Safe Packaging of Chemically Reactive Radioactive Waste – Addressing the Data Needs - 17487

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ABSTRACT

Industry-standard thermal hazard screening is an effective, cost efficient approach to quickly obtain the required data typically utilized for safe scale-up of chemical processes and to accommodate changes to process recipes. Such thermal hazard screening is directly relevant to the packaging, transport, and storage of radioactive waste that is or can become chemically reactive. For such waste streams it is vital to identify safe temperature and pressure conditions and quantify adiabatic heat and gas generation rates in order to safely accommodate (or preclude) thermal instability within the waste package or storage facility. This paper illustrates widely-used thermal hazard screening bench-scale techniques that lend themselves to quickly identifying reactive hazards while providing directly scalable data for package/storage facility design. Example data are presented with discussion of how the data are analyzed for application to safe packaging and storage.

INTRODUCTION

Safe packaging, transport, and storage of chemically reactive materials require knowledge of energy and gas release rates for systems under upset conditions. The Design Institute of Emergency Relief Systems (DIERS) program provided the chemical process industry with analytical tools necessary to gather such data which cannot be predicted from first principles [1, 2]. These same principles and well established technology can be applied to radioactive chemical waste where thermal stability is required.

The Vent Sizing Package 2 (VSP2™) and the Advanced Reactive System Screening Tool (ARSST™) are standard laboratory instruments for rapidly screening and characterizing reactive chemical systems while providing directly scalable relief-system (vent) design data. These data are amenable to kinetic modeling and can reduce or eliminate the need for time consuming and costly large scale experiments. Outside of a thermal runaway, systems that evolve gas such as hydrogen are of concern when designing and implementing waste storage techniques. Experimental data provide key input to traditional design and safety case modeling efforts to underpin safe process design and minimize risk from thermal instability and flammable gas.

ADIABATIC CALORIMETRY DESCRIPTIONS
Vent Sizing Package 2 (VSP2)

The Vent Sizing Package (VSP) calorimeter was introduced in 1985 as the original DIERS Bench Scale Apparatus for characterizing runaway chemical reactions. The design has been updated since its original release (hence VSP2). Key features of the VSP2 include a lightweight test cell (for low thermal inertia, i.e. low Φ factor), adiabatic tracking (and automatic pressure balancing for closed cell test operation), and heat-wait-search capabilities. (The Φ factor is the ratio of the heat capacity of

the sample-plus-test-cell to the heat capacity of the sample alone; Φ approaches a value of 1 for a very lightweight test cell.) A detailed description of the VSP2 and its design principles is available elsewhere [3, 4, 5, 6, and 7].

The basic design of the VSP2 (Figure 1) typically utilizes a liquid or solid sample size of 60-100 grams in a lightweight cylindrical test cell with a volume of approximately 120 ml. Gas or liquid can be added or removed during a test. There are multiple materials of construction (e.g. 304 or 316 stainless steel, Hastelloy, Titanium, or glass-lined) for the test cells and the configurations are customizable (e.g. baffled, dip-tubes, multiple fill lines, vent lines, etc.) allowing for numerous test design options. The test cell can include either a Teflon or glass encapsulated magnetic stir bar (overhead mechanical stirring is also an option) and is mounted within an auxiliary heater (used to heat the sample to a set temperature or at a particular rate, say for fire exposure simulation) and a guard heater (to maintain adiabaticity) and then installed in a 3.8 L containment vessel. The VSP2 apparatus records the sample temperature(s) and pressure, from which reaction self-heating rates and gas evolution rates are readily calculated using included data reduction software.

