THE APPLICATION OF LARGE SCALE TESTING TO THE DESIGN OF AN EMERGENCY RELIEF SYSTEM

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Synopsis

Powder decompositions in driers are in many cases initiated thermally, and commonly, from localised hot spots such as frictional heating, due to the inclusion of tramp material or failure of a bearing. As the gas generation and heat release from such an event is not homogeneous but proceeds at a finite rate throughout the drier contents, the maximum rate of gas generation during such a decomposition will be less than that encountered in an en-masse reaction commonly associated with runaway reactions. This paper presents the findings of an emergency relief system sizing exercise which indicated that classical DIERS sizing techniques for two phase flow from a gassy system was over conservative when employed in drying operations, and that a substantial reduction in the vent area could be achieved based on experimental data obtained from large scale simulation of the relief process.

Keywords:- Driers, Vent Sizing, Thermal Decomposition, Direct Scaling

1. Introduction

Emergency Relief systems within the process industries are common place and are well accepted as a means of protecting vessels from overpressure, the net result of a process deviation such as loss of cooling or agitation and resulting in a runaway reaction.

This paper presents the finding of a vent sizing assessment conducted by this laboratory involving the drying of a thermally sensitive fine chemical. The vent was sized initially using classical experimental methods involving adiabatic dewar calorimetry and DIERS calculation techniques. The outcome was to vastly oversize the required relief area vent and to make it's inclusion in the plant impossible. A laboratory based experimental programme employing direct scaling techniques was then initiated to explore the possibility of reducing the required relief area. In order to increase confidence in the encouraging laboratory predictions, large scale (100 litre) tests were conducted using specially designed test vessel and vent configuration.

2. Classic Vent Sizing Involving Two Phase Flow

The classic method of vent sizing will normally encompass the following steps :

- Identification of the worst case
- Classification of the system to determine the mode of pressure generation
- Identify nature of discharge, single or two-phase flow
- Choice of set pressure
- Runaway characterisation
- Calculation of required relief area
- Correction for down stream effects

Identification of the worst case will normally come from a process hazard assessment and is intended to ascertain the conditions under which a runaway will take place, but must be based on feasible plant circumstances. Classification of the system and determination of the nature of the discharge will, in most cases, result from an experimental investigation, as will characterisation of the runaway itself. Experimental methods for conducting such investigations are described elsewhere in some detail.[1,2,3]

2.1 DIERS and Sizing for Runaway Reactions

The sizing of the required relief area will usually be conducted, employing experimental data obtained during the characterisation exercise, using DIERS design principles for two phase flow [4]. This is a technique that assumes that heat is released in the reaction mass in a homogeneous manner, ie, it is released at an infinite number of reactive centres and that the rate of reaction and consequent rate of heat release at these points is equivalent and exhibiting self accelerating Arhenius characteristics.

2.1 DIERS and Sizing for Thermal decomposition of single components.

Two phase flow resulting from thermal decompositions in driers provides complex problems in sizing the relief device. The application of DIERS calculation methods for gassy systems can vastly oversize the orifice under certain conditions, particularly if the mode of initiation of the decomposition does not exhibit homogeneous characteristics and results from a localised hot spot in the drier that then propagates a decomposition through the reaction mass.

3. The Process Problem

A Rossenmund type filter / drier of 5 m^3 volume had been employed for a number of years for the filtration and drying of a thermally sensitive fine chemical. The material in question had a history of incidents involving thermal decompositions, and indeed, thermal decompositions had occurred in the filter drier on a number of occasions. These events had resulted in complete decomposition of the batch and ejection of a multi phase mixture of solid, vapour and gas into the emergency relief vent and containment system.

3.1 Plant and Materials Data

The vessel was equipped with a 6" diameter burst disk arrangement and convoluted vent line configuration. Although on a number of previous occasions total batch decomposition had occurred in the drier due to a number of differing reasons, the existing vent configuration had coped without the vessel design pressure being exceeded and with no resultant release outside the containment system.

