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Defining the consequences of exothermic behavior in large-scale equipment utilizing DIERS technology [1]

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Abstract

In addition to knowing the thermal effects associated with reactive systems, it is important in many chemical manufacturing operations to understand the potential consequences of these systems, particularly in regards to their pressure generating potential. Knowing this information, appropriate actions can then be taken to insure that, if loss of thermal control occurs, no damage to plant facilities or harm to personnel results. A method for investigating these consequences is technology developed by the Design Institute for Emergency Relief Systems (DIERS), a sponsored research activity of the American Institute of Chemical Engineers (AIChE). An important aspect of this technology is that temperature and pressure can be measured on a laboratory scale and the results can then be utilized to determine an appropriately sized vent which can safely relieve pressure should it unexpectedly develop in processing equipment. Experimental apparatuses employed in the DIERS technology are the vent sizing package (VSP) and the reactive systems screening tool (RSST). In this paper, both devices are reviewed, together with their application in a process safety testing program. In addition, factors considered and criteria utilized for establishing the need for this testing are discussed. Finally, applications to real plant situations are presented.

INTRODUCTION

After determining the exothermic behavior associated with reactive systems, i.e., magnitude, rate, and initiation temperature, utilizing such thermal analysis techniques as differential scanning calorimetry (DSC), differential thermal analysis (DTA) and accelerating rate calorimetry (ARC), it is important in many cases to understand the consequences of this behavior especially in terms of pressure. This results because it is the

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uncontrolled build up of pressure that typically results in unwanted discharges or damage in large-scale chemical manufacturing equipment.

Technology developed by the AIChE Design Institute for Emergency Relief Systems (DIERS) is especially suited for this characterization. The technology allows maximum temperatures and pressures occurring in large-scale plant equipment due to exothermic behavior to be measured using laboratory bench-scale equipment. Equally important, the DIERS technology provides a method, which requires little physical property and kinetic data, for sizing emergency relief devices to relieve safely any pressure that may develop. Typically this release of pressure involves two-phase liquid/gas flow and requires more vent area than a simple gas or liquid discharge. Two commonly utilized experimental tools used for data collection in the DIERS technology are the vent sizing package (VSP) and the reactive systems screening tool (RSST).

VENT SIZING PACKAGE

The vent sizing package (VSP) is a bench-scale test apparatus which consists of three principal parts: a main console, a satellite test stand, and a containment vessel [1, 2]. The main console has the controls and computer to operate many of the VSP functions and collect data during an experimental run. The satellite test stand, usually located under the containment vessel, contains the thermocouple amplifiers, gas inlet/outlet valves and a magnetic agitator base. The containment vessel is the novel element of the VSP (see Fig. 1). It consists of a 4000 cm^3 stainless steel

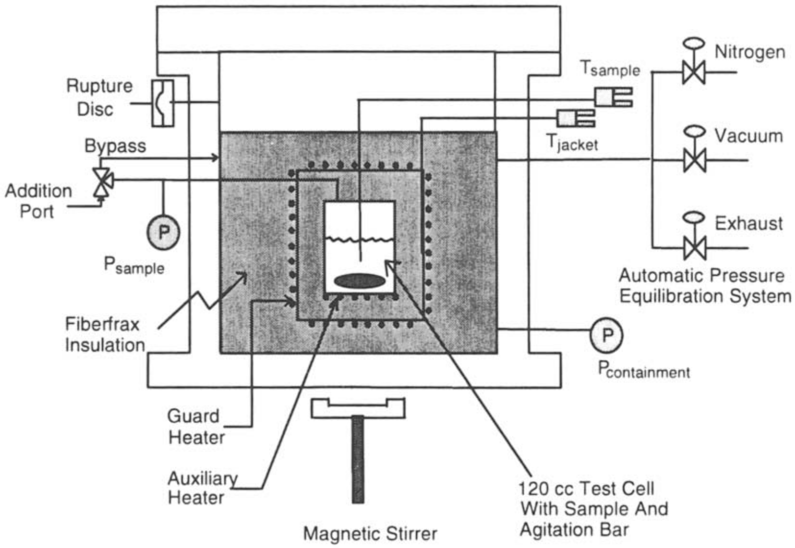

Fig. 1. Schematic of VSP 4000 cm^3 containment vessel.

vessel which can withstand pressures over 13.7 MPa; inside the containment vessel is a test cell, 120 cm^3 in volume, which holds the material under investigation. The test cell also has a magnetic agitator bar to provide mixing during a run and it rests inside a heater which consists of two parts, the auxiliary and the guard. The auxiliary is used to raise the temperature of the test cell contents; the guard is employed to keep the wall temperature of the test cell equal to the internal temperature, thus maintaining the system adiabatic.

