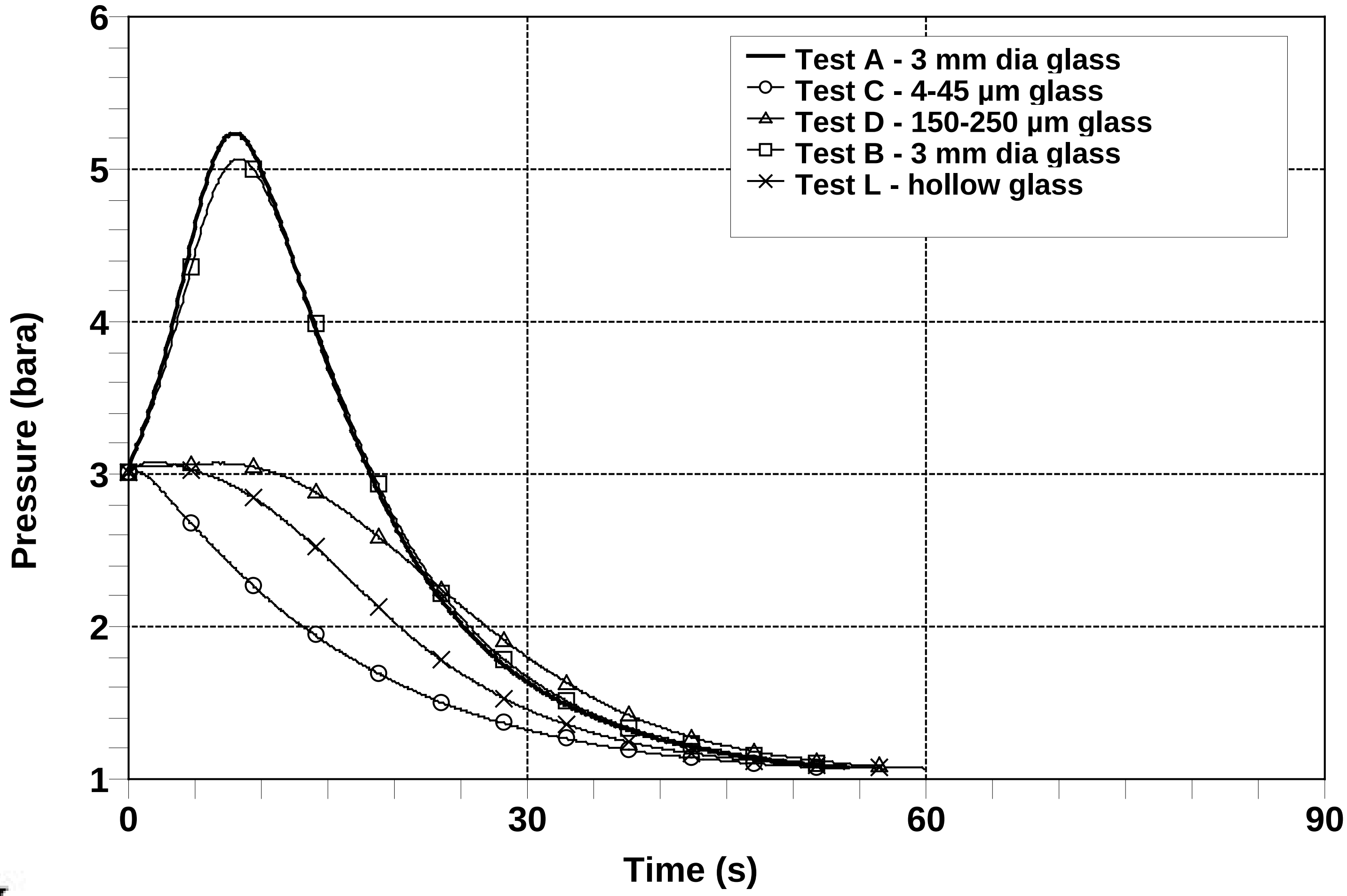

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Figure 3. Temperature profile for venting of reacting system tests at low fill level

10 litre scale, 5750 ml charge (5000 ml reactants + 15% by volume glass), water and acetic anhydride (mole ratio 1.5) 9 mm nozzle, 200 rpm stirring