Because of the nature and value of the material, the thermal properties of the material were the subject of an extensive and ongoing experimental investigation. Small scale thermal stability screening tests using Carius tube technology had indicated that the thermally initiated onset temperature was in excess of 110°C and the material generated in excess of 120 $dm^3.kg^{-1}$ of a non-condensible gas. Accelerating Rate Calorimetry and Adiabatic Dewar Calorimetry had indicated that the first detectable onset of any thermal decomposition under adiabatic conditions, ie, those that would be encountered on the manufacturing scale, was in the region of 80°C.

The drying operation was normally conducted at ambient temperature with towns water at 20°C circulating around limpet coils on the outside of the vessel. This resulted in the vessel and its contents being maintained at a temperature significantly below that where runaway problems might first be encountered. Nevertheless runaways had occurred in the vessel resulting in the bursting disc operating.

Circumstances dictated that the existing 6" vent configuration be addressed and it's adequacy be determined in light of current emergency relief system sizing techniques. In addition it was proposed to alter the existing vent line geometry to improve the efficiency of the existing vent.

4. Laboratory Based Experimental Investigation

Once the worst case scenario had been identified, and initially in this case that was thought to be en-masse decomposition of the drier batch, the experimental investigations were started. The DIERS programme has shown that all vent sizing assessments need to be conducted based on experimental data that was generated under conditions that most accurately simulate the manufacturing environment. Consequently the initial temperature, pressure, time data required for sizing was generated using sealed cell Adiabatic Dewar Calorimetry techniques.

4.1 En-Masse Decomposition.

The kinetics of the thermally initiated runaway when conducted under adiabatic conditions was dramatic. Initially the dry feed material was charged to the calorimeter at ambient temperature and the unit sealed. The material was heated in a "heat, wait, search" profile until exothermic activity was detected. At this point the heating was isolated and the material maintained under adiabatic conditions. This was normally at a batch temperature of approximately 100°C. A typical decomposition trace is shown in Figure 1.

Employing the DIERS calculation methods for gassy systems, the required relief area to cope with an En-masse decomposition was 1.6m^2, 1.4 m in diameter, clearly much larger than the existing 6" vent, a system that had already been confirmed as being able to cope on the manufacturing scale without rupture and loss of containment. In addition, no consideration was given in the calculations to the effect of flow uncertainties in the vent line, a factor which will significantly increase the required relief diameter further.

In considering the outcome of these results the validity of the system being tested needed to be addressed as emergency pressure relief was obviously unacceptable as a basis of safety if this en-masse decomposition was the most feasible worst case scenario.

4.2 Hot Spot Initiated Decompositions.

Decompositions in driers which contain known thermally sensitive materials are rarely initiated by heating the drier contents to its decomposition temperature, as was simulated here. However such events have been known to be initiated by a localised hot spot due to the inclusion of tramp metal in the drier or failure and resultant over heating of a bearing.

Any decomposition initiated in this manner does not behave as an en-masse reaction but the decomposition front propagates at a finite rate throughout the reactor rather that the whole mass decomposing simultaneously. Credit can be taken for this phenomenon and consequently the maximum rate of gas generation and hence the required relief area will be substantially less than that encountered with an en-masse decomposition.

By considering these points, the assessment centred on examining the kinetics of the runaway when initiated by a hot spot present in the material which was at ambient temperature. Modification of the Adiabatic Dewar Calorimeter allowed the inclusion of a resistance wire in the reaction mass. The decomposition was then initiated by applying an electrical potential to the wire resulting in a localised hot spot in the reaction mass.

The rate of gas generation for the decomposition was then calculated, making the assumption that, in an enclosed vessel , the decomposition gasses obeyed the ideal gas law. By examining the rate of gas generation for this form of decomposition and applying DIERS methods for gassy systems, the required relief area was substantially reduced and was $0.16m^2$ or 0.46 m in diameter, but still with no correction for vent line Clearly, however, it was still much larger than that already employed on the vessel.

4.3 Closed Cell Tests - Conclusions

This work confirmed the supposition that the required relief area could be substantially reduced compared with that based on an en-masse decomposition, however further work was required to ensure that the existing vent was capable of coping with all feasible decompositions within the drier. By this stage it was clear that the possibility of an en-masse initiated decomposition was eliminated from the assessment.