One of the main advantages of the VSP is that it possesses a relatively low thermal mass. As a result, a significant portion of the heat generated goes to raising the temperature of the reaction mass. This is what normally occurs in a plant environment. Little of the thermal energy goes to heating the reaction sample holder or test cell as is common with many laboratory calorimeters. The low thermal mass of the VSP is possible because the test cell is made typically of thin metal, such as stainless steel or Hastelloy C. Being constructed of thin metal, however, the VSP test cell cannot withstand significant internal pressure if run in a closed, completely sealed, mode. To overcome this limitation, the pressure inside the containment vessel is maintained very close to the pressure inside the test cell by evacuation and/or introduction of nitrogen gas utilizing an automatic pressure equilibration system.

The closed sealed mode of the VSP is normally employed for testing because it can provide the most accurate data. The VSP, however, can also be operated in the open mode where the test cell is freely vented to the containment vessel. In this open mode, nitrogen pressure is normally introduced into the containment vessel to minimize evaporation of the sample under investigation. One of the main uses for the open mode is the study of very energetic systems. With very energetic systems, the containment vessel automatic pressure equilibration system usually cannot maintain the proper differential across the test cell wall and rupture of the closed test cell results. The VSP can also be modified to conduct specialized testing, such as blow down tests, to check flow characteristics and to simulate various plant conditions.

REACTIVE SYSTEM SCREENING TOOL

The reactive system screening tool (RSST) is a bench-scale test apparatus similar to the VSP but simpler in design and operation [3, 4]. The RSST utilizes a small controller for heating as well as for amplifying the temperature and pressure signals. In addition, a computer is employed to record data and supervise the controller. The RSST also possesses a containment vessel (400 cm^3) and a test cell (10 cm^3). However, it employs only one temperature thermocouple and a single pressure transducer (see

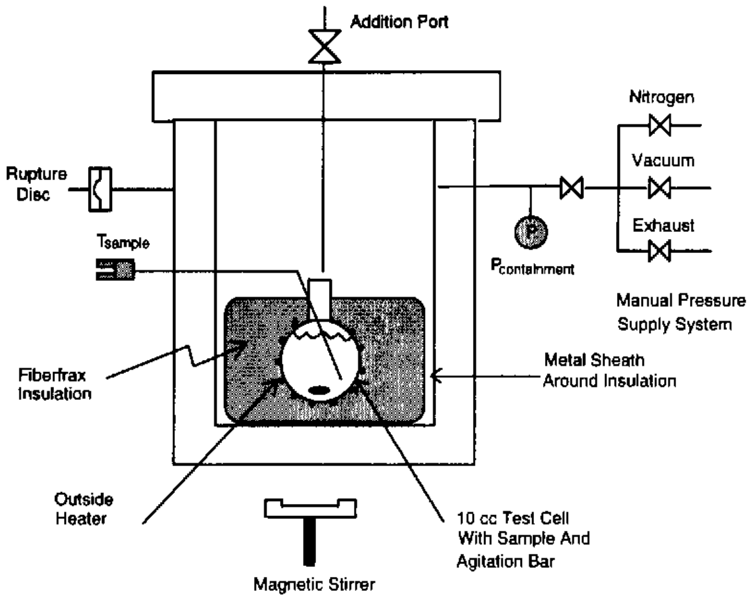

Fig. 2. Schematic of RSST 400 cm^3 containment vessel.

Fig. 2). The spherical test cell used with the RSST is typically made of glass and is fitted with an internal or external heater.

The RSST is not a true adiabatic calorimeter like the VSP because it does not try to eliminate heat losses to its surrounding. Instead it attempts to compensate for these losses by adding additional energy determined by calibration through the heater. The amount of additional heat needed varies with temperature and pressure as well as sample properties. The RSST is often used for testing with systems which possess rapid temperature or pressure rise rates as it is easier to set up and operate.

