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Safe Venting of " Red Oil " Runaway Reactions (U)

by

D. F. Paddleford

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

H. K. Fauske
Fauske and Associates, Inc., Burr Ridge
IL USA

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Authors:

D.F. Paddleford
Westinghouse Savannah River Company
Centennial Corp. Center
Aiken, South Carolina, 29801

and

H. K Fauske
Fauske and Associates, Inc
16W070 West 83rd Street,
Burr Ridge, Illinois, 60521

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D.F. Paddleford, WSRC, Aiken, SC
H. K Fauske, FAI, Burr Ridge, IL

Calorimetry testing of Tri-n-butyl phosphate (TBP) saturated with strong nitric acid was performed to determine the relationship between vent size and pressure buildup in the event of a runaway reaction. These experiments show that runaway can occur in an open system, but that even when runaway is induced in the TBP/HNO_3 system, dangerous pressure buildup will be prevented with practical vent size.

Introduction and Summary

In follow-up to the 1993 damaging explosion at the Tomsk-7 nuclear fuel reprocessing plant in Russia[1],[2], operations at the Savannah River Site (SRS) involving tri-n-butyl phosphate (TBP) and nitric acid (solutions a.k.a. "red oil") were carefully reviewed with respect to potential for runaway reactions, and safety procedures and safety documents updated. Various safety precautions are available and taken to prevent a "red oil" runaway. These include among others: preventing accumulation of significant masses of TBP, preventing significant interaction with strong nitric acid, stirring during additions and sampling, maintaining low temperature, maintaining cooling system effectiveness, and keeping TBP/HNO_3 mixed with, or thermally coupled to, aqueous layers.

Finally, and the focus of this paper, in the unlikely event of failure of the above preventive measures, it was desirable to know whether the tanks had (or could be made to have) adequate venting to handle a runaway of the maximum credible amount of red oil that could accumulate and be heated, without building up explosive pressures. With adequate venting, even with runaway the vessel would remain intact, respirable aerosol generation would be minimized, and confinement and filter integrity assured.

To experimentally determine the required vent size, Fauske and Associates, Inc. (FAI) performed a number of tests with their Reactive System Screening Tool (RSST)[3] and Vent Sizing Package (VSP)[4] calorimeters. These small (15 ml and 110 ml respectively) calorimeters have been specifically developed to be essentially adiabatic for purpose of studying runaway reactions and determining the vent sizes to support safe design. These experiments[5] show that even when runaway is induced in the TBP/HNO_3 system, dangerous pressure buildup will be prevented with practical vent size. In particular, tests in which TBP saturated with strong (70%) nitric acid was induced to runaway indicated the pressure would remain low (<22 psig) provided the vent area was greater than 0.005 in^2/Kg of TBP/HNO_3. By contrast an identical test with closed system, i.e. no vent, was destructive, and an identical test with the vent but a two atmosphere back pressure to simulate the Tomsk-7 control valve opening pressure resulted in large over pressure and severe bulging of the test vessel.

A range of vent sizes and materials (additives) were investigated. This paper presents typical thermal and pressure response transients, the relationship between peak pressure and reactant mass per unit vent area, and conclusions drawn.

Experience With TBP

Tri-n-butyl phosphate (TBP) is an important organic solvent utilized in acidic extraction steps in separations processes at reprocessing facilities. Complexes of TBP and HNO3 (known as "red oil" because of the colors formed) undergo exothermic reactions which can thermally "run away" if heated to temperatures where the heat of reaction exceeds heat losses. In fact there have been several instances of explosive type reaction with the TBP/HNO3 system in industrial processes [6], [7], [8], [9], [10] . The most recent occurrence (1993) was at the Tomsk-7 facility in Russia[1],[2] at which faulty operations is believed to have resulted in the runaway of a solution of up to 500 liters of TBP inadvertently saturated with strong nitric acid and heated, resulting in explosive failure of the storage vessel and subsequently blowing out a wall of the reprocessing building . The damage to the building is believed to have been a result of the deflagration of flammable gases, most likely butene and CO, released from the initiating explosion.

Prior Work

Substantial previous research has been conducted on the TBP/HNO3 system reaction to characterize its hazards [11], [12],[13], [14], [15]. In particular, Nichols [11] experimentally measured the gas composition and release rates for the decomposition of TBP/HNO3 at constant temperatures up to 160 C in sealed tubes. From these he determined Arrhenius model reaction rate constants and calculated the heat of reaction. With a simple model and limited experimental heat transfer measurements he developed estimates of the mass vs Temperature limits that would preclude runaway with only natural convection heat loss from the storage vessel. Gordon [13] conducted heating tests at high temperature (160-200 C) in a sealed pressure vessel and observed high, fast pressure and temperature reactions characteristic of an ignition.

Recent/Current Work

Subsequent to the Tomsk-7 explosion there has been substantial additional work initiated in the US as well as Russia related to characterizing the various safety aspects of TBP/HNO3 reactions, much yet still to be published. DTA, DSC, and butene release rate experiments have been performed at Hanford [16]. Los Alamos National Lab has conducted red oil stability studies [17], and studies of reaction kinetics at constant volume[18]. WSRC has completed or sponsored several recent projects related to red oil safety, in addition to the FAI adiabatic heating/venting tests described herein. These include:

- Bench tests to characterize the reaction and provide qualitative and quantitative analysis of the residue and gaseous products were conducted at SRS [19], [20].

- Isothermal heat and composition balances for a single layer of TBP/HNO3 in the range of 100 to 125 C, and heat balance and mass transfer tests for a two layer (organic layer over aqueous layer) system were performed at Savannah River to determine coolability [21], [22].

- Georgia Tech, under SRS contract, is measuring gas release and compositions of both constant volume and constant pressure systems.

Hyder[23] has provided a summary of both, incident experience and research relevant to red oil safety.

FAI TBP/HNO3 Venting Tests

Prior research indicated that although abrupt explosions yielding high temperature and pressure can occur with TBP/HNO3 in closed constant volume systems, transients were slower and mild by comparison in open systems. Reasons for this are:

(1) With open systems a portion of reactants (HNO3, NO2, NO, etc.) escape leading to incomplete reaction.

(2) With the open system, much of the reaction energy can be absorbed in the vaporization of the water and nitric acid in solution reducing temperature increase. Furthermore the reaction products include generation of gas bubbles throughout the reaction zone that are sites enhancing this vaporzation[21].

(3) The temperature will not exceed the atmospheric pressure boiling point of the solution. Even though this increases to the TBP atmospheric pressure boiling point of approximately 260 C during the transient as the more volatile water and nitric acid vaporize from solution, this is far lower than the 700+ C temperature that could be reached if boiling were surpressed. With the Arrhenius type dependence on temperature the resulant reaction rates are much lower at the reduced temperatures achieved in the open system.

For performing safety studies it is essential to know the magnitude of venting area required to provide these open system benefits. The various process tanks at SRS with potential to contain significant red oil are equipped with process header vents and overflow line vents with total vent areas ranging from 10.75 in2 to over 20 in2. Furthermore, there was potential for making use of spare ports to increase vent area if necessary. Probabilistic risk studies[24] have determined the maximum credible mass of red oil that could be inadvertently accumulated in a tank and accidently heated to a temperature necessary for a runaway reaction to be 3000 lbs. It was desired to know what vent area could accomodate this mass of material undergoing runaway without generating high pressure that could place the tank integrity in jeopardy.