Experiments are run in either a closed or open test cell mode. Closed cell tests are typically run on reactions that are not expected to generate large amounts of non-condensable gas, and are advantageous because vapor pressure data can be obtained throughout the reaction. In this configuration, the pressure balancing system is used to maintain a low pressure differential between the test cell and the containment vessel, which prevents test cell rupture. This allows for use of lightweight thin-walled test cells (hence the low Φ factor). Open cell testing is used for systems expected to generate copious amounts of non-condensable gas. Using this methodology, the test cell is vented to the containment vessel which provides a larger volume for accumulation of non-condensable gas and for direct venting simulation. It is also possible to connect the outlet of the test cell to a mass flow meter or to analytical equipment in order to obtain gas composition.

The key feature of the VSP2 adiabatic design is the low heat capacity of the sample container relative to that of the sample. Thus the heat released by the chemical reaction goes to directly heat up the sample reactant mass, with negligible energy absorbed by the test cell itself. As a result the measured data can be directly applied to larger process (or waste package) scale without mathematical correction for thermal inertia and associated assumptions regarding extrapolation of observed kinetics to higher temperatures beyond the measured range. This is important because the data are exactly representative of what would occur inside a waste container under worst-case conditions.

Common process upset scenarios generally include: loss of cooling or agitation, accumulation or mischarge of reagents, contamination, process/recipe change, thermally initiated decomposition, resident incubation time, and fire exposure heating. Although some of these process upsets are not applicable to radioactive waste storage, they could be relevant to other waste processing steps. Calorimetry data can be used to determine the rate of noncondensable gas generation during a

chemical reaction (to determine venting requirements), onset temperature (to guide alarm systems), adiabatic temperature rise (to understand the ramifications of a runaway reaction), vapor pressure data, and heat of mixing or reaction (perhaps for initially loading waste containers or understanding required cooling capacity). Other data applications include kinetic modeling, thermal stability (important for transportation or storage), time-to-maximum-rate (TMR), temperature-of-no-return (TNR), self-accelerating decomposition temperature (SADT), and vent sizing evaluations (relief size required to properly vent vessels during an upset scenario).
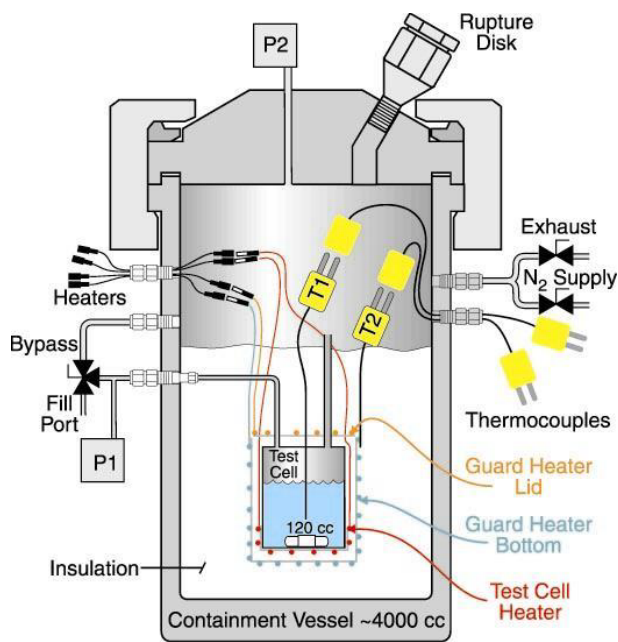

Fig. 1. VSP2 Schematic

Advanced Reactive System Screening Tool (ARSST)

Like the VSP2, the Advanced Reactive System Screening Tool (ARSST) is a low thermal inertia adiabatic calorimeter used to obtain critical process upset design data, but the ARSST was designed to be a simple and inexpensive alternative. A detailed description of the ARSST and its design principles is available elsewhere [8, 9, 10, and 11].

