DEVELOPING ROBUST AND RAPID COMPATIBILITY TESTING GUIDANCE FOR THE WASTE BULKING AND TREATMENT INDUSTRIES

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A number of unexpected, reportable adverse reaction incidents have occurred in the waste treatment industry in recent years. The incidents have been caused by the mixing of incompatible wastes in bulking vessels which have reacted together to generate heat and/or gas. The waste industry is particularly prone to such incidents due to several unique features of the sector:

- handling wastes of varying, and often uncertain, composition
- large scale bulking operations often involving large un-agitated, and often poorly instrumented, vessels
- wide variety of wastes received on a day-to-day basis
- general lack of thermochemical knowledge and understanding to implement robust compatibility testing procedures
- rapid turnaround time between waste receipt and bulking

The Environment Agency and Health & Safety Executive are acutely aware of the unique hazards posed by waste treatment processes and have been proactive in providing guidance to the industry to improve the level of understanding. In recent years, interim guidance on compatibility testing has been jointly issued by HSE & Environment Agency (HSE, 2009) with outline requirements also summarised in the Environment Agency Sector Guidance Note S5.06 (Environment Agency, 2004). In 2011, the Environment Agency and HSE jointly published definitive guidance on compatibility testing procedures. Chilworth Global prepared the new guidance, under contract, utilising their intimate knowledge of hazards testing and data scale-up.

This paper summarises the contents of the guidance and explains the proposed procedures for compatibility testing. Simple methods for hazards prediction are discussed, as are experimental procedures and methods for evaluating the validity of test data for scale-up. The main challenge in defining experimental procedures is that they must be simple, yet scientifically sound and they must dovetail with other testing and documentation requirements in this highly regulated sector. The testing strategy and assessment of result validity is equally applicable to other chemical mixing and storage situations.

KEYWORDS: Compatibility Testing, Waste Compatibility, Calorimetry

INTRODUCTION

In the waste treatment industry, diverse ranges of industrial wastes are processed. The first step of treatment, on receipt, normally involves "bulking up" operations to transfer the individual received waste into a vessel containing similar streams. Reactions must not be intentionally performed in bulking operations. Reactions can only be knowingly performed in **treatment** processes. It is, however, a possibility that reactions may occur unintentionally due to the wide variety of potential components present in the received waste, or in the waste with which this will be bulked. Exothermic or gas generating reactions between waste streams are termed "adverse" reactions when they occur in vessels that are not adequately designed for removing heat and/or preventing gas release to atmosphere (e.g. in simple bulking operations).

A significant number of incidents have occurred in the waste treatment industry, many during bulking operations, and the Environment Agency has produced a review of a number of these to demonstrate the primary causes and effects (Environment Agency, 2009). In addition, a paper presented by the Health and Safety Executive (HSE) in 2008 reviews incidents associated with unplanned adverse reactions (Etchells, 2008). The Environment Agency review examines the incidents and identifies departures in procedures from the standards established in the Sector Guidance Note (Environment Agency, 2004). One incident (March 2007, Heysham Works) from the review illustrates some of the issues involving adverse reactions during waste bulking.

The incident occurred in 2007 when a tanker offload of 21 tonnes of hydrocarbon light distillate (HLD) in a bulk tank led to exothermic reaction, pressurisation, venting and a loss of over 4 tonnes of the vessel contents to atmosphere. This was a repeat load of HLD – with 16 previous loads having been satisfactorily accepted from the same customer.

The incident investigation revealed a number of failures in the operator's procedures including:

- The pre-acceptance information collected by the operator was incomplete.

- The HLD waste was highly variable from consignment to consignment and the use of a generic HLD sample for compatibility testing was inappropriate.
- There was inadequate instrumentation on the large scale bulking tanks to provide any indication of internal reaction.

This incident occurred due to adverse reaction of the HLD waste consignment with a component in the bulk storage tank. The exothermic reaction caused heating of the tank contents, significant and prolonged vapour generation and venting of the tank direct to atmosphere. Reliable acceptance procedures, which would clearly highlight variability in the load, should trigger the need for compatibility testing. This testing would almost certainly have identified the potential adverse reaction and pressurisation risk, and this should have led to rejection of the load or its quarantine in a dedicated tank.