Because of the complexity of the several reactions taking place, as well as the elevated temperature, mixture vapor pressures, and mass transfer considerations, the venting was studied experimentally instead of analytical modelling of theoretical heat and mass balance equations that could be subject to question. A total of 30 small scale tests were conducted investigating various degrees of venting, back pressures, sample masses, and sample compositions (TBP/nitric acid/diluent/decomposition product). From these test results a relationship between red oil mass per unit vent area and the resultant pressure increase is developed that scales directly to plant conditions. In some of the tests gas samples and reaction residues were collected and analyzed at SRTC laboratories.

Equipment Description

Scoping tests were performed utilizing FAI's Reactive System Screening Tool (RSST) which has a 15 ml spherical glass reaction vessel open to the confinement vessel. Tests with closed vents or partial venting were performed utilizing FAI's Vent Sizing Package (VSP) which has a 110 ml thin steel cylindrical shell can shaped reaction vessel with an integral magnetic stirrer. The VSP vessels included a 1 inch long drawn tubing vertical vent, ranging from 0.022 to 0.125 inch in inside diameter, welded to a penetration through the top of the can. Both of these are widely-used industry tools, designed for implementing the AIChE-DIERS (Design Institute for Emergency

Relief Systems) methods to quantify runaway reactions and determine vent sizes to support safe design in the commercial chemical industry [3],[4]. Key features include a combination of thermal insulation and temperature compensated heaters to avoid heat loss and maintain the adiabacity of the sample, pressure and temperature data recording with automatic on line data processing and graphing via computer, and the ability to prepressurize the confinement vessel to simulate the backpressure caused by a closed vent valve prior to reaching set pressure and being driven open.

Test Procedures

A measured quantity of pure TBP was saturated with 3 parts by volume nitric acid by vigorous stirring and allowed to settle. The organic layer was decanted off and the weight and volume gain measured. The desired quantity of organic was inserted into the test vessel using a syringe. In several tests DBP (7 vol. %) and butyl nitrate (4 vol. %) were included to simulate decomposition products. Neither these additives nor first saturating TBP with ceric ammonium nitrate (to simulate metal nitrates possibly present) had any apparent affect on the reaction compared with the identical RSST or VSP tests on samples absent these ingredients.

Even though the plant normally uses only 6 M nitric acid or less, the tests used concentrated, 70 weight %, nitric acid since this is conservative and covers all possible abnormal situations. RSST scoping tests performed with lower concentration nitric acid in the TBP confirmed this.

Similarly, in the plant TBP is normally mixed with an organic diluent (parrafin hydocarbons such as dodecane) and the organic mixture is only 30 vol. % TBP. All the tests conservatively used pure TBP except for two RSST scoping tests: one which included 30% TBP with 70% commercial dodecane, and the other which included 30% TBP with 70% actual diluent supplied from SRS. These tests resulted in milder reaction than corresponding tests with pure TBP due to: (1) the greater heat capacity per unit mass of TBP reactant provided by the diluent, and (2) the lower nitric acid oxidant solubility with the diluent.

As indicated, the VSP includes a temperature compensated guard heater to prevent heat loss and an auxiliary heater to control the sample heatup rate. Typically the sample is heated (by auxiliary heater) on a ramp of 1 to 2 C per minute to the 100 C range at which a heat-wait-search mode is initiated to determine whether the reaction is sufficient to self heat. If so, the auxiliary heater is left off for the remainder of the transient. Otherwise the sample is heated approximately 5-10 more degrees and the heat-wait-search repeated. Typically for the vented cases boiling-like behavior is evidenced between 115 and 125 C with no self heating until 130 C. For the closed system self heating was initiated at 116 C, however.

Typical Test Results

The non-vented VSP data are shown in Figures 1 through 5 which represents the adiabatic behavior of a 50 gm equilibrium sample of TBP saturated with HNO3. In this case the can burst when the pressure reached 690 psi. The peak temperature recorded is 700 C. The self heat rate exceeded 10,000 C/min. The peak pressurization rate recorded is on the order of 1000 psi/min.

In contrast to the above data, Figures 6 through 8 show vented VSP data with a 0.040 inch diameter vent and a 75 gm equilibrium sample. In this case the peak temperature is 250 C and the pressure rise only 0.5 psi. The peak heat rate is only 20 C per minute, a factor of 500 less than with no vent. The dramatic effect the pressure has on the temperature transient resulting from a non-vented configuration is illustrated in Figure 9 which compares the two temperature transients.

This effect is further illustrated by the temperature rate equations for the closed and open system configuration, respectively

$$\dot{T} = 3.24 \cdot 10^{15} e^{-13{,}500 / T_R}$$
and
$$\dot{T} = 6.27 \cdot 10^{12} e^{-12{,}000 / T_R}$$

where $\dot{T}$ (C/min) is the rate of temperature rise at reaction temperature T_R(K).

Nichols [1960] had estimated Arrhenius rate equation parameters for the reaction of TBP saturated with up to 11 M nitric acid.

$$\lambda = s \cdot e^{-E / R \cdot T_R}$$

The Nichols activation energy, E, of 26,800 cal/gm-mole-K with the gas constant , R, value of 1.987 cal/gm-mole-K yields the identical temperature dependence as the VSP closed system test, i.e. E/R=13,490 vs 13,500 from fitting VSP data. Nichols also estimated the frequency factor, s, to be 2.58×10^{12}/min for TBP equilibrated with 6-11 M nitric acid. This coupled with his calculated heat of reaction of approximately 200 cal/gm of solution, as more recently updated to 340 cal/gm by Hyder [20], and a TBP/HNO3 heat capacity, c_p, of approximately 0.7 cal/gm-C yields

$$\dot{T} = \frac{\lambda H}{c_p} \cong 0.7 - 1.3 \cdot 10^{15} e^{-13,490/T_R} \quad \text{degree C/min,}$$

which is approximately 20 to 40 % of the VSP closed system result for TBP saturated with 15 M nitric acid. Thus the VSP closed system transient results are relatively consistent with but 2 to 5 times more energetic than the earlier isothermal sealed tube results. On the other hand, the VSP open system rates are only about 5% to 10 % of the closed system heat rates. These rates are compared graphically in Figure 10.

Venting Requirement

Through variation of both, the mass of red oil, and the vent diameter, in the VSP test series it was possible to cover a broad range of red oil mass to vent area ratios that yielded from essentially no pressure rise, to high disruptive pressures. Figure 11 illustrates this in terms of the pressure increase vs the ratio (red oil mass/vent area). The rupture pressure of the SRS tanks is estimated to exceed 200 psig. The data point with 22 psi pressure rise, at a mass/vent area of 312.5 gm/mm2, is well within this structural capability and serves as a best estimate for the safe vent area. However because the curve above this point is very steep and there is uncertainty in extrapolating small scale results to plant equipment size, a margin of a factor of 1.5 on vent area is judged appropriate. Consequently the SRS tank vent areas were increased such that the mass loadings are below the dashed line at 208 gm/mm2. This corresponds to a vent area of 14 sq inches to accomodate 3000 lb of red oil.

Interpretation of Tomsk-7 Incident

Reconstruction of the Tomsk incident suggests that up to 500 liters of TBP saturated with strong nitric acid (~ 15 Molar) was involved in the runaway scenario [1],[2]. Considering that TBP can absorb about 55.8 wt% nitric acid, the involved reactants amount to about 780 kg. The effective vent line diameter of the Tomsk-7 incident vessel is believed to have been 70% of 7 cm which corresponds to 417 gm/mm2. Comparing this value to the overpressure relationship shown in Figure 11, clearly suggests that the Tomsk-7 incident resulted from insufficient venting capacity. This conclusion can be made without requiring the need for postulating two-phase flow or foaming. According to Russian reports significant swell and foaming were not observed. Nor was evidence of significant foaming seen in the FAI tests.