The basic components of the ARSST (Figure 2) include a spherical glass test cell with an internal volume of about 12 ml, a surrounding bottom heater, insulation, thermocouple(s) and pressure transducer, and a 350 ml (or 450 ml) containment vessel that serves as both a pressure "simulator" and safety vessel. Adiabatic tests are typically run using open test cell methodology (kits are available to perform closed cell ARSST screening tests). In the open configuration the test cell is vented to the containment vessel, and volatilization of the test sample is prevented by imposing an inert backpressure in the containment vessel. A magnetic stir bar is normally placed inside the test cell (and has been used for example to mix mixtures of nitric acid and ion exchange resins). The sample temperature and the containment temperature and pressure are measured, and the wetted parts can be made of different materials (e.g. Teflon coated, Hastelloy, stainless steel, or glass). An

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external fill tube can be used to add liquid reagents to the test cell either before or during the test.

The simple ARSST design allows for easy test setup and quick test turnaround time. Since the containment vessel is compact and portable, the test setup can be accomplished in a dry box, hot cell, or inert atmosphere. Operation at low temperatures can be accomplished by simply placing the containment vessel in a cold bath or freezer. Tests can be run with alternative test cell materials (e.g. Titanium, stainless steel, or Hastelloy test cells) by using standard ARC© bombs in place of the glass test cell (useful for quick screening of potentially energetic pressure-generating systems such as may arise from defense waste streams).
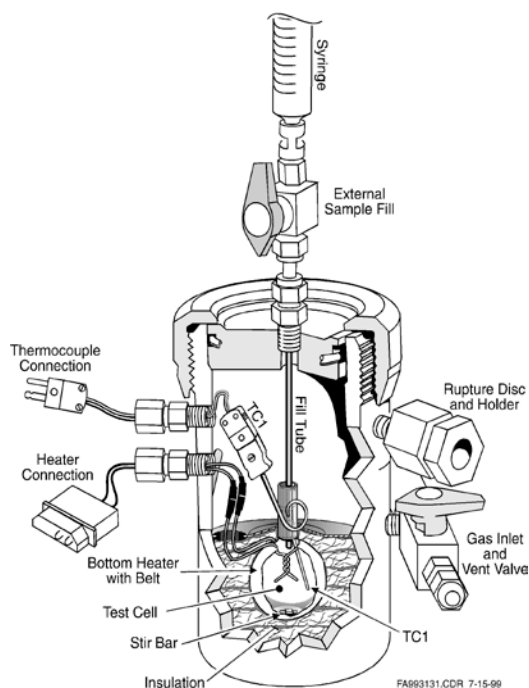

Fig. 2. ARSST Schematic

THERMAL DATA APPLICATIONS AND EXAMPLES

For radioactive waste evaluations, adiabatic calorimetry testing (such as with the VSP2 and ARSST) is a convenient way to develop vent sizing data for reactive systems or simply to screen for chemical reactivity under adiabatic conditions. Collecting this type of data is crucial to safe packaging, transportation, and storage of chemically reactive radioactive waste. It is vital to identify safe working conditions (i.e. temperature and pressure) in order to adequately design storage vessels or preclude thermal instability. The waste associated with radioactive processes (i.e. remediated wastes from recovery, purification, decontamination, decommissioning, etc.) can often be chemically active and under certain chemical conditions or additional trigger mechanism(s) can lead to runaway reactions or chemical decompositions resulting in breached containers. Further, because of the complexity that is often found in waste mixtures, thermal stability issues can be studied experimentally in a more cost efficient way instead of by analytical modeling of theoretical heat and mass balance equations that could be subject to question.

Identifying potential reactivity, as well as potential triggers or upset scenarios, can help prevent unexpected releases. There have been several incidents of released radioactive material due to thermal or pressure generating reactions under abnormal conditions [12, 13, 14, 15]. The following section provides example data with discussion of how the data are analyzed for application to safe packaging and storage.