Over the period spanned by the HSE review, there were on average 10 reportable incidents per year in the UK relating to waste treatment, 70% of which occurred during simple bulking up operations where reactions should not occur. In recognition of the magnitude of the problem, and the lack of detailed guidance on testing, the Environment Agency and HSE jointly sponsored the preparation and publication of specific guidance on waste compatibility testing for bulking operations in the waste treatment industry. The guidance (Environment Agency, 2010) was prepared by Chilworth Global. The waste treatment sector is already highly regulated and one of the challenges of the guidance was to ensure that it dovetailed with existing requirements.

The remainder of this paper summarises the guidance and procedures recommended for compatibility screening and testing. The guidance focuses solely on adverse reaction identification and quantification it does not address issues involving toxicity, ecotoxicity, solid waste handling or flammability.

OVERVIEW OF THE ASSESSMENT STRATEGY

Adverse reaction assessment should be performed at the two distinct stages. The first stage, ***pre-acceptance***, is the contract discussion and specification stage where the waste company considers the receipt, storage and treatment methods for the specific load and provides a price to the customer.

Whilst the characterisation of the waste may be carried out using a range of standard chemical analyses, compatibility testing requirements are generally less defined at the pre-acceptance stage. Compatibility assessment will determine if there are any adverse reactions from the new waste when bulked with the intended existing wastes.

Testing at the second stage of the process, ***acceptance***, will then compare the incoming waste to the pre-acceptance sample as a measure of acceptability to authorise off-loading. Acceptance testing is fulfilling a different purpose. Ideally, it will:

- Assess the waste characteristics to confirm the load is (compositionally) similar to the pre-acceptance sample and is within the limits previously set.
- Test the compatibility of the incoming load with site fluids present at the instant of off-loading.

This latter aspect is more difficult to assess and is often not a routine operation in current practice. Its importance is to evaluate the nature of the actual waste received and its compatibility with the current composition in the bulking tank and hence elimination of adverse reactions.

The compatibility of the incoming stream with the existing streams with which it will be bulked with must be assessed at either pre-acceptance or acceptance – or both. Figure 1 indicates three routes which may be followed. In the first route, desktop screening of the waste compositions can indicate whether adverse reactions are likely. For simple compositions, this may be an adequate level of assessment, negating the need for physical testing. For more complex wastes, or where the possibility exists of adverse reaction, physical testing may be performed at the pre-acceptance stage. If the waste composition changes, this may require repetition at the acceptance stage. The final option is only to conduct compatibility testing at acceptance. This route is not desirable without some pre-screening as it leads to a heightened prospect of load rejection (or need to quarantine) if the wastes are found to be incompatible at this late stage.

The choice of compatibility assessment option would typically follow a comprehensive risk assessment covering variability of composition, complexity of the waste, extent of data availability and commercial aspects.

SCREENING WASTES FOR REACTIVITY

Some reactions can be readily identified as being potentially adverse. Examples include:

- Acid/base reactions or neutralisations. This can be predicted by significant difference in the pH of the two streams and will result in exothermic reaction.

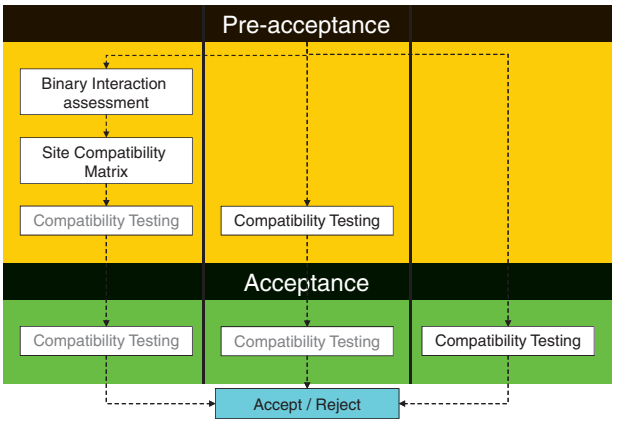

Figure 1. Assessing compatibility – the options

- Chlorinated waste/aqueous base resulting in exothermic reaction.
- Metals (particularly light metals such as aluminium, magnesium and sodium) contacting with water or acid resulting in hydrogen gas generation.