The above conclusion is further supported by the measured overpressure resulting from a vented VSP test with a vent line diameter of 0.022 inch subjected to an initial backpressure of 2 atmospheres in order to simulate the set pressure of the pressure control valve during the Tomsk incident. Consistent with the pressure sensitivity illustrated in Figure 11, the modest increase in back pressure of 2 atm resulted in a very large overpressure (~300 psi) as compared to a similar vented VSP test with initially atmospheric pressure which resulted in a peak overpressure of only 22 psi.

General Conclusions

Based on calorimeter tests the following general conclusions concerning the TBP/HNO3 runaway reaction can be made.

1. Runaway is possible in open system, i.e. at atmospheric pressure, where self heating was observed at temperatures in vicinity of 130 C.

2. Energetics is a strong function of pressure, i.e., does not depend on temperature alone.

3. Pure TBP saturated with 15 molar nitric acid is a conservative representation of potential red oil runaway reactions:

   -Energetics increases with increasing concentration of HNO3,

   -Dilution of TBP with parafin-dodecane decreases energetics.

4. No measurable effect is produced by introducing DBP, butyl nitrate, or saturating TBP with ceric ammonium nitrate.

5. Similar runaway behavior is observed between single-phase organic layer and two-phase organic aqueous layer tests, although it is apparently necessary to boil the aqueous layer away prior to achieving runaway when using small scale apparatus.

6. A gas sample collected prior to reaching peak temperature (~250 C) in a VSP open system test showed very little, if any, butene. The sample collected after the peak temperature was mostly butene. This is consistent with pyrolysis of TBP at high temperature.

6. The relationship between vent size, reaction mass and overpressure has been obtained with TBP saturated with 15 molar HNO3 (considered worst case condition) as shown in Figure 11.

The FAI venting tests have provided important input to the safety bases[24] for adequacy of tank vents to accomodate a runaway reaction of TBP/HNO_3 solution.

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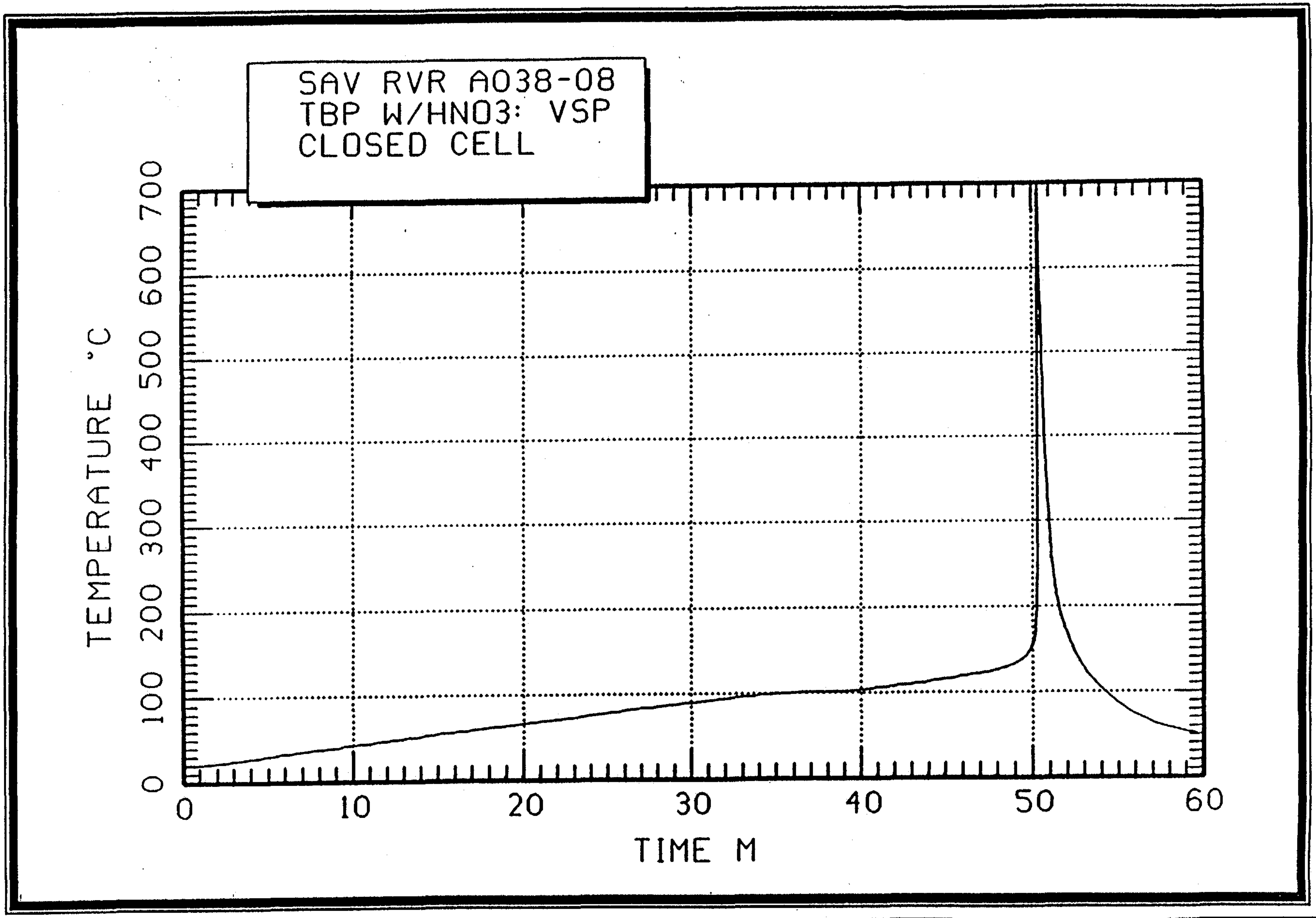