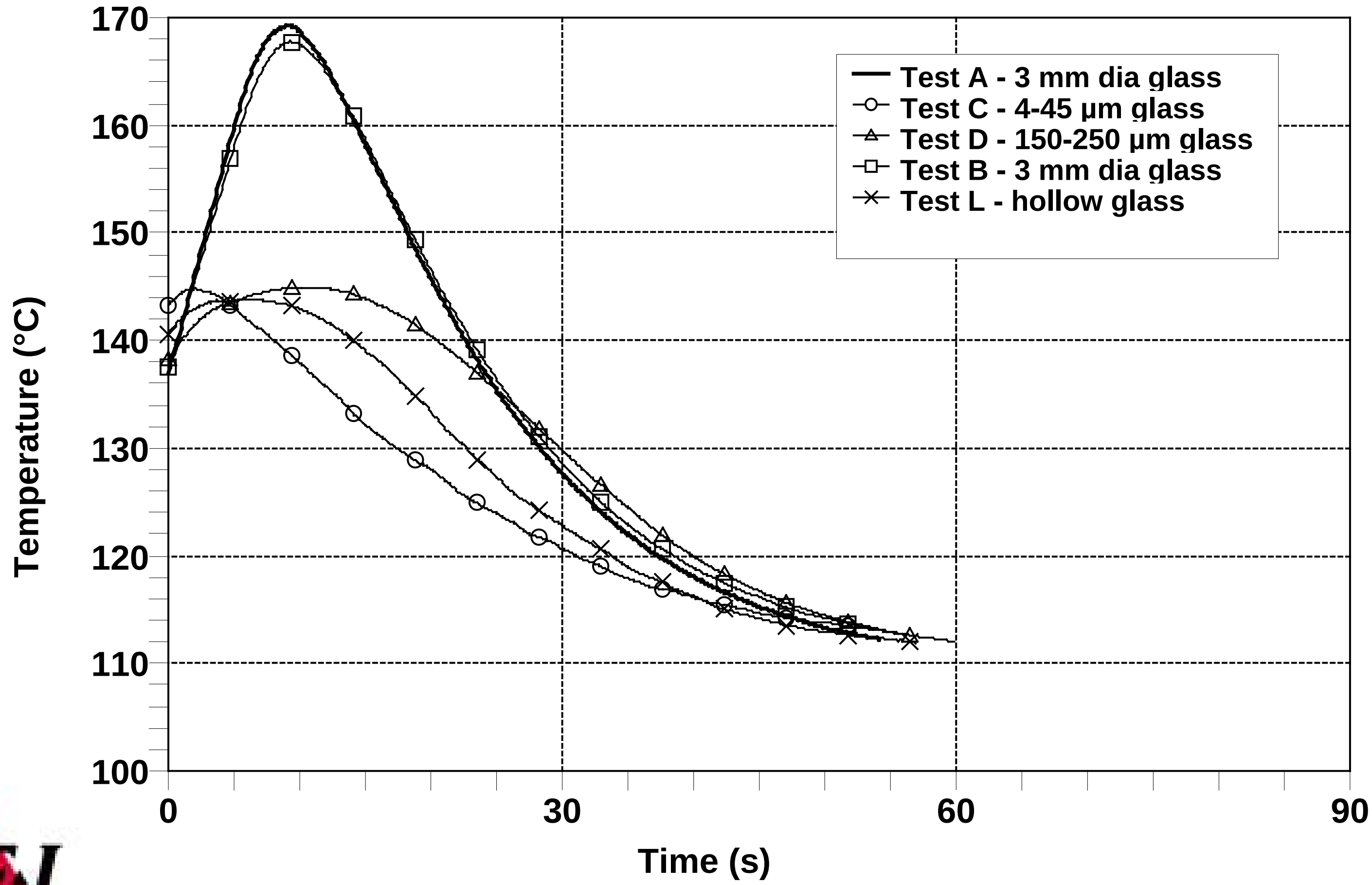

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Figure 4. Heat-rate profiles of reacting system tests at low fill level

10 litre scale, 5750 ml charge (5000 ml reactants + 15% by volume glass), water and acetic anhydride (mole ratio 1.5) 9 mm nozzle, 200 rpm stirring