In addition, some specific chemicals and groups of chemicals will present a high risk of adverse reaction when present in appreciable concentration. Examples include the following (with the nature of the potential adverse reaction in brackets):

- Nitric acid solutions in combination with various solvents and acids (to produce unexpected unstable nitrations and/or gas generation)
- Other concentrated acids such as sulphuric acid or oleum solutions (exothermic reaction and gas generation)
- Peroxides – including aqueous hydrogen peroxide, organic peroxides and hydroperoxides (exothermic reaction and gas generation)
- Oxiranes – specifically epichlorohydrin, ethylene oxide and propylene oxide (exothermic reaction)
- Unsaturated monomers – for example, acrylic acid, styrene, methacrylic acid, methyl methacrylate and any other acrylate or methacrylate monomers (exothermic reaction)
- Hypohalites – for example, sodium hypochlorite with acids (exothermic reaction and gas generation)
- Hydrides – for example, sodium/potassium borohydride, sodium hydride, lithium aluminium hydride (gas generation)
- Acid chlorides – for example, thionyl chloride, acetyl chloride, phosphorus oxychloride (exothermic reaction and gas generation)
- Sulphides (gas generation)

When these compounds and groups are present, in significant concentration, physical testing should be immediately considered unless the received waste is to be mixed with material of a very similar composition. An example of this is where a bulk tank is dedicated to a specific and compositionally consistent stream from a specific customer.

Other reactions are also possible and must be assessed. One simple technique for examining binary compatibility is to use compatibility and reactivity software such as the NOAA Chemical Reactivity Worksheet (NOAA, 2009). Mixing of streams with significant pH changes or where heat of neutralisation effects may be substantial should also be assessed.

If a reaction is predicted from initial screening, it is necessary to predict the size of the reaction and then decide if it presents an unacceptable risk. In this assessment, only the magnitude of the hazard is considered, not its rate. Within the Environment Agency guidance, relatively stringent limits are recommended for temperature rise (10 K) and gas generation ($25\ \mathrm{cm^3_{(of\ gas)}} \cdot \mathrm{kg^{-1}_{(of\ mixed\ waste)}}$). Bulking should be rejected if either of these criteria is exceeded. [Strictly, any identified reaction should be re-classified as a treatment process. *Intentionally* performing reactions in bulking processes may be in contravention of the companies permit]. The general flowchart and decision tree for desktop binary interaction assessment is provided in Figure 2.

Physical compatibility testing must be performed if:

- desktop screening is not performed
- any component is suspected of being thermally unstable near the proposed storage temperature
- any potential interactions (including neutralisations and heat of solution effects) are identified by desktop screening but the predicted magnitudes are below the specified limits for rejection
- the waste composition is variable or the received waste differs from the initially assessed waste.

TESTING FOR COMPATIBILITY

Where physical compatibility testing is required, the methods employed must produce valid results. Laboratory simulation of plant scale processes must therefore be conducted under low heat loss conditions to match the plant scale. For this reason, sensitive calorimetric methods are required in the laboratory and simple glassware experiments are wholly inadequate due to the inability of the equipment to simulate the industrial scale operation. They may however, provide useful pre-screening information. Testing methods for waste compatibility screening should be:

- rapid – especially at the acceptance stage where the load is waiting
- low heat loss
- inexpensive
- simple to conduct and relatively easy to interpret
- agitated – to avoid stratification
- capable of measuring evolved gases accurately.

These requirements are most readily met using Dewar flask based calorimeters which are designed to be low heat loss. In some cases, typically for smaller plant vessels, non-adiabatic Dewar testing will be adequate. However, in the case of larger vessels, with lower heat losses, adiabatic testing may be necessary (or provision made for a "safety margin").

The experimental set-up of a non-adiabatic Dewar system is described below and depicted in Figure 3. The essential components of the system are:

- Glass Dewar vessel – typically 500 or 1000 $\mathrm{cm^3}$ (designed for laboratory testing) fitted with a leak tight head and fittings. The heat losses of the flask can be reduced by wrapping it in insulation. This would extend the validity of the data to larger scales.
- Thermocouple – capable of measuring to $+/-$ 0.1 K.
- Immersion heater and DC power supply – for calibration, capable of delivering up to 50 W to the immersed section only.