Chemical investigation of the products of decomposition indicated that although the bulk of the material was carbon monoxide, carbon dioxide, other complex gasses and solid carbonaceous waste, there was a significant proportion of volatile tars and low molecular weight aliphatic aldehydes generated. It was felt possible that the presence of these volatiles may well temper the runaway process by removing heat as latent heat, subsequently moderating the kinetics of the decomposition, effects that would not be observed using the sealed cell tests reported above. The outcome of any such phenomena would be to further reduce the required relief area.

In order to determine the effect of any tempering that may be present and to concurrently simulate the effect of a propagating hot spot decomposition, direct scaling tests were conducted.

5. Vent Sizing by Direct Scaling Techniques

The sizing of emergency relief systems by direct scaling has, in the past, provided a means as to increasing confidence in the proposed vent system[5]. The method normally involves an adiabatic calorimeter equipped with a relief device of known cross-sectional area. The relief area employed is chosen based on the batch charge, provided that the gassy system under study has a high superficial gas velocity.

5.1 Experimental Techniques

The test apparatus was based on that used with sealed cell hot spot tests, but was further enhanced by provision of scaled relief vent and vent pipe. The pipe was of the same diameter as the vent and was present to ensure that flow conditions at the point of relief were those that might be encountered on the large scale. All tests were initiated employing the electrical hot spot as this was now the accepted worst case scenario. The experimental configuration is shown in Figure 2.

A number of trials involving approximately 50 g of material were conducted, simulating a reduction in the vent diameter from 0.26 m to 0.15 m (the existing 6" vent), examining the ability of the different vent orifices to cope. These vents corresponded to diameters ranging from 5mm to 2mm on the scale of test employed.

The criteria for ascertaining the ability of the vent to cope was the maximum pressure in the calorimeter during the venting operation did not exceed the design pressure of the drier. In all cases the scaled vent was capable of coping with the decomposition, inferring that on the plant scale of operation the existing 6" vent was adequate and indicating that there could well be some tempering taking place during relief. However, there was some evidence to suggest that these small scale tests were not simulating the relief process accurately. Multi-phase release was not always observed, ie, the relief was sometimes gas phase only, a phenomena that had never been observed in the plant. In addition, and perhaps most significantly, vent line blockage due to tarry decomposition products was observed in some of the tests.

Although the outcome of these tests was encouraging, the areas of concern relating to single phase release and vent line blockage, thought to be due to the effect of scale, meant that confidence in the existing 6" vent was not total.

In order to fully understand the decomposition and relief process and to confirm that the existing 6" vent system was sufficient for a hot spot initiated decomposition, an experimental programme, involving hot spot initiated decompositions of kilogram quantities of the material of concern was initiated in a 100 litre scaled model of the filter / drier.

6. Large Scale Hot Spot Initiated Decompositions

In order to ensure that the large scale testing directly simulated the manufacturing operation, a 1/64 scale model of the filter drier was constructed in mild steel.

In choosing a scale of 1/64, consideration several factors were considered :-

- Appropriate pipe diameters were required that scaled to the existing 6" vent configuration (based on a batch charge to vent area ratio)

- The batch size was of a sufficient quantity such that there was a finite time for propagation of the decomposition front through the reaction mass.

- The batch size was sufficiently small so as not to impose severe cost constraints in decomposing kilogramme quantities of high value product.

- The testing could be conducted safely

6.1 Vessel and Process Details

The vessel was hydraulically pressure tested to 10 barg and equipped with :-

- An appropriately scaled internal agitator (static)
- An orifice scaled to simulate the full scale 6" vent
- Bursting disk holder attached to the orifice
- A vent pipe geometrically configured to simulate the plant operation
- A down stream catch-pot and scrubber
- Facilities for pressure and temperature measurement within the vessel and vent pipe
- A resistance wire hot spot within the batch for initiation of the decomposition.

Finally the vessel was equipped with a 3" diameter graphite bursting disk, vented directly to atmosphere, to prevent the generation of excess pressure within the vessel and subsequent possible rupture in the event of vent line blockage during testing. A schematic of the unit with the original vent configuration is presented in Figure 3. Note the right angled vent pipe and 'T' junction at the vessel outlet.