Figure 1 Temperature data from closed cell test

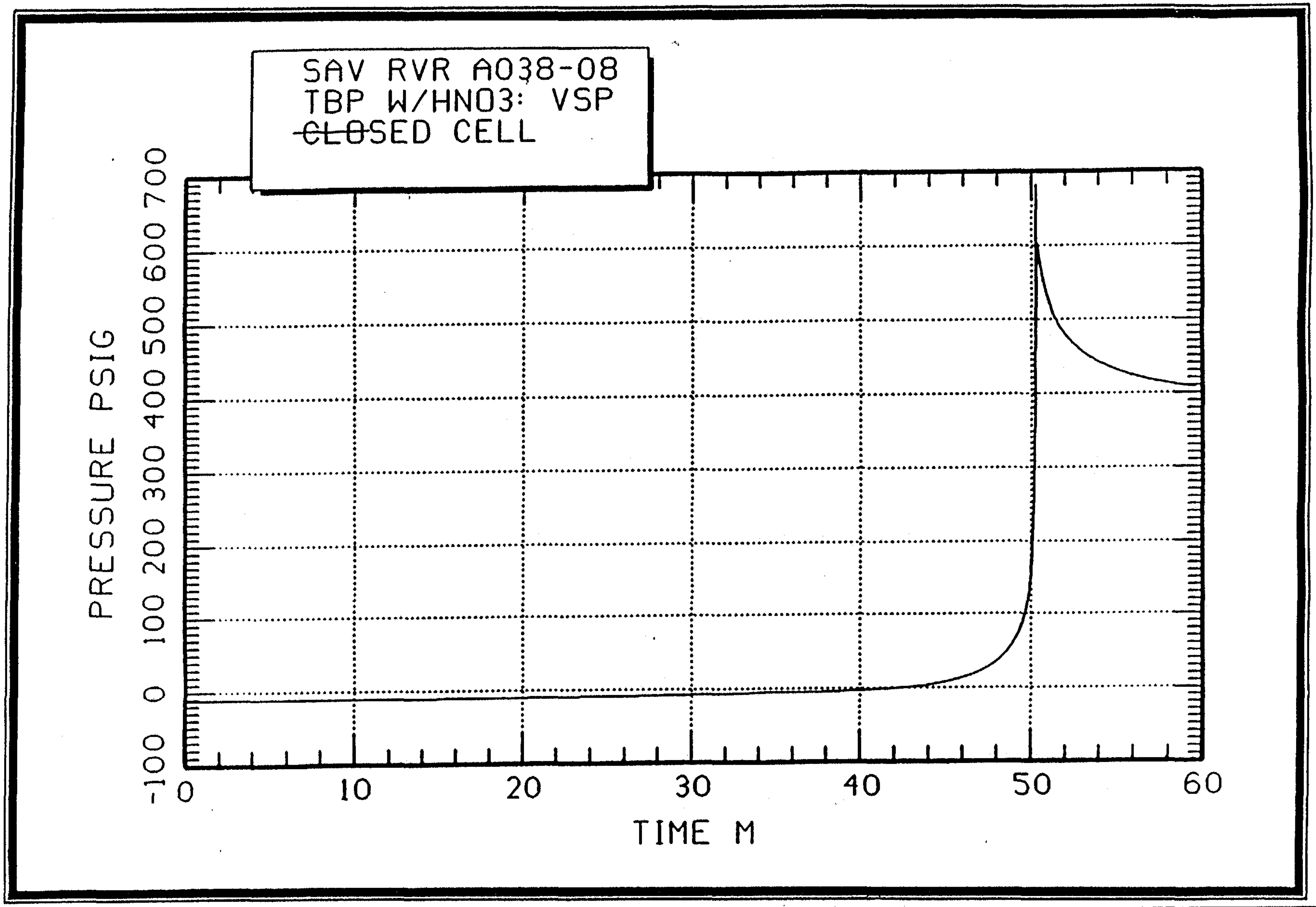


Figure 2 Pressure data from closed cell test

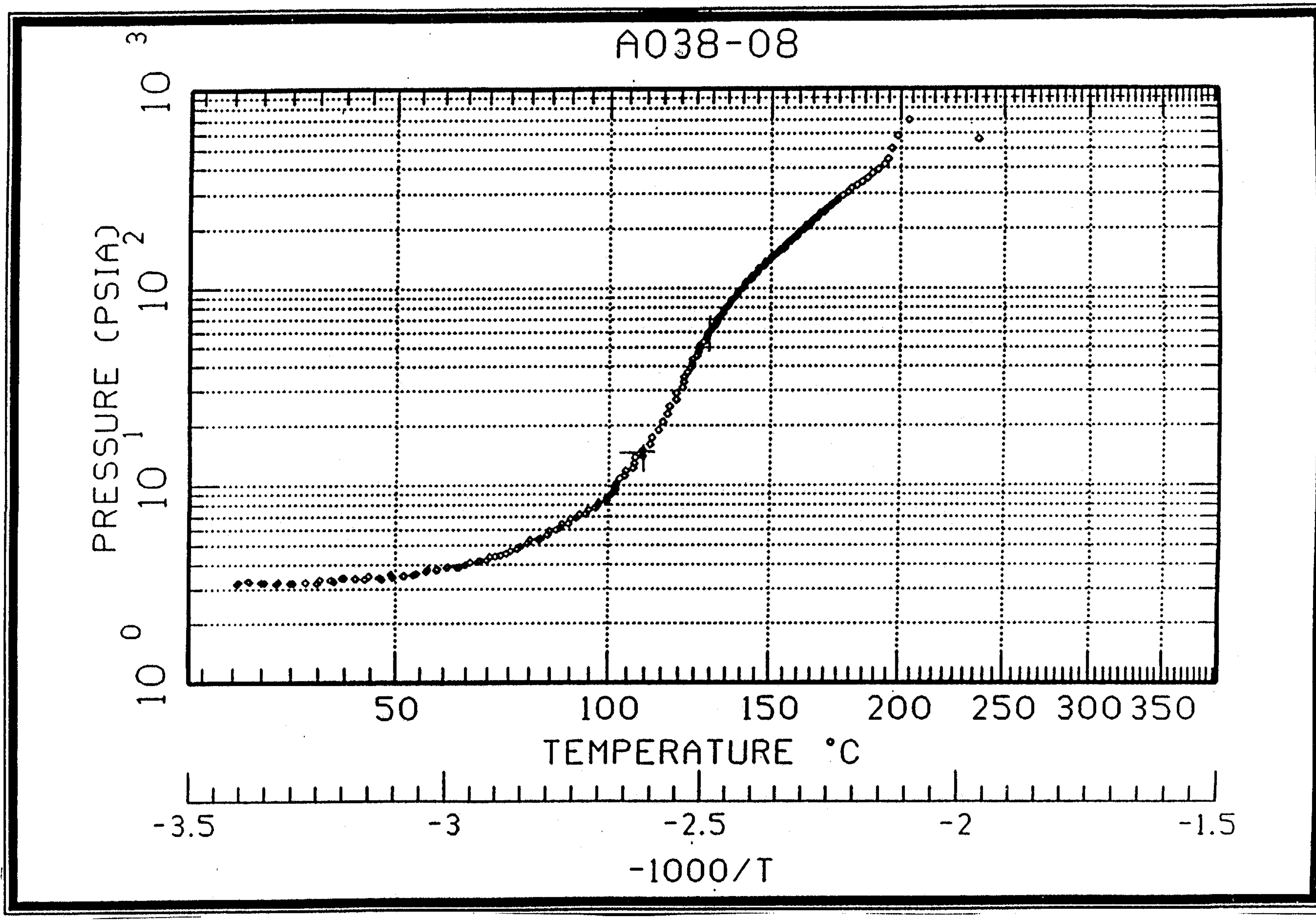


Figure 3 Pressure-temperature data from closed cell test