TESTING CANDIDATES

One method of selecting candidates for testing in either the VSP or RSST is based on standard thermal analysis techniques. Usually, processes to be run in large-scale equipment are examined for exothermic activity by testing streams utilizing such devices as differential scanning calorimetry (DSC), differential thermal analysis (DTA), or accelerating rate calorimetry (ARC). Typically, however, these thermal techniques, cannot measure directly the pressures and temperatures that can develop in large processing equipment. As a result, if any exothermic activity of concern is seen when utilizing these thermal analysis techniques, then additional testing should be considered with the VSP or RSST. If significant pressure is measured in either the VSP or RSST, then the need to relieve pressure safely in plant equipment, utilizing a properly sized emergency relief device able to handle two-phase flow, must be evaluated.

A second way of selecting candidates for VSP or RSST testing is through hazard identification reviews. These reviews normally employ techniques such as failure mode and effect analysis (FMEA) and HAZOP (hazard and operability study) [5, 6]. If, in the course of conducting one of these reviews, an upset scenario that can occur in large-scale chemical manufacturing equipment is identified but its potential for generating pressure is unknown, then the VSP or RSST can, in many cases, be very effective in determining the consequences of the identified upset. Examples of a plant upset which can be studied in the VSP or RSST are water intrusion to water-reactive materials, rapid addition of materials leading to uncontrolled exothermic activity, the over or under addition of reactants or the charging of materials in the wrong order. Many plant upsets can be studied in the VSP or the RSST because both designs include a line that allows materials to be added during an experimental run.

DATA ANALYSIS

For standard VSP and RSST studies, the significant data collected are temperatures and pressures as a function of time. Employment of this data, especially for sizing emergency relief devices, depends on how the pressure from exothemic behavior is generated. If the pressure is due to the vapor pressure of volatile components (called a tempered system), then the rate of temperature rise data is important. If the pressure is due to gaseous by-products generated as a result of the exothermic behavior (called a non-tempered system), then the maximum rate of pressure rise data are significant. If pressure results from both high vapor pressure components and gaseous by-products generation (a hybrid system), both temperature and pressure rise rates are required.

Once the data has been obtained, a number of methods can be utilized to size the emergency relief device needed to handle two-phase flow. One that is relatively straightforward to use involves simplified expressions derived by Leung and Epstein [7–9]. In this method, emergency relief design is based on stagnation conditions, that is conditions just before there is a release of pressure from the plant vessel or equipment. In addition, only a single parameter is employed to describe the stagnation conditions. Included in the simplified relationships are a number of important assumptions. One is that flow during venting is homogeneous two-phase, i.e., liquid and gas or vapor are uniformly mixed throughout. This tends to lead to conservative designs. In addition, it is assumed that the system is not highly viscous because the venting of two-phase flow for these systems is complex and the application of simplified expressions is not well established.

The size of the emergency relief devices from VSP or RSST data utilizing Leung's or similar methods is normally specific for defined plant conditions. Therefore, if a parameter such as vessel charge changes, the emergency relief device size needs to be redetermined. With most methods, the determination can be done without the need to conduct additional experimental work. It is important also to note that many emergency relief device sizing methods determine an ideal vent, that is, no fractional losses are assumed. For the plant, this ideal vent must be corrected for actual frictional losses [10]. These frictional losses include not only the relief device itself but also the associated inlet and outlet piping.

EMERGENCY RELIEF DESIGN EXAMPLES

Non-temperature (gaseous) system

In a study of a new process to be introduced in a large-scale chemical manufacturing facility, it was established, through ARC testing, that in a batch distillation, the final residue possesses exothermic activity which initiates as low as 180°C. Because the maximum expected normal operating temperature in the plant for this stream could be over 150°C, a closed VSP test was conducted to determine the pressure build-up associated with this exothermic activity. During the course of the closed test, the test cell ruptured due to the excessive rate at which pressure was generated. As a result, a second open VSP test was conducted.