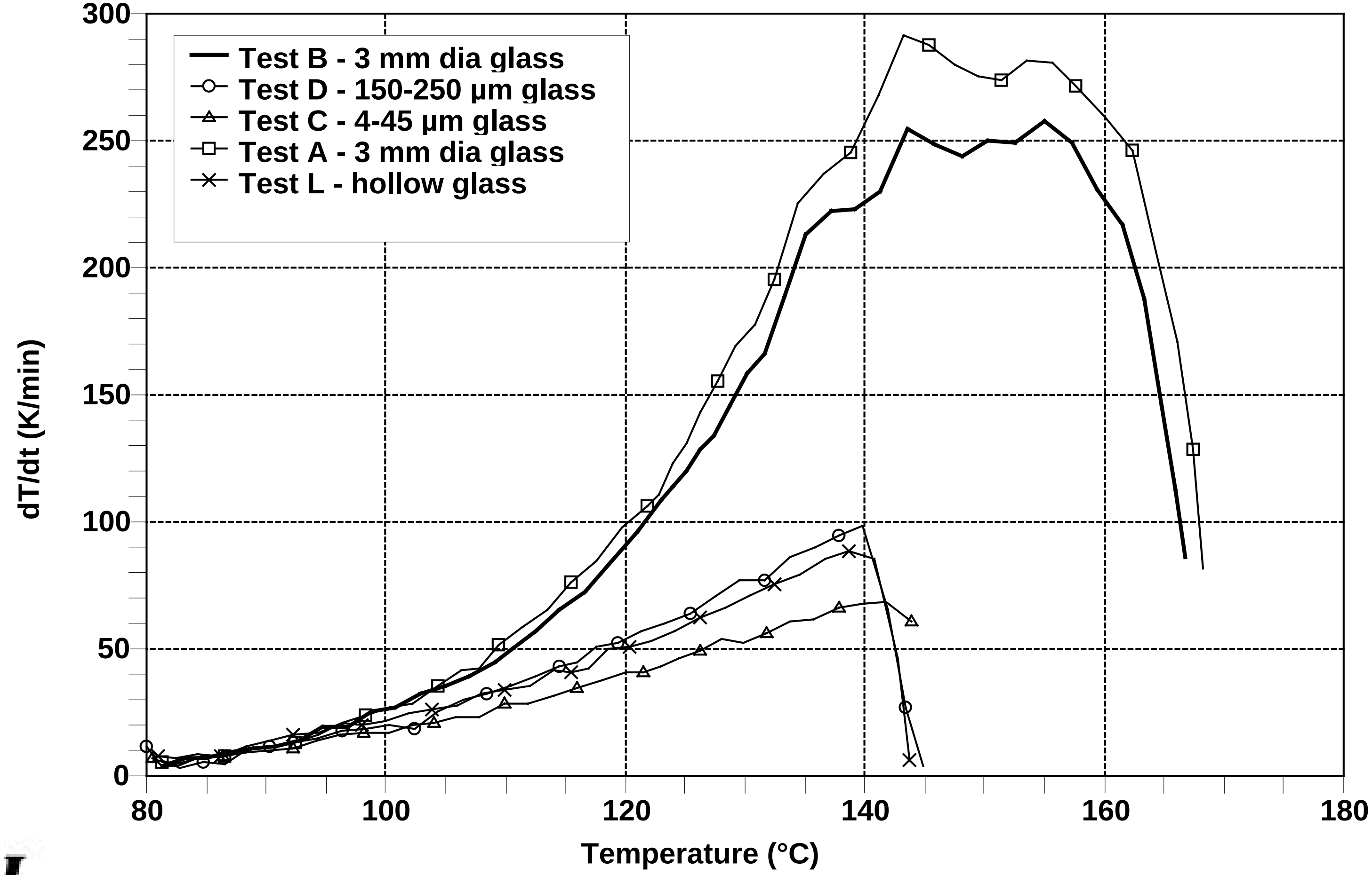

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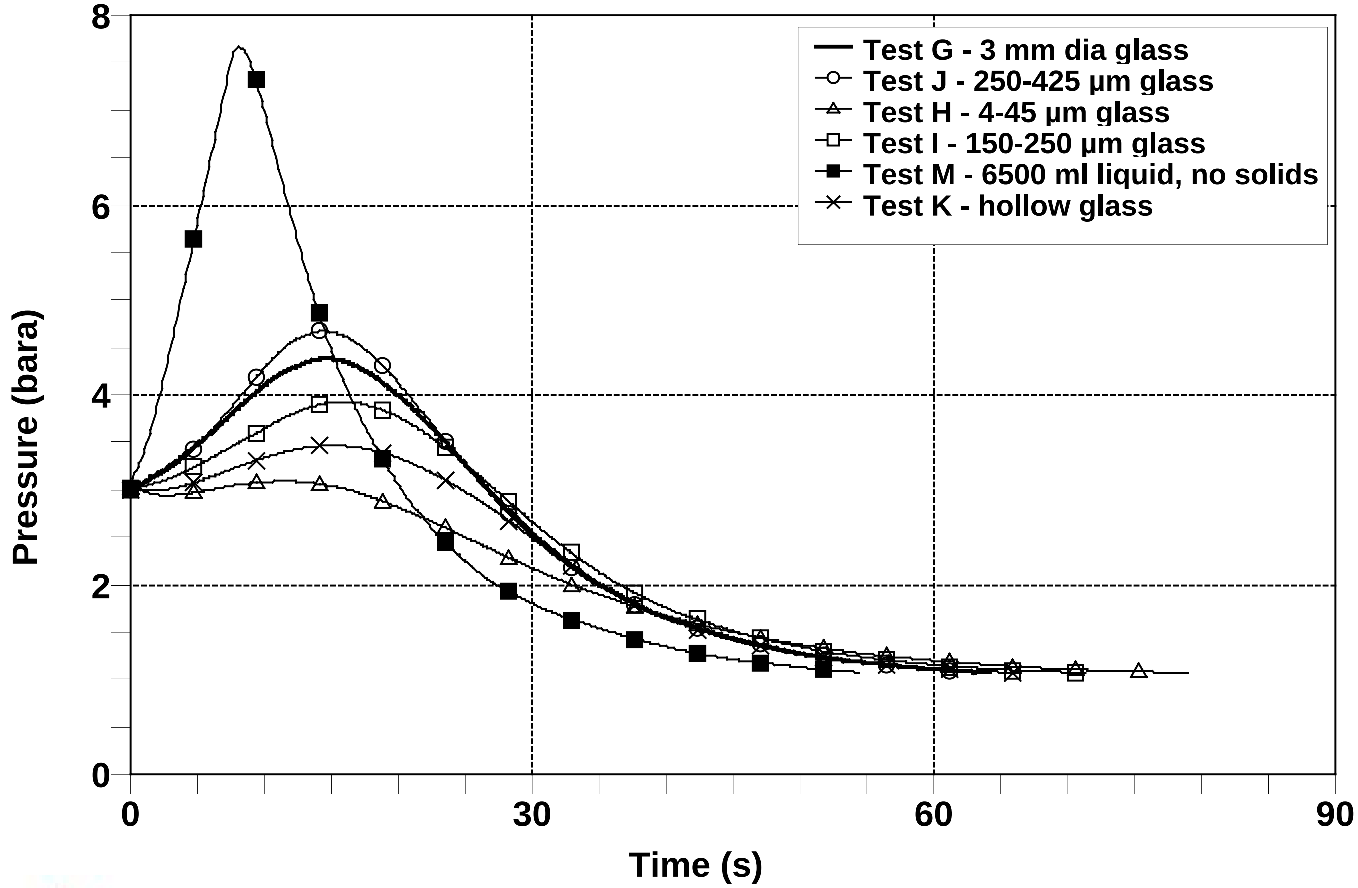
Figure 5. Pressure profile for venting of reacting system tests at high fill level

10 litre scale, 7475 ml charge (6500 ml reactants + 15% by volume glass), water and acetic anhydride (mole ratio 1.5) 9 mm nozzle, 200 rpm stirring.



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3 PHASE VENTING: liquid/solid/vapour or gas

We have not looked at:

- **Experiments on a scale larger than 10 litres**
- **Solid deposition in vent line or downstream equipment**
- **Solids that are involved in the reaction**
- **Enhanced solid concentrations in the reactor (and hence reaction rates?) due to flashing of vapour or preferential discharge of liquid**

INITIAL CONCLUSIONS FROM 10 LITRE REACTION STUDIES

- **Comparisons between homogeneous and heterogeneous systems are hard. Adding solid is like adding an inert diluent. The phi factor is increased and the reaction rate reduced: thus dP/dt and dT/dt are lower**
- **Because the thermal properties of the solid and liquid are different, different amounts of vapour are produced**
- **At large values of dT/dt, T_{liquid} and T_{glass} are not the same. Similarly the $T_{reactor}$ may lag behind T_{liquid}. As a result the effective phi factor varies during the runaway**
- **Collect adiabatic calorimetry data at the correct phi factor. Use averaged physical property data (density, specific heat, etc.) for the 2 and 3 phase mixtures.**

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Table 6
Selected mass balance data from acetic anhydride/water tests.