The scale of operation was such that the scaled emergency relief vent and vent line was 1" diameter and the batch charge was 5 kg of material. The total quantity of gas liberated during an en-masse decomposition was in excess of 600 dm^3 at STP, sufficient to raise the pressure in the vessel to in excess of 88 barg in the event of vent line blockage. Consequently all testing was conducted in a safe manner, well away from habitation and by remote operation under video surveillance.

An experimental programme was conducted to examine the mode of excess pressure generation, both in the vessel and pipe run, during decomposition and relief. The existing vent configuration, a design which had a number of flaws, was first examined (Figure 3), and then subsequent vent line configurations were examined where less convoluted vent geometry at the vessel outlet was employed (Figure 4).

6.2 Testing Outcome

All decompositions exhibited the same basic pressure profile. Approximately 20 seconds after the decomposition was initiated, the pressure in the vessel had reached the burst disk set pressure. In most cases the pressure in the vessel subsided on rupture. There was considerable noise and a two phase mixture discharged down the vent line to the scrubber and catch pot, with approximately 50% of the batch contents being ejected. The time of relief was normally 30 seconds following disk rupture.

All tests exhibited a characteristic second pressure peak following the disk operating. It was felt that this was due to the propagating decomposition front being suddenly dispersed within any un-reacting material as pressure was suddenly released, vastly increasing the points of decomposition and hence rate of decomposition.

A typical experimental trace comparing the vessel pressure for the two vent pipe configurations is shown in Figure 5. It was immediately apparent that the supposition that the existing emergency relief vent was adequate although there was some evidence of flow restriction in the vent pipe, particularly at the end of the relief process when the vented material velocity was reducing. Of significant interest however, is that redesign of the vent pipe enabled a significant reduction in vessel pressurisation during the decomposition.

7. Conclusions

In vent sizing assessments it is of great importance to accurately define the worst case situation based on feasible plant circumstances. In this case en-masse decomposition was inappropriate resulting in emergency relief venting being prohibited due to engineering constraints.

This vent sizing assessment has shown that once the correct assumptions have been made about the process, the application of a structured experimental programme involving a number of different experimental techniques and simulations can provide a high degree of confidence in an emergency relief system that, at the outset, may appear prohibitively large for inclusion in an engineering design.

References

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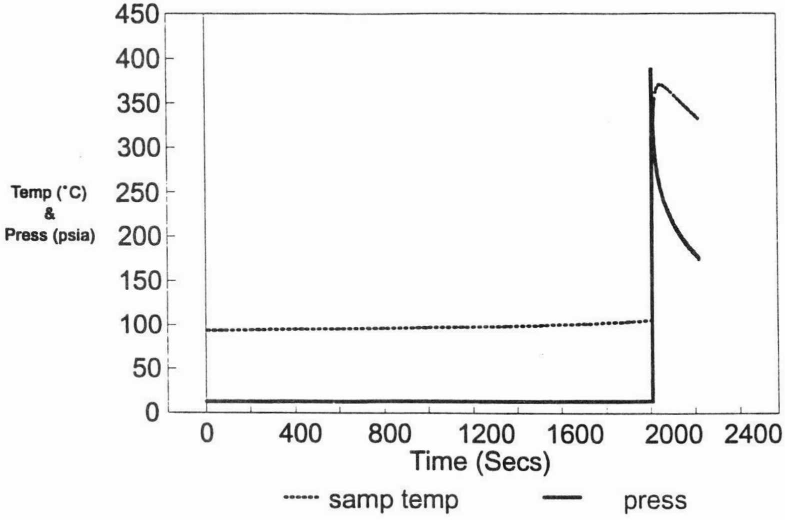