Red Oil Case Study

VSP2 testing of tri-n-butyl phosphate (TBP), also known as Red Oil, saturated with strong nitric acid was performed to determine the relationship between vent size and pressure buildup as follow-up to the 1993 damaging explosion at the Tomsk-7 nuclear fuel reprocessing plant in Russia [16]. TBP is an important organic solvent used in acidic extraction steps in separations processes at reprocessing facilities. Solutions of TBP, hydrocarbon diluent, and nitric acid (known as "red oil" because of the color of nitrated hydrocarbons) can thermally runaway if heated to temperatures where the heat generation is greater than the heat removal capabilities. The tests were conducted in order to determine if, in the unlikely event of failure of various safety precautions (e.g. preventing significant interaction with strong nitric acid, preventing significant accumulation of TBP, stirring during additions and sampling, maintaining low temperature, etc.), the tanks had adequate venting to handle a runaway caused by the worst-case scenario [17, 18].

Figure 3 shows the temperature rate versus temperature from four open cell VSP2 tests on TBP saturated with nitric acid. The first three tests varied the concentration of the nitric acid (70 wt.%, 43 wt.%, and 24 wt.%). The fourth test used a mixture of TBP, with 70 wt.% nitric acid, and 8.9 wt.% butyl nitrate (to simulate decomposition products). Each test showed two separate exothermic reactions. In each case the first exotherm (not shown in Figure 3) was fairly mild (less than 1°C/min), beginning around 80 to 90°C and leading to a tempering period around 100°C due to evaporation of dissolved water. The second thermal event was more significant (although still less than 10°C/min) and data comparisons are shown in Figure 3. The peak temperature rates were decreased by lowering the concentration of nitric acid to 24 wt.% or adding small amounts of butyl nitrate. However, these changes do not significantly alter the measured self-heat rate versus temperature curve, given that all the curves have the same slope (activation energy) up to approximately 160°C and rise to a peak temperature of approximately 240°C. Thus the variations in the process recipe did not greatly affect the thermal stability of the mixture. Data like these can be used to calculate the required vent area as well as to manage process changes.

The above TBP tests have a key feature in common: each is performed near atmospheric pressure (i.e. "open" style testing) such that tempering (evaporation) occurs. Tempering generally provides a cooling effect, removing chemical reaction heat as latent heat and minimizing increases in temperature and pressure. In a "closed" configuration (as for example if a process vessel relief is plugged or has a high set point) the results can be very different. Figure 4 compares self-heat rate data from a closed and an open test. Unlike in the open test, the closed test reaction does not temper and the reaction rate continues to increase exponentially, eventually rupturing the test cell (handled safely by the VSP2 containment vessel).
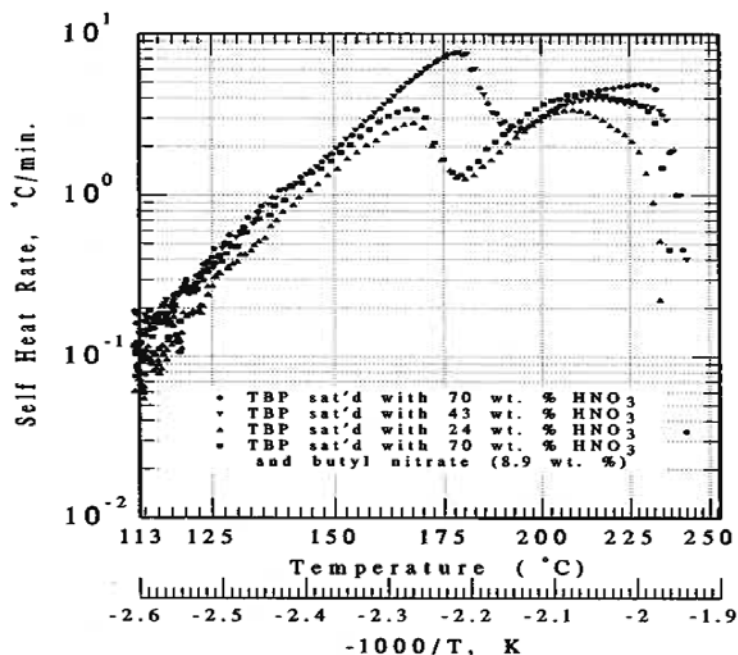
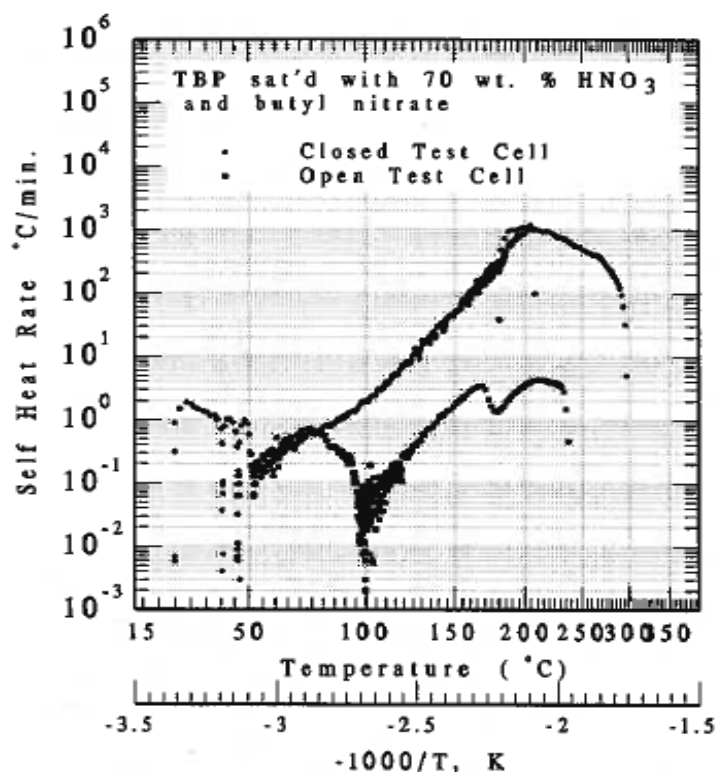Fig. 3. Self-Heat Rate versus Temperature for TBP-Nitric Acid Mixtures