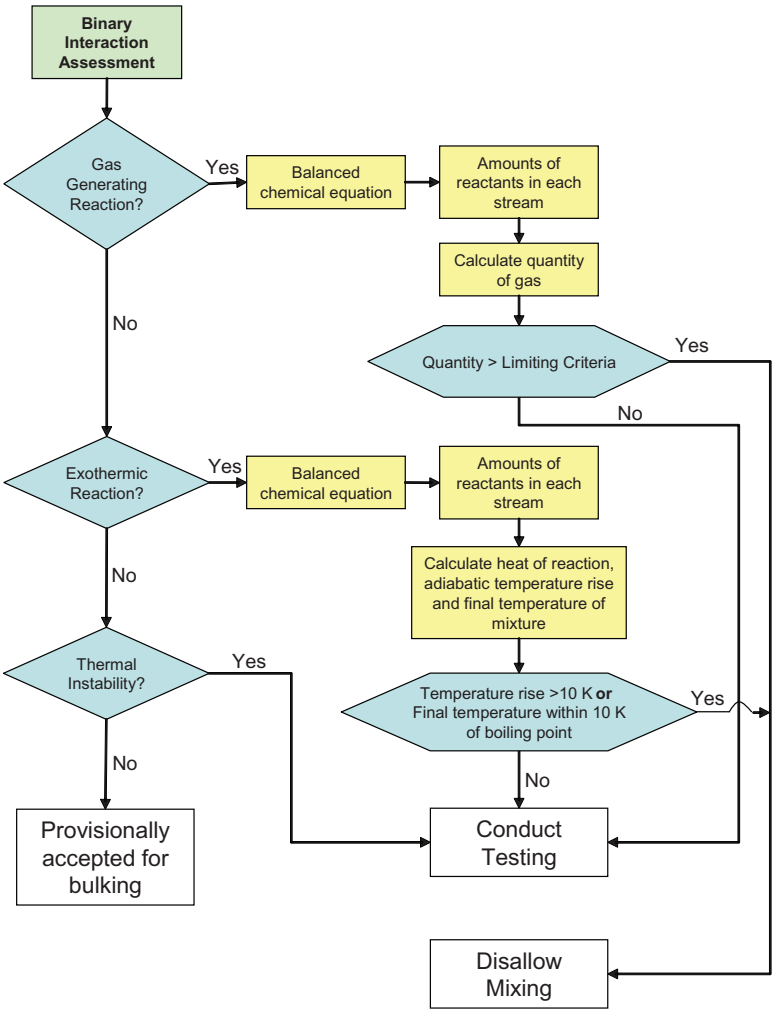

Figure 2. Desktop binary interaction assessment flowchart

- Agitator – impellor system is ideal but anchor may be necessary for viscous systems. Typically rotating at modest speed (ca. 50 rpm).
- Gas measuring system – capable of resolving to $+/-$ 5 cm^3.
- Pump, syringe or gravity feed system for the second waste to be added.
- Data acquisition and control system.

To measure the gas accurately, it is important that the whole system is leak tested. The apparatus should be operated behind a safety shield and ideally within a fume hood. All components in contact with the waste streams should be chemically inert and compatible and appropriate personal protective equipment (PPE) should, of course, be worn by the operator.

Tests are performed by stabilising the temperature of the "existing" waste in the Dewar at the desired temperature and then adding the "received" waste over a short