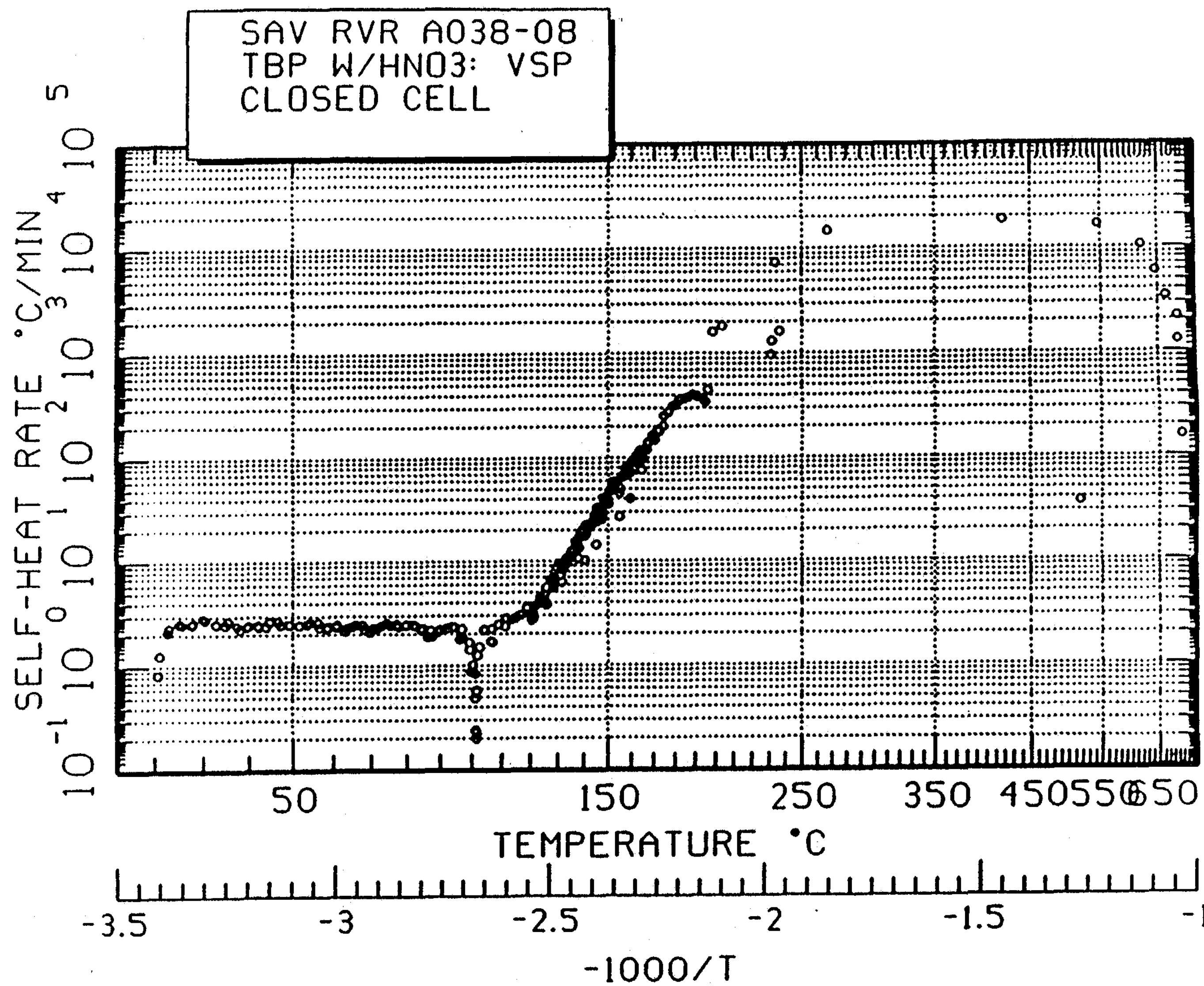


Figure 4 Self-heat rate data from closed cell test

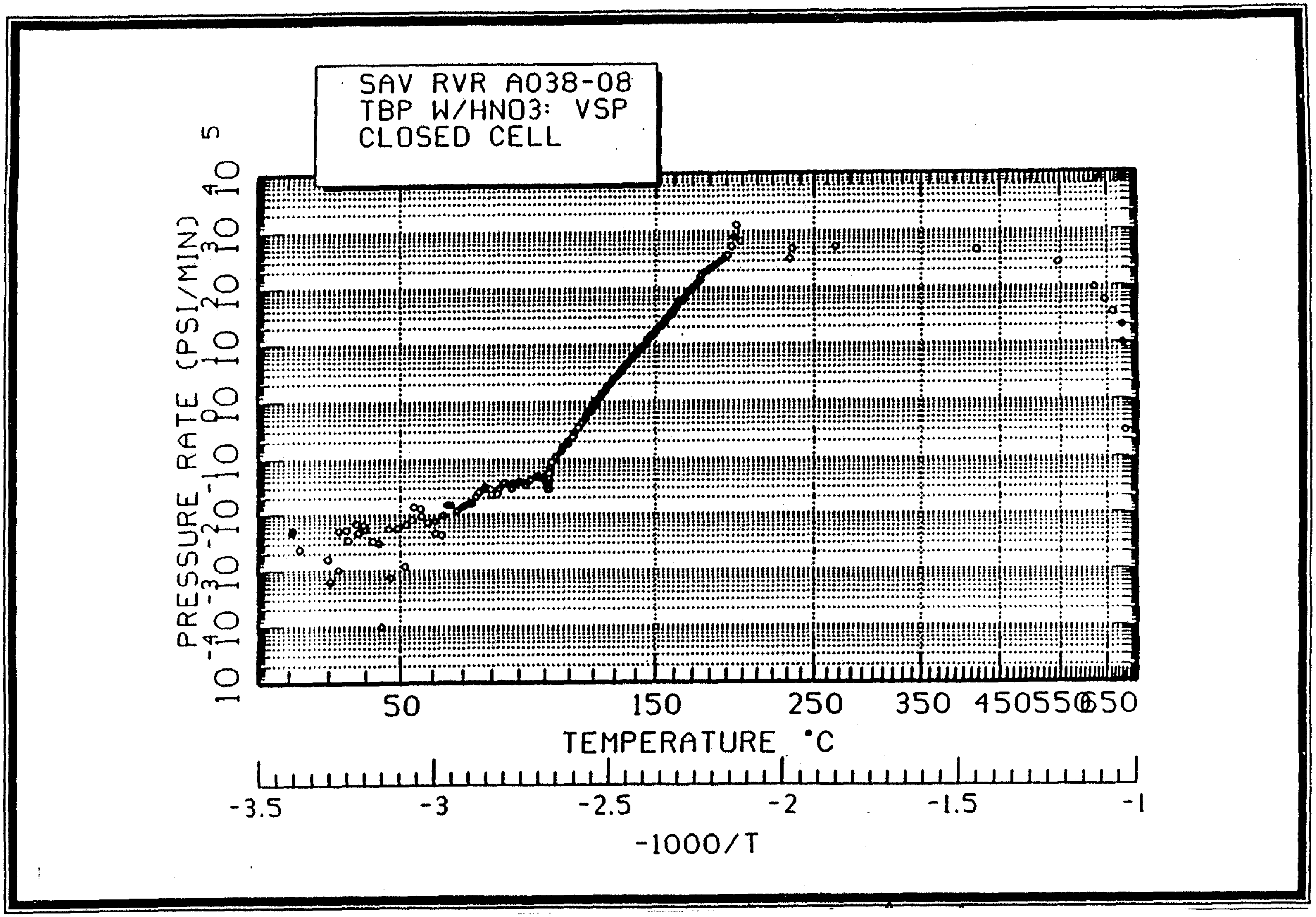


Figure 5 Pressure rise rate data from closed cell test

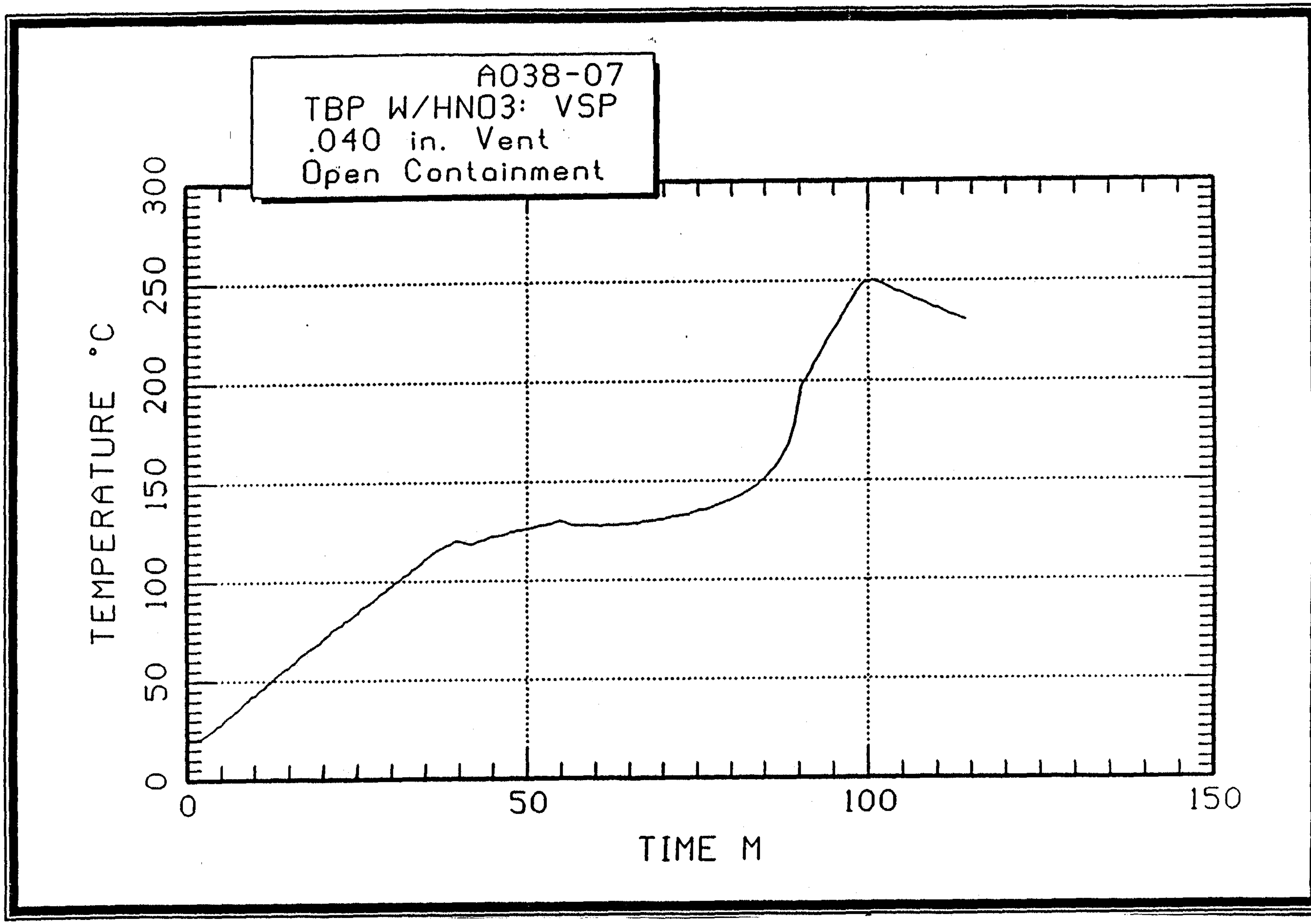