Fig. 4. Self-Heat Rate versus Temperature for Open and Closed TBP Tests

Examples of Estimation of Simple Kinetics

The safe transport and storage of various materials can be evaluated using the calorimetry tools presented above to determine the reaction kinetics. Two key parameters for kinetic evaluations are the pre-exponential factor, A (K/min), and

activation temperature, B (K). Values of these kinetic parameters are easily derived from ARSST data [19]. An example of such data is shown in Figure 5 for a 10 g sample of t-butyl peroxybenzoate. In the low temperature range of interest, i.e. negligible chemical conversion, the reaction rate $\dot{T}$ (K/min) is well represented by $\dot{T} = Ae^{-B/T}$. Correcting for the external heat-up rate of approximately 1°C/min, the slope indicated in Figure 5 can be readily determined, resulting in A= 1.2 x 10^{21} K/min and B =17,700 K.
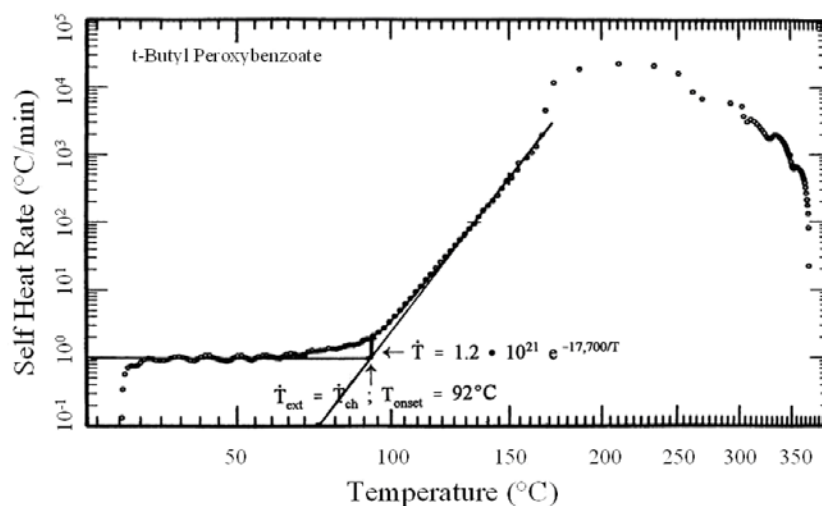