Figure 1 :- En-masse Runaway in the Adiabatic Dewar Calorimeter

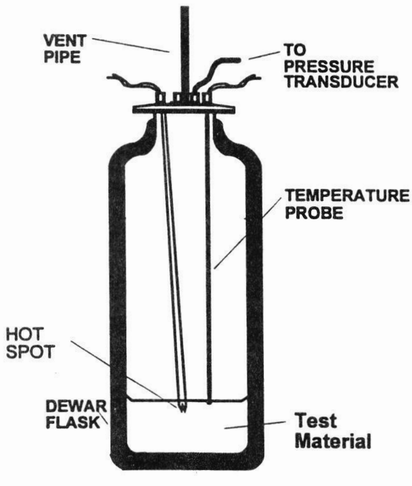

Figure 2 :- The Vented Dewar Calorimeter

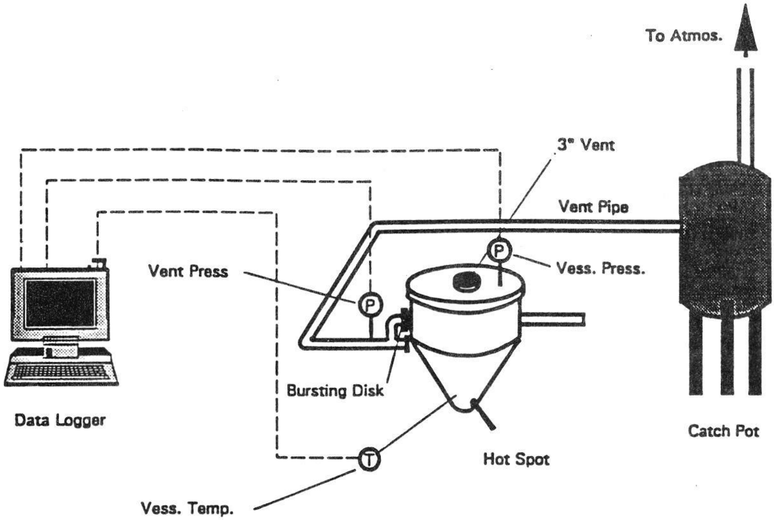

Figure 3 :- **Schematic of the Large Scale Experimental Configuration**

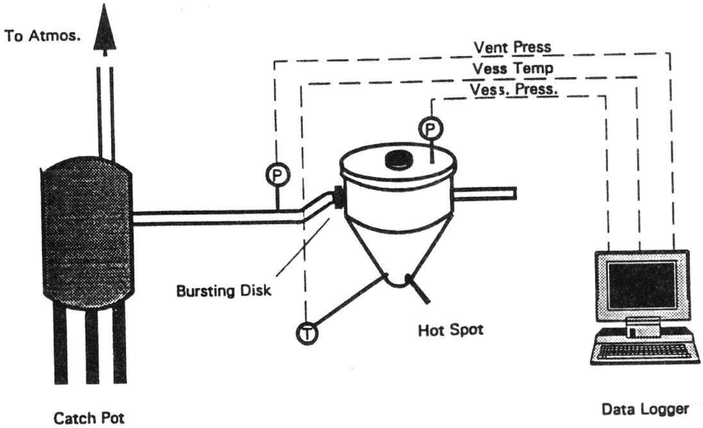

Figure 4 :- **Improved Vent Line Configuration**

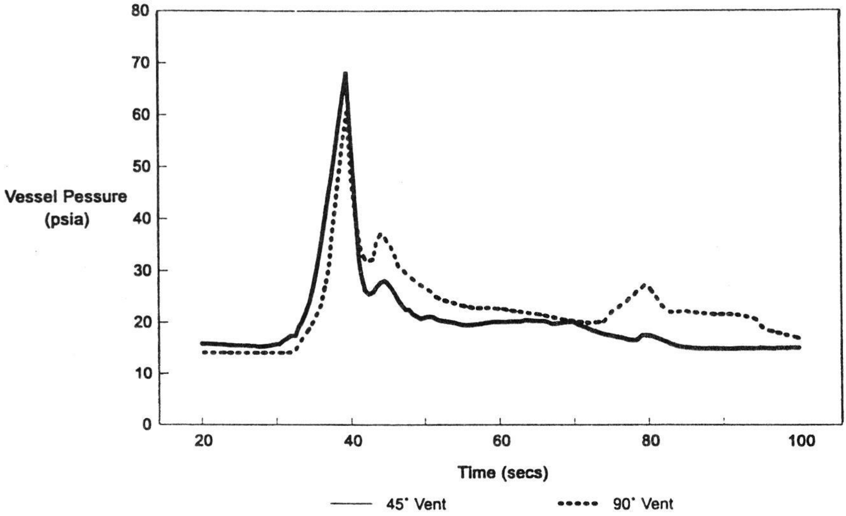

Figure 5 :-   Large Scale Tests, 90° and 45° Vent Configurations