After the open VSP test was completed, the residual pressure at ambient temperatures inside the containment vessel was 0.43 MPa versus the initial back pressure of 0.29 MPa. This indicated that substantial amounts of gas were generated during the test. The pressure generation was, therefore, characterized as non-tempered/gaseous. For sizing an emergency relief device, the maximum rate of pressure rise was thus required. This was determined from the pressure versus time plot from the open VSP test (see Fig. 3) as 0.227 MPa min^{-1}. Using this information, along with the additional VSP test and plant data given in Table 1, the ideal vent required to prevent over-pressurization of the plant vessel from the exothermic activity observed with the distillation residue was found to be 0.150 m in diameter. Because of the size of the device, it was decided to employ a rupture disk as the emergency relief device in the plant. After correcting the ideal vent for the frictional losses of the rupture disk that had a discharge coefficient of 0.62, plus the frictional losses of the plant vent line, which had a length to diameter (L/D) ratio of 200, the final device needed in the plant was determined to be at least 0.221 m in diameter.

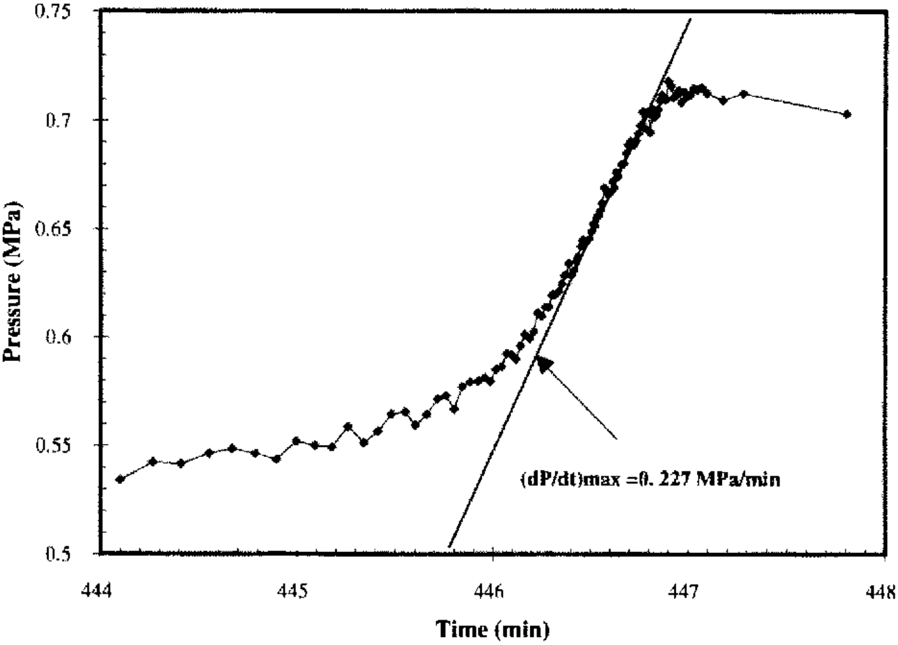

Fig. 3. VSP data for non-tempered (gassy) system.

TABLE 1

Data for non-tempered (gassy) vent sizing calculation

Plant parameters	
Volume of plant vessel	3.785 m^3
Maximum allowable pressure of plant vessel	1.13 MPa
Charge to plant vessel	2271 kg
Volume of vessel charge	1.893 m^3
Bulk density of vessel charge	1200 kg m^{-3}
Discharge pressure	0.101 MPa
Relief device set pressure (P_{set})	1.17 MPa
Maximum pressure accumulation ($P_{turn\text{-}around}$)	1.29 MPa
VSP test information	
Test cell sample charge	0.0451 kg
Free board gas volume during test	4000 cm^3
Temperature during peak pressure rise	360°C
Correction for cooler containment	1

Tempered (vapor) system

During a HAZOP review of a Grignard reaction conducted in tetrahydrofuran, an upset considered as credible in the plant was the addition of all reactants before initiation occurred. To determine the consequences of this upset, a closed VSP test was conducted in which all reactants were added rapidly to the test cell. A short time after the addition, initiation occurred and a significant increase in temperature and pressure was observed. After the test was completed and the test cell cooled to ambient temperatures, the residual pressure was found to be essentially equivalent to its starting value. As a result, the observed pressure increase during this test was considered primarily due to the volatilization of reaction mixture components, particularly the solvent tetrahydrofuran. Therefore, the situation during emergency relief venting in the plant would be a tempered/vapor one. For vent sizing determinations, the rates of temperature rise both at the plant vessel's emergency relief device set pressure and at the maximum pressure accumulation, were required (see Fig. 4).