Fig. 5. Self-Heat Rate versus Temperature for t-Butyl Peroxybenzoate

Similarly, the ARSST can be used to develop simple kinetics for chemically reacting systems which are much less energetic then the neat peroxide described above. For example, Figure 6 shows ARSST self-heat rate data for 10% di-tert-butyl peroxide (DTBP) in toluene. The plot shows the rate data, the data corrected for the 1°C/min external heating rate, and the first-order rate constant results. The slope of the rate constant curve can be used to calculate the activation energy for decomposition of DTBP, resulting in a measured activation energy value of 37 kcal/mol which is consistent with published literature values. Also included in Figure 6 are four sets of very reproducible rate constant data developed from closed cell experiments on 25°C DTBP in toluene using the VSP2. The activation energy results are again very consistent.

Such kinetic parameters can be used in many ways to underpin safe transport or storage of chemically reactive radioactive waste. For example, the parameters can be used with the Semenov ignition theory to determine the self-accelerating decomposition temperature (SADT) or the time-to-maximum rate (TMR) or to identify the onset temperature of thermal or pressure generating decomposition [19].
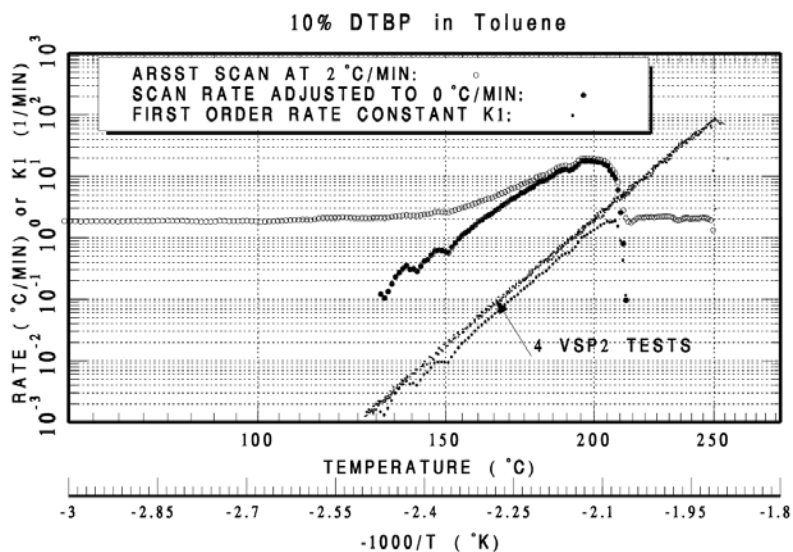
Fig. 6. Self-Heat Rate versus Temperature for DTBP Diluted in Toluene

Effect of External (or Internal) Heating

In chemical process safety an external fire is often considered to be a credible upset scenario for which the process equipment must have adequate overpressure protection. Industry standards such as those from NFPA (National Fire Protection Agency) or API (American Petroleum Institute) may be used to estimate the fire heat load. In adiabatic calorimetry experiments this heat load is easily simulated by imposing a constant background "fire heating rate." (The data in Figure 5 reflect a 1°C/min external heating rate, although in that case it was imposed for convenience to quickly "scan" the sample as one might do for chemical reactivity screening.) Fire heating pushes the chemical reaction to higher temperatures with less chemical conversion, generally leading to higher peak temperatures, higher peak reaction rates, and larger vent requirements.