Test	Glass diameter (μm)	Initial glass charge (g)	Glass carryover to catch tank (g)	Glass remaining in reactor (g)	Fraction of initial glass remaining in reactor	Fraction of initial liquid charge remaining in reactor
A	3000	1875	0	1868	1.00	0.54
B	3000	1875	0	1870	1.00	0.38
C	4-45	1875	45	1782	0.95	0.76
D	150-250	1875	20	1806	0.96	0.51
E	70-110	1078.1	20	1042	0.97	0.45
F	70-110	1078.1	20	992	0.92	0.48
G	3000	2437.5	0	2421	0.99	0.39
H	4-45	2437.5	299	2078	0.85	0.52
I	150-250	2437.5	25	2354	0.97	0.35
J	250-425	2437.5	0	2362	0.97	0.43
K	0-65 (hollow glass)	585	220	346	0.59	0.44
L	0-65 (hollow glass)	450	70	383	0.85	0.66

Figure 5. Temperature and pressure versus time from PHI-TEC test (phi = 2.45)

Water and acetic anhydride (mole ratio 1.5) with electrical heating to 90°C at ~3 °C min^{-1}

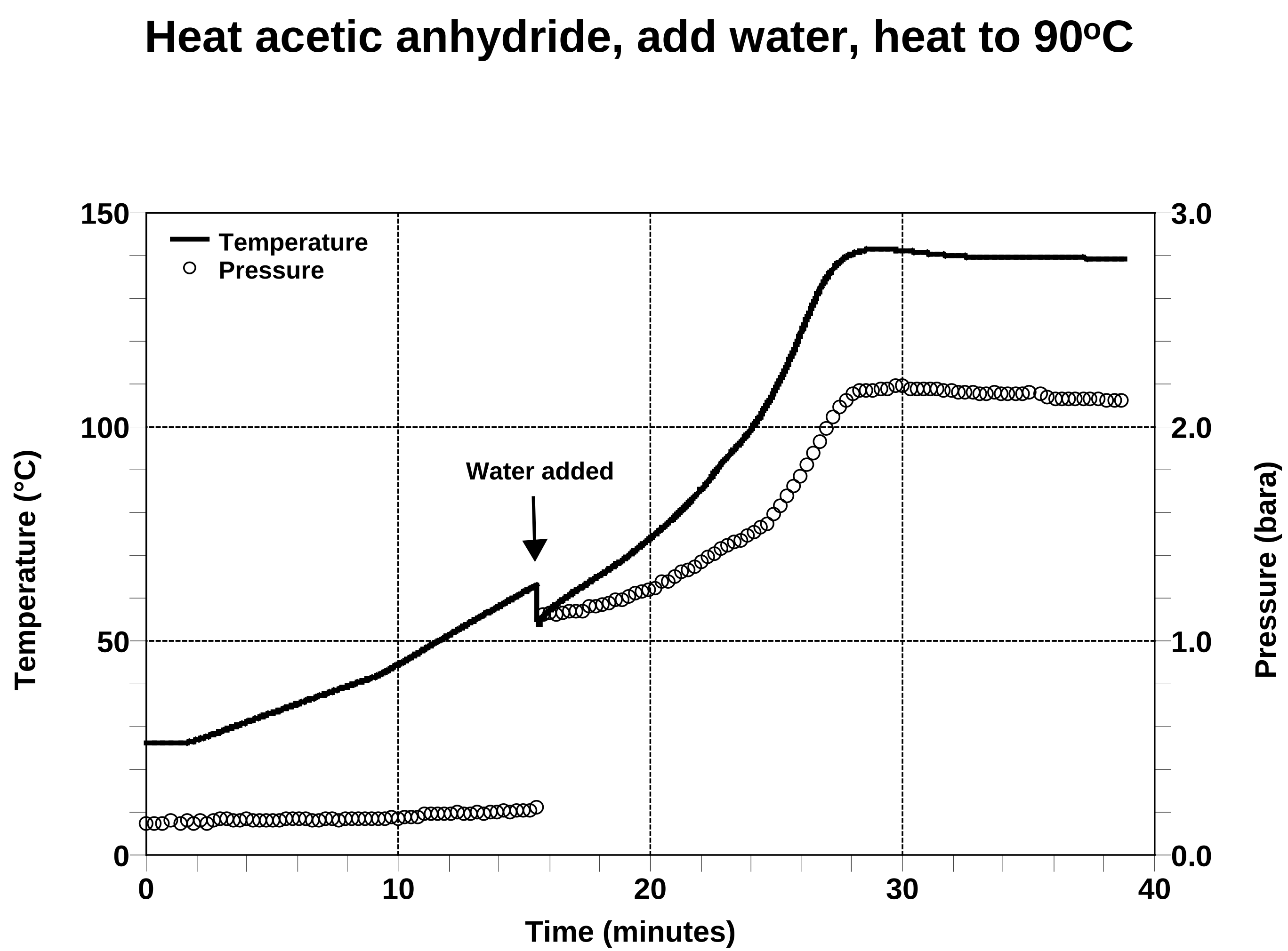

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Figure 11. Temperature and pressure profiles from closed test in 10 litre vessel

Water and acetic anhydride (mole ratio 1.5) addition of water at 50°C and electric heating to 80°C, phi factor = 2.45

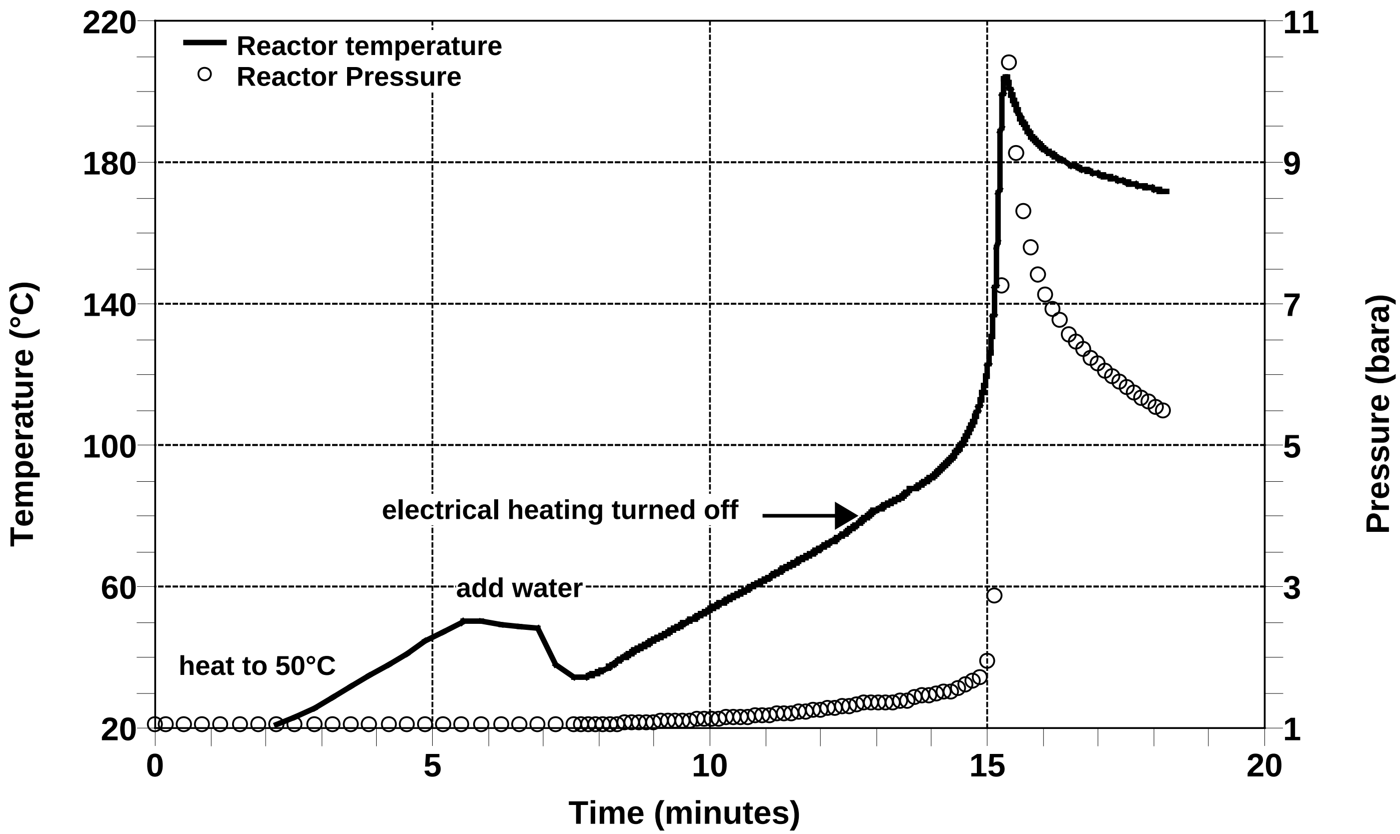

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Figure 6. Self heat rate against temperature, from PHI-TEC test (phi = 2.45)