This information, together with the additional plant and test data given in Table 2, showed that an ideal vent 0.051 m in diameter would be sufficient to prevent over-pressure of the plant vessel. Because of the size of

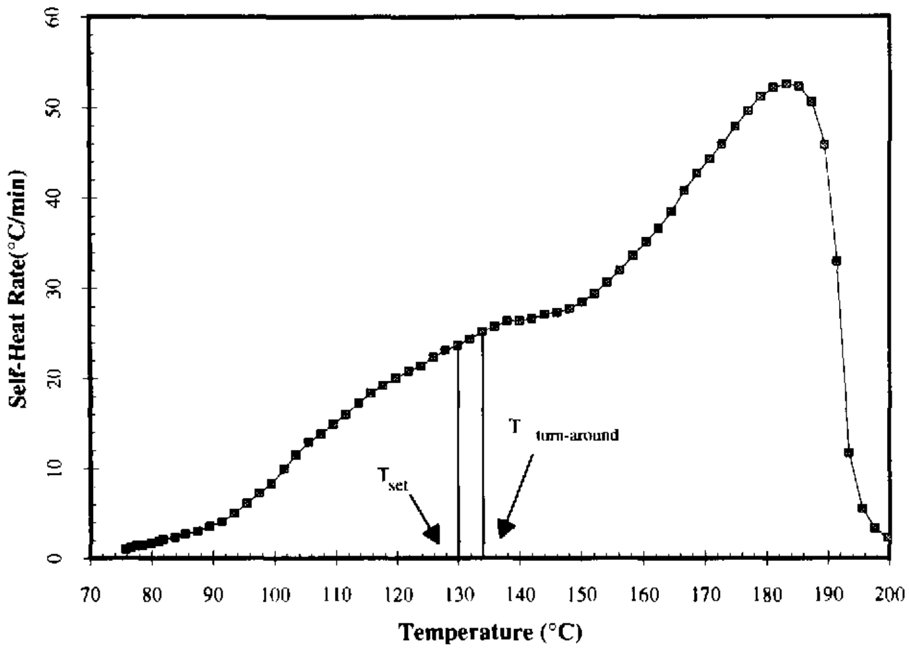

Fig. 4. VSP test data for tempered (vapor) system.

TABLE 2

Data for tempered (vapor) vent sizing calculation

Plant parameters	
Volume of plant vessel	1.1355 m^3
Maximum allowable pressure of plant vessel	0.515 MPa
Charge to plant vessel	363 kg
Volume of vessel charge	0.3528 m^3
Bulk density of vessel charge	1029 kg m^{-3}
Discharge pressure	0.101 MPa
Relief device set pressure (P_{set})	0.536 MPa
Maximum pressure accumulation ($P_{turn\text{-}around}$)	0.581 MPa
VSP test information	
Test cell sample charge	0.0425 kg
Free board gas volume during test	73 cm^3
Relief set temperature (T_{set})	130°C
Temperature rise rate at relief set temp.	22°C min^{-1}
Turn-around temperature ($T_{turn\text{-}around}$)	134°C
Temperature rise rate at turn-around temp.	25°C min^{-1}
Tetrahydrofuran physical properties (ref. 11)	
Latent heat of vaporization	364,008 J kg^{-1}
Density of saturated vapor	11.6 kg m^{-3}
Heat capacity	2100.0 J kg^{-1}°C^{-1}
Antoine equation	$T = \frac{1202.29}{6.995 - \log P} - 226.25$ (P in mm Hg and T in °C)

the required device, it was decided that a rupture disk would be employed for the plant equipment. After correcting for the frictional losses of the relief device that had a discharge coefficient of 0.62, plus the losses in the plant vent line, which had a length to diameter (L/D) ratio to 200, it was found that the rupture disk required for the plant would need to be at least 0.071 m in diameter.

CONCLUSIONS

Both the VSP and RSST are powerful bench-scale tools for determining the maximum temperatures and pressures that can take place in large-scale equipment as a result of exothermic activity. With the information obtained with the VSP and RSST and utilizing techniques developed by the Design Institute for Emergency Relief Systems (DIERS), emergency relief devices that can safely handle the two-phase flow that typically occurs during emergency release with these systems, can then be sized for large-scale processing equipment.

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