A similar background heating effect could result from radionuclide activity within the reaction mixture itself. For example, if alpha-emitters were expected to generate non-trivial heat in the above red oil case the experiments on non-active materials could be performed with a corresponding imposed heating rate to simulate that activity. Another approach is to mathematically manipulate the kinetic model, which can be derived from adiabatic data on inactive surrogate materials, to predict the system behavior if activity were present. Finally, the calorimeters described here, in particular the smaller ARSST device, might be used with real active chemicals in a hot cell.

Effect of Contamination

Contamination can greatly increase the rate of reaction for many chemical systems. A relevant example is the general class of condensed phase organic-nitrate reactions. Such reactions have been the subject of safety assessments for the Hanford high level waste tanks where the presence of organic complexants like sodium acetate along with oxidizers like sodium nitrate present the potential for

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spontaneous runaway reactions of the Arrhenius type and propagating reactions initiated by a local ignition source [20, 21]. Figure 7 shows data from the RSST (the predecessor of the ARSST) where the tested material was a mixture of sodium acetate in sodium nitrate and waste tank simulants (total organic carbon about 6%). Significant exothermic activity is noted at about 200°C which leads to a runaway reaction exhibiting Arrhenius dependence on temperature up to about 300°C. At this temperature a dramatic step change is observed in the temperature rise rate; this is interpreted as a threshold for rapid wave-like reaction propagation and the temperature of 300°C is referred to as the ignition temperature.
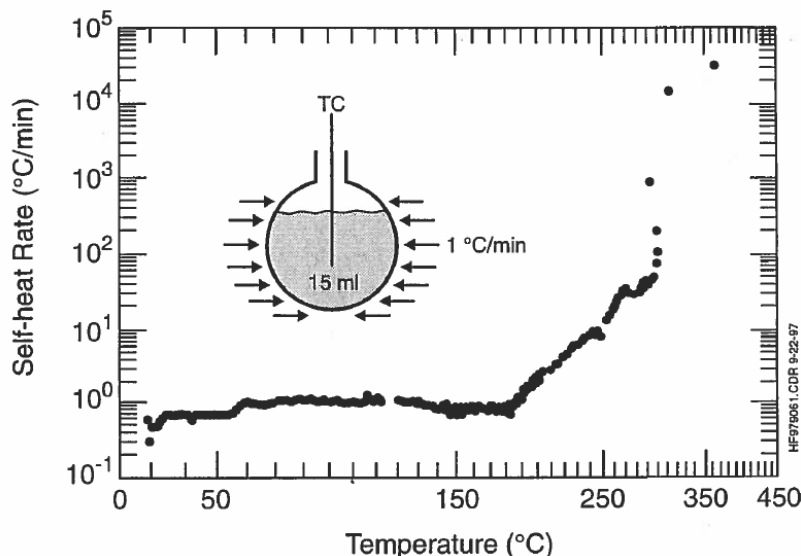

Fig. 7. Illustration of Test Cell and Organic-Nitrate Ignition Temperature Data

Ammonium nitrate is another common oxidizer that has been involved in extremely destructive large scale industrial accidents and is potentially explosive when mixed with organic fuel. Two sets of ARSST data are presented below to illustrate the effect of adding a small amount of organic material (plastic scraps) to ammonium nitrate. Scanning tests were run with and without contamination. Figure 8 compares the sample temperature, gas temperature, and containment pressure versus time, while Figure 9 compares the self-heat rate (temperature rise rate) data versus temperature on a logarithmic scale.

The first test (represented by triangles) was conducted by heating approximately 10 ml of ammonium nitrate in a test cell with a background heating rate of 2°C/min under a pressure of 160 psig. The data show that the sample melts around 170°C and then decomposes beginning at 250°C. The maximum temperature rise rate reached during the test was approximately 5,000°C/min. The second test (represented by circles) was conducted by heating approximately 10 ml of ammonium nitrate with 1.5% polyethylene "contamination" also at 2°C/min. Again, the data show the melting point of the mixture at 170°C and the decomposition begins at around 250°C. The reaction with contamination, however, appears to be autocatalytic and reaches a maximum temperature rise rate of approximately 18,000°C/min (3.5 times greater than the non-contaminated sample). Clearly if this