Figure 6 Temperature data from 40 mil vent test

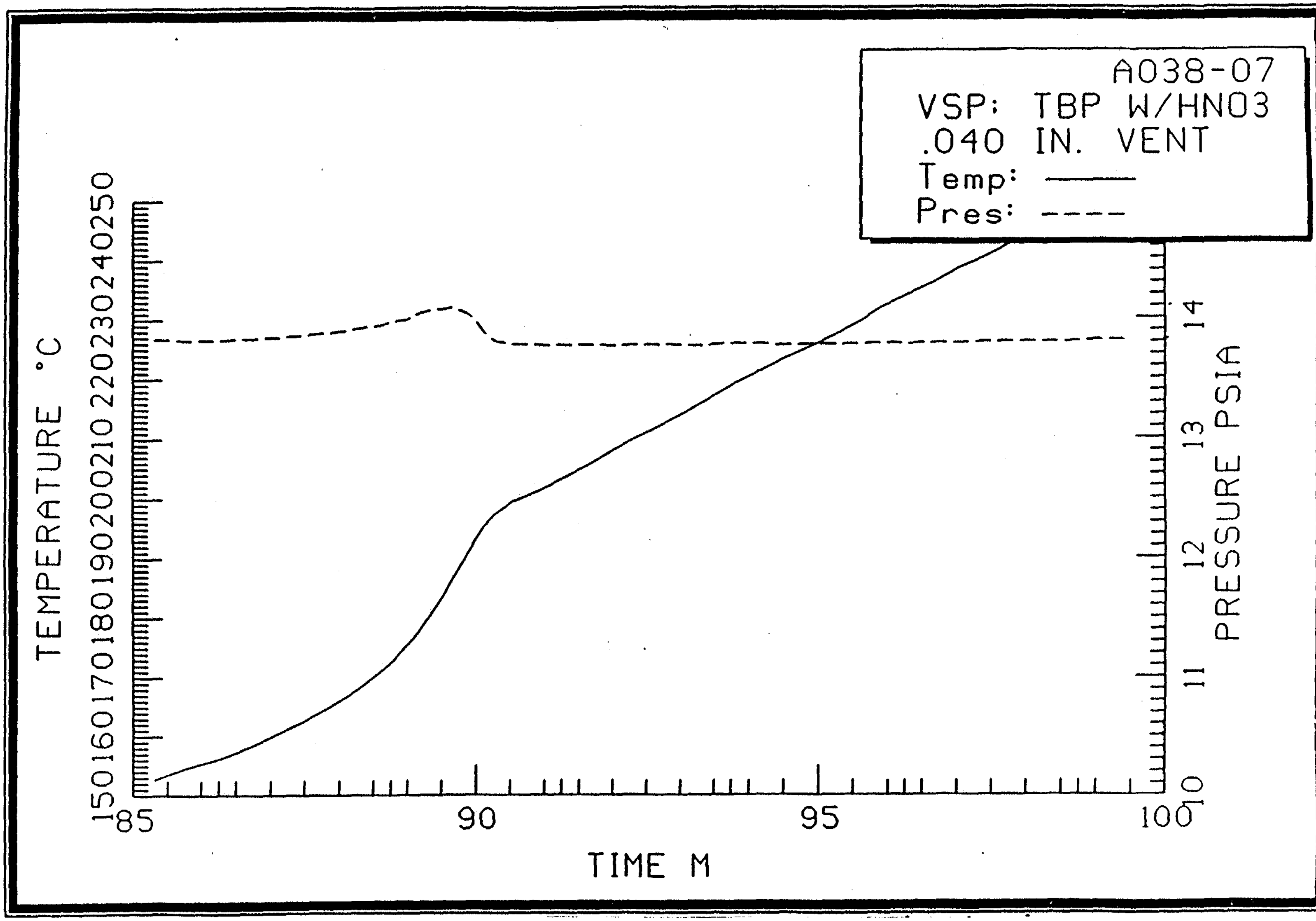


Figure 7 Temperature/pressure data from 40 mil vent test

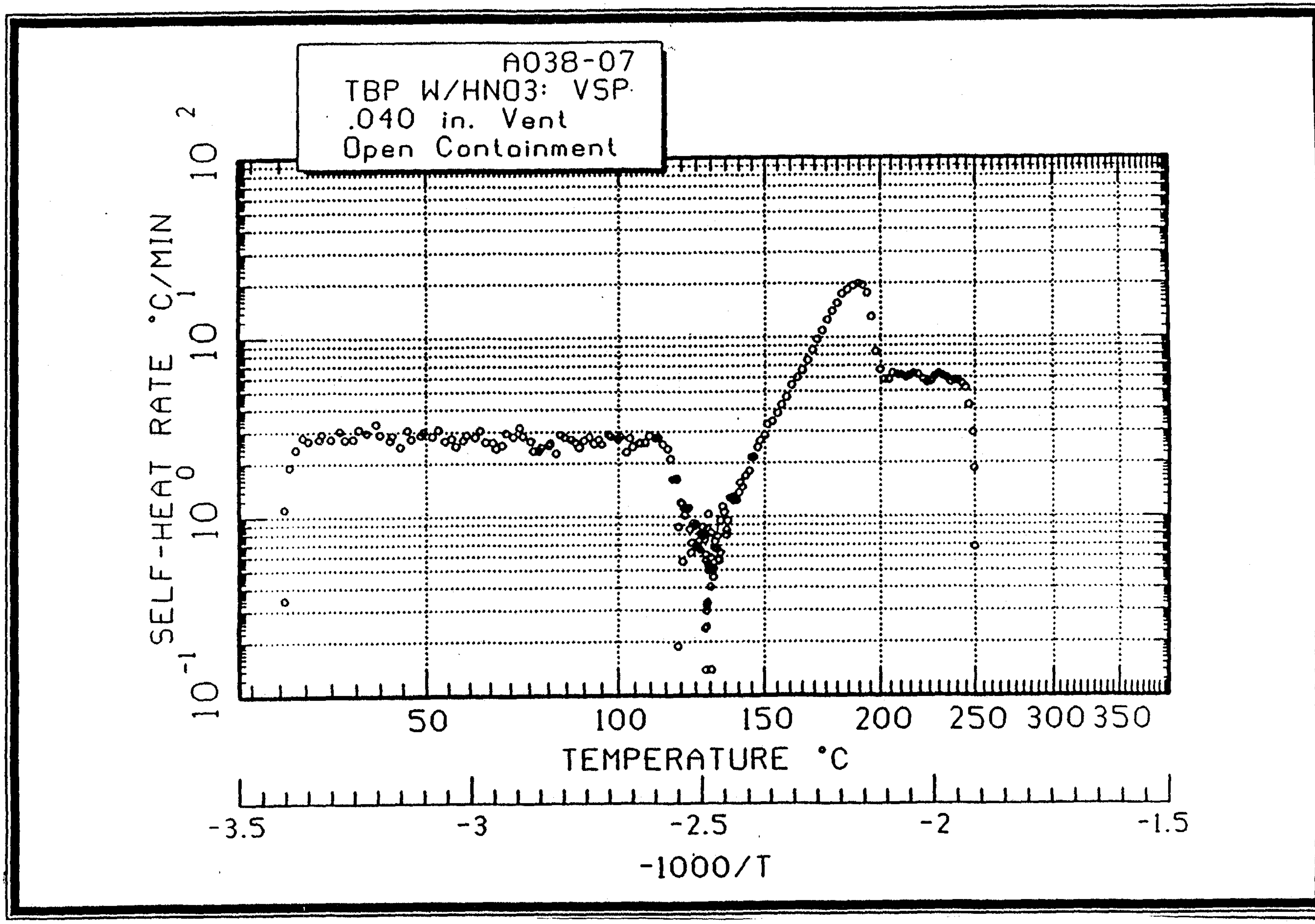


Figure 8 Self-heat rate data from 40 mil vent test