Water and acetic anhydride (mole ratio 1.5) with electrical heating to 90°C at ~3 °C min^{-1}

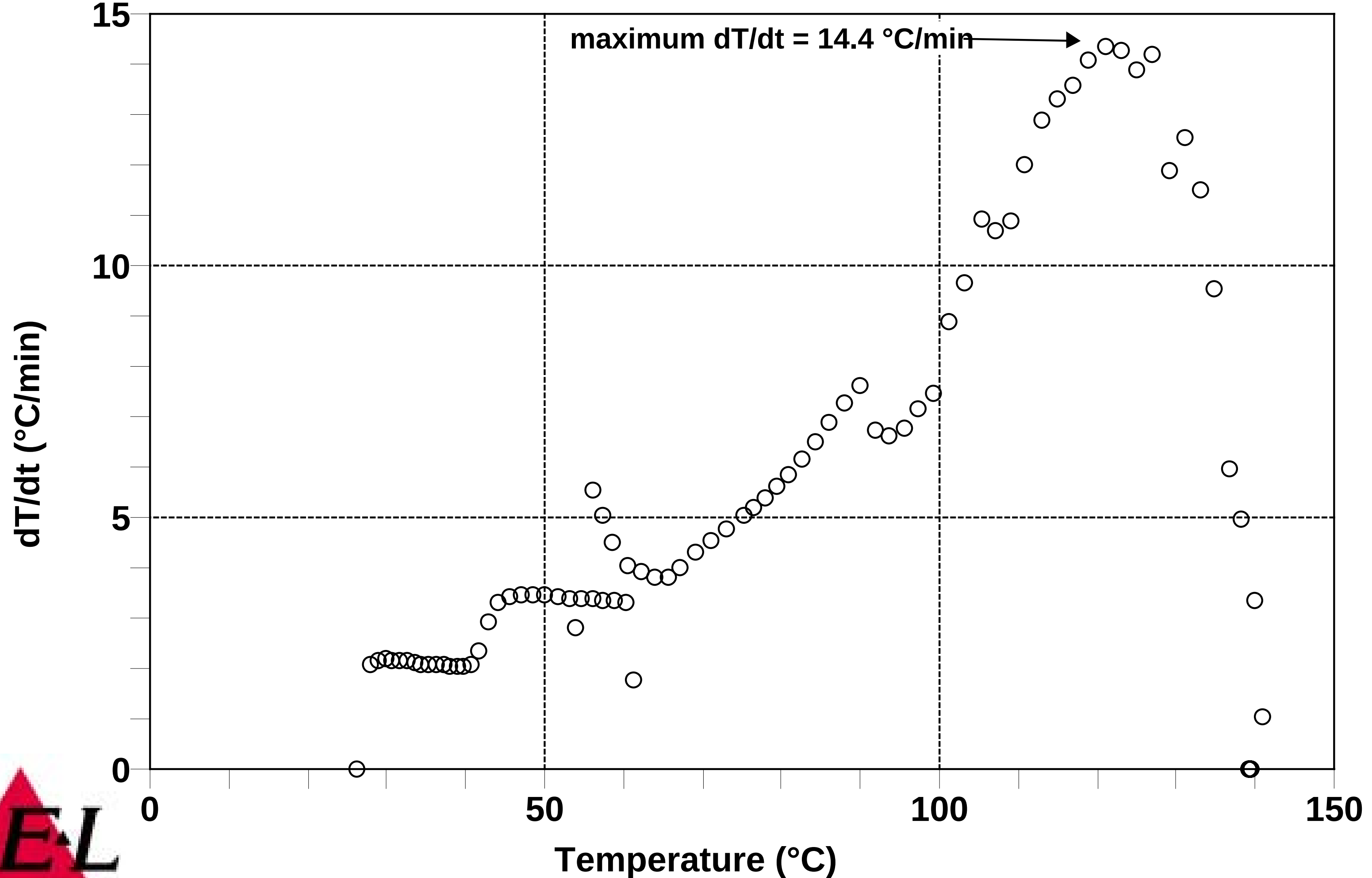

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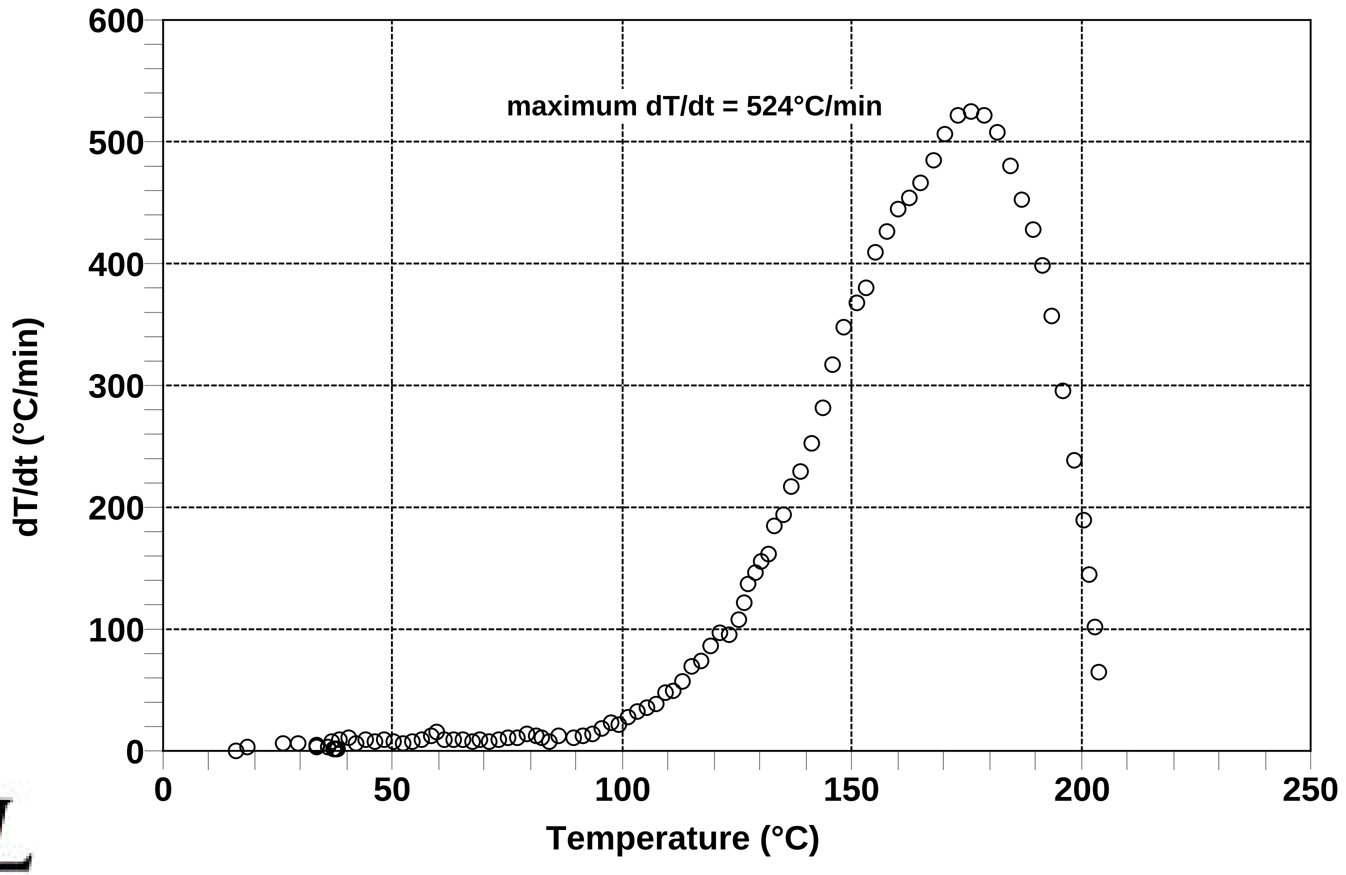
Figure 12. Self heat rate against temperature from closed test in 10 litre vessel

Water and acetic anhydride (mole ratio 1.5) addition of water at 50°C and electric heating to 80°C, phi factor = 2.45

Approximately 36 times faster than a small scale test at phi = 2.45. Why?



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Buchi, 1 litre, jacketed, oil heated, 60 bar reactor

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Magnetic drive, pneumatically actuated ball valve, pressure relief valve, nozzle holder