or similar material was to be transported or stored it is crucial to avoid contamination and to provide adequate cooling or venting capability to accommodate potentially high reaction rates [22].
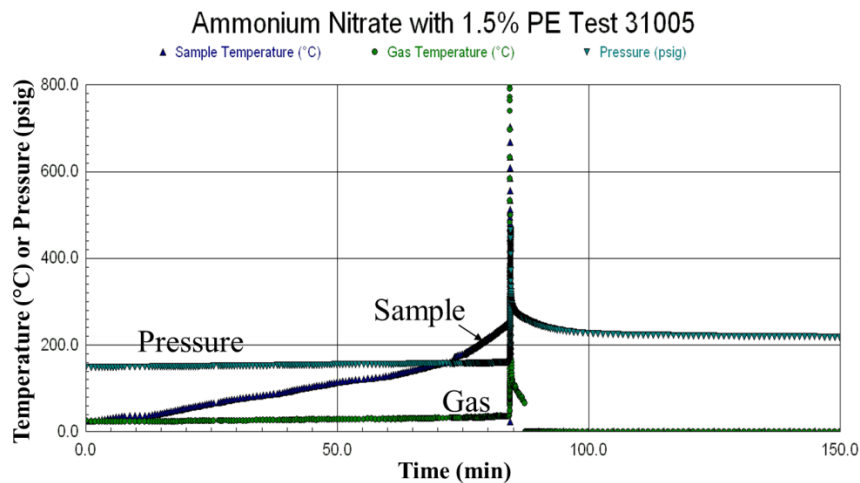

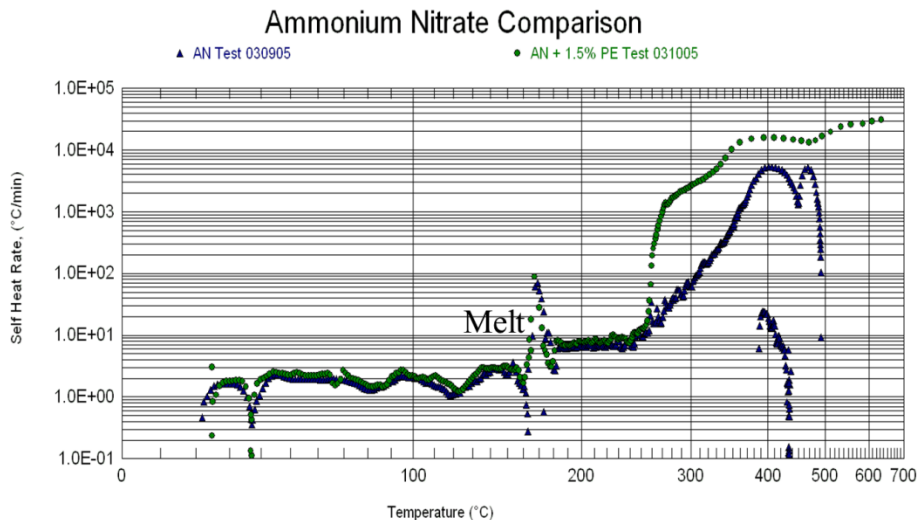Fig. 8. Temperature and Pressure Data for Ammonium Nitrate Contaminated with Polyethylene

Fig. 9. Self-Heat Rate Data for Ammonium Nitrate with and without Contamination

CONCLUSION

The methods presented here are relatively simple techniques to safely and quickly develop a variety of critical safety data for management of thermal hazards. The low Φ factor design of the ARSST and VSP2 allows the data to be scaled up directly. These two instruments are well suited for a variety of applications including evaluation of thermal stability, self-heat rate, generation rate of noncondensable gas (including hydrogen), onset temperature, condensed-phase ignition temperature, adiabatic temperature rise, kinetic parameters, self-accelerating decomposition temperature (SADT), and data for vent sizing.

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