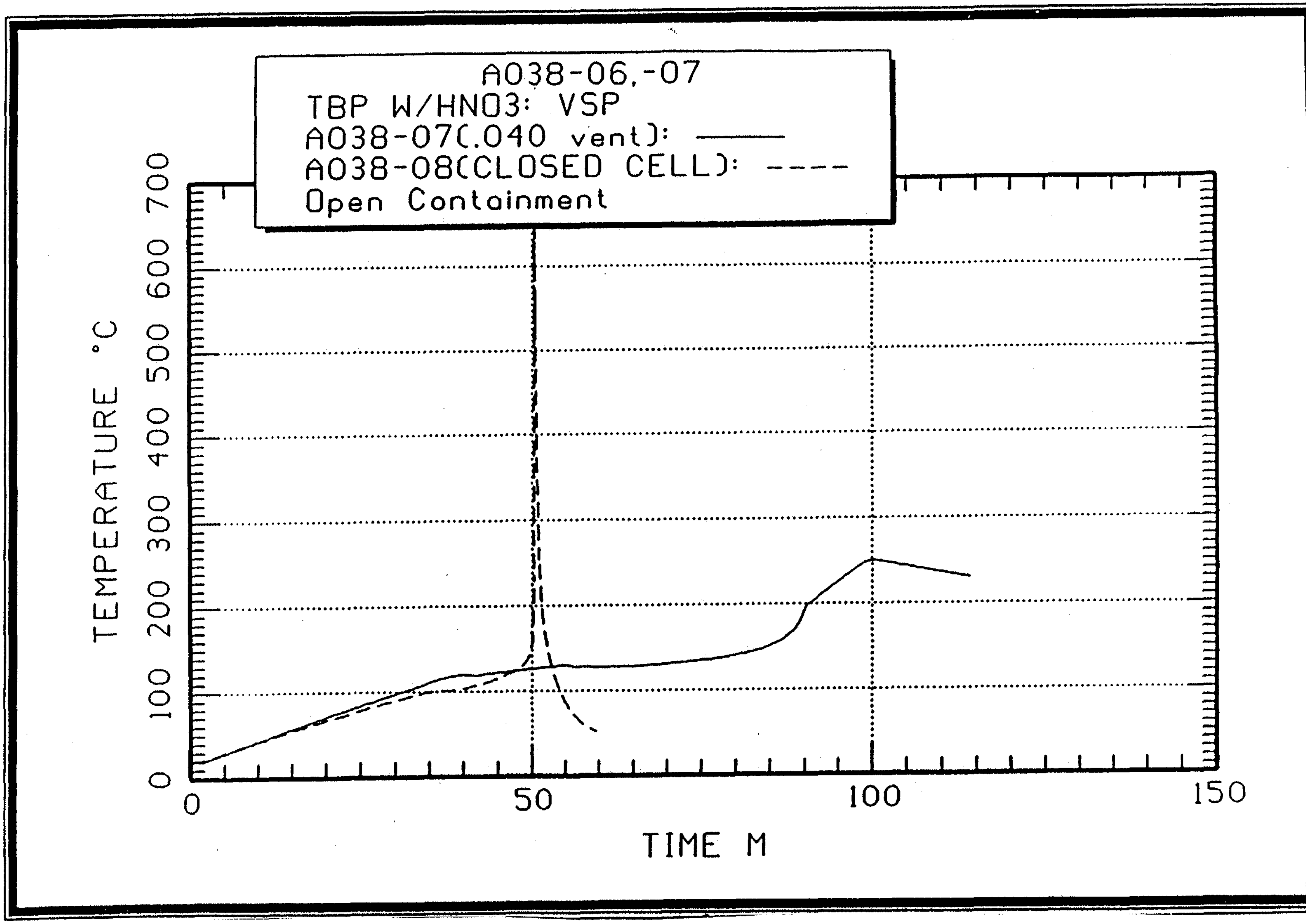


Figure 9 Comparison of Temperature data from open and closed cell tests

Figure 10 Comparison of Heat Rate Equations

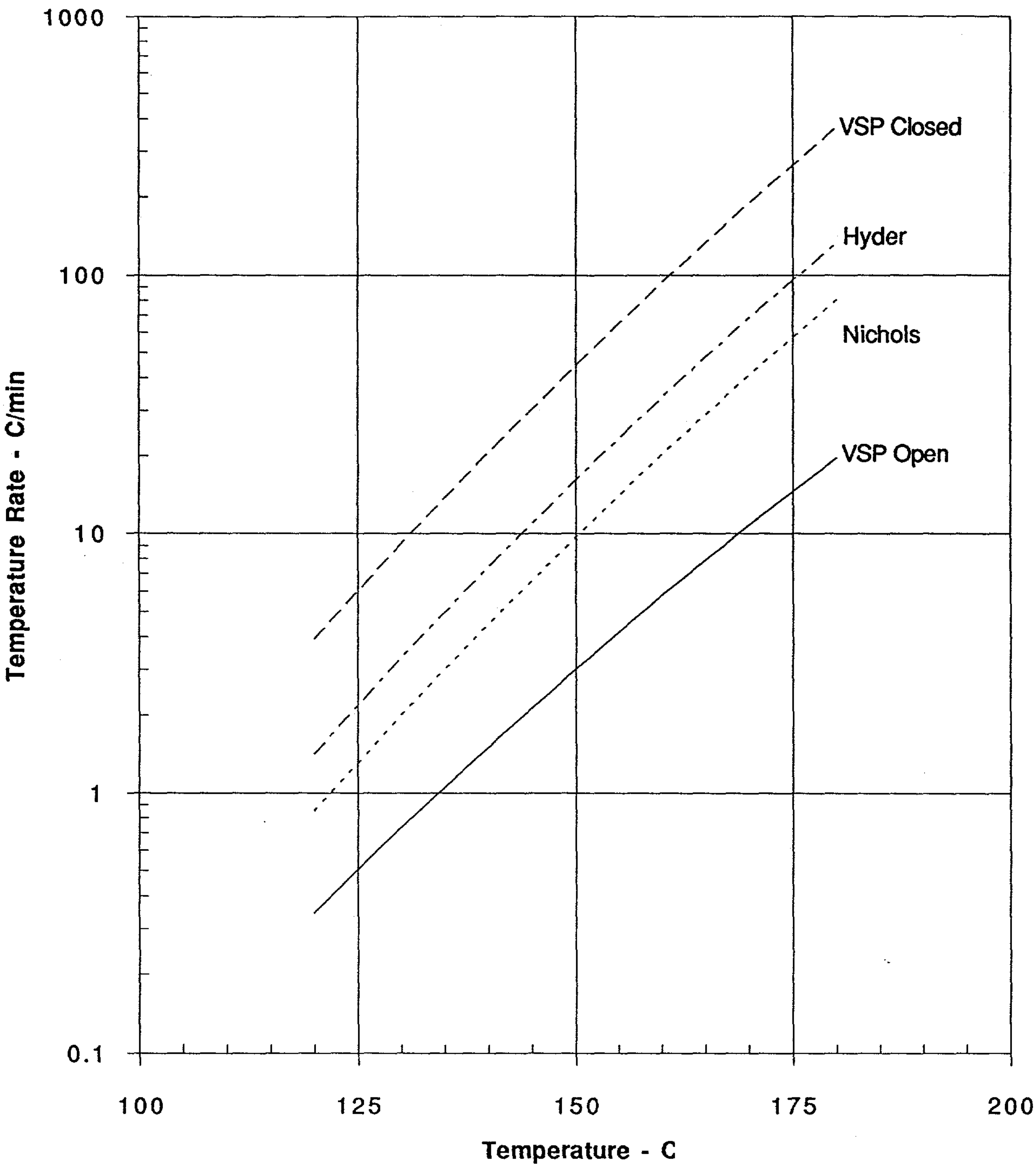
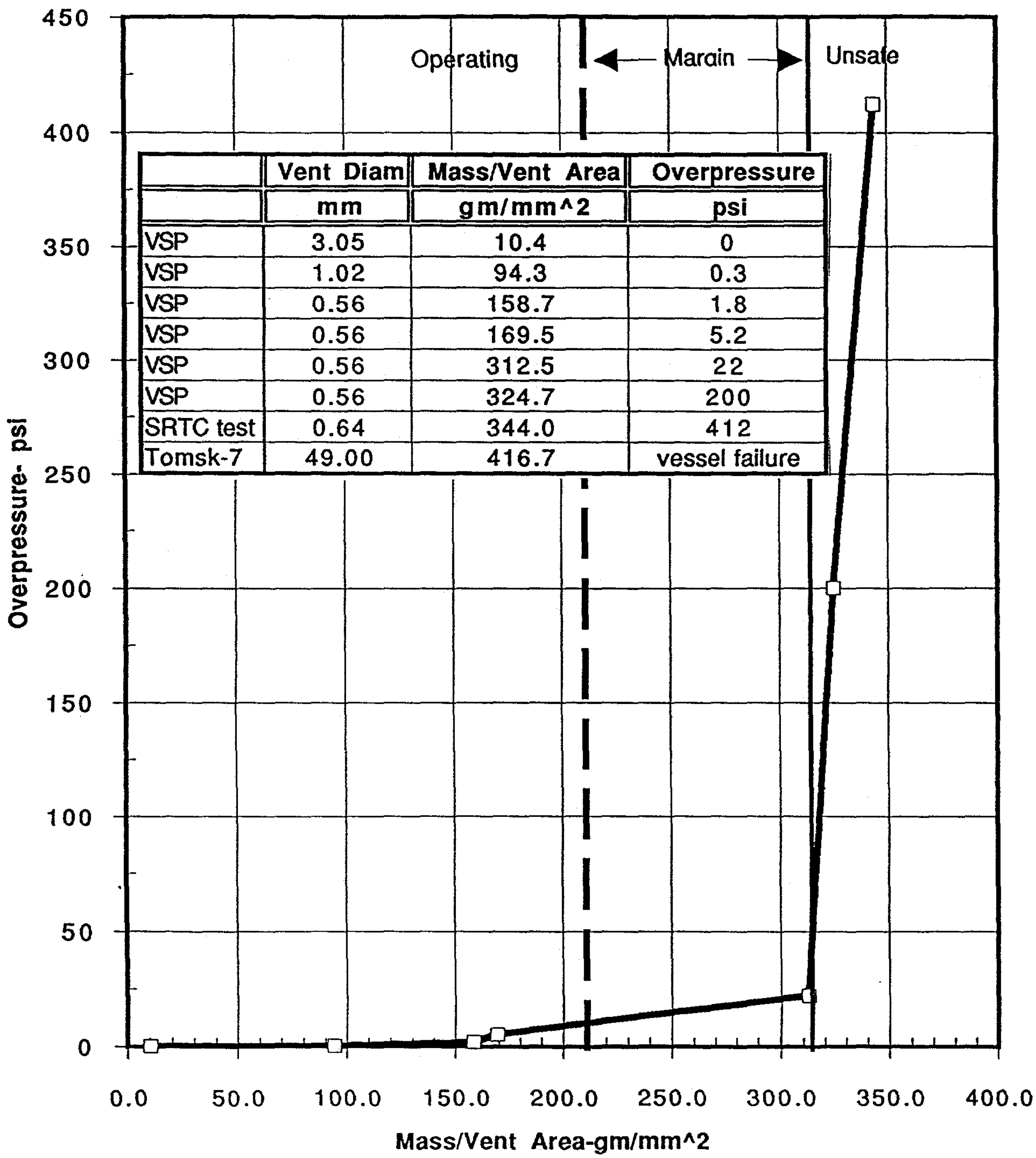


Figure 11 Pressure vs Mass/Vent Area Ratio



	Vent Diam	Mass/Vent Area	Overpressure
	mm	gm/mm^2	psi
VSP	3.05	10.4	0
VSP	1.02	94.3	0.3
VSP	0.56	158.7	1.8
VSP	0.56	169.5	5.2
VSP	0.56	312.5	22
VSP	0.56	324.7	200
SRTC test	0.64	344.0	412
Tomsk-7	49.00	416.7	vessel failure