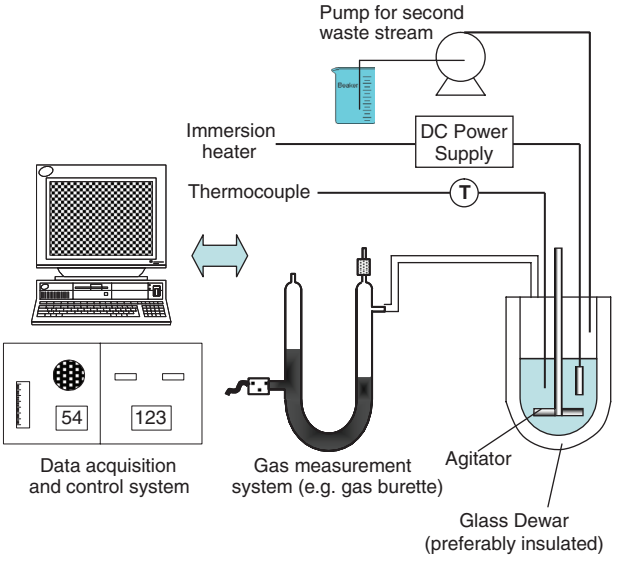

Figure 3. Typical configuration for non-adiabatic testing

period of time (up to 2 minutes but not instantaneously). Criteria recommended in the guidance for the monitoring period and threshold criteria are:

- monitor behaviour for a minimum of 20 minutes.
- If an exotherm is detected, allow it to proceed to completion (i.e. until there is no further temperature rise)
- If no exotherm is detected, increase temperature by 15 K and monitor for another 20 minutes
- If no exotherm is detected, increase temperature by 15 K and monitor for another 20 minutes.

The temperature steps are designed to accelerate any "slow-to-initiate" reactions or reactions that start to be detectable just above the test temperature, thereby facilitating their identification. If a temperature rise of >10 K, or a gas quantity of >25 $cm^3 \cdot kg^{-1}$ are observed in a **VALID** simulation, then the proposed bulking operation is disallowed.

A critical element of the testing is to determine if the test result is valid. Validity is determined by comparing the estimated heat loss and heat capacity (phi factor) of the large scale storage vessel with the heat loss and phi factor of the non-adiabatic test.

CALIBRATING THE HEAT LOSSES AND PHI FACTOR OF NON-ADIABATIC DEWAR FLASKS

A simple calibration and calculation procedure should be applied to evaluate the heat loss and phi factor of the test equipment. The calibration is performed by running heating/cooling curve trials at an appropriate starting temperature using (non-reactive) liquids representative of those used normally on the site. Liquids such as water or a light hydrocarbon such as toluene may be considered representative of aqueous or organic feeds, respectively. The calibration would typically involve the following steps:

- Assemble the apparatus, complete with calibration liquid of known mass and heat capacity.
- Use the internal immersion heater to raise temperature in discreet steps from ambient temperature to typically 80 to 90°C (but not nearing the liquid boiling point). Two to three heating steps should be used with an equilibration period between each.
- Allow the liquid to cool naturally back towards ambient temperature.

Rapid cooling of a vessel may be indicative of a loss of vacuum in the flask – rendering it useless for calorimetric purposes. It is not realistic to calibrate each vessel before each use, but the vessel should be subject to full re-calibration after several experiments (with spot checks of vacuum integrity before each test). Records should be maintained of all Dewar vessels used, their usage history, calibration dates and calibration results.

The data obtained in the test can be used to determine the approximate heat capacity and heat loss value of the Dewar. Figure 4 illustrates a typical experimental profile from a calibration experiment.

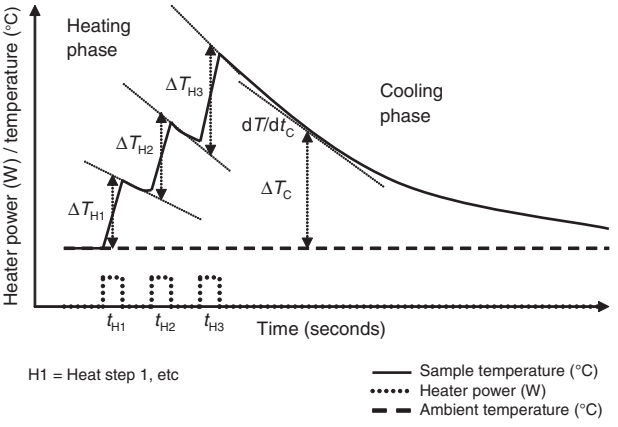

Figure 4. Dewar vessel calibration-experimental profile

Heat Capacity Determination

The difference between the energy applied by the heater and the energy absorbed by the liquid during heat steps provides a direct measurement of the heat capacity of the vessel (HC_{vessel} in $J \cdot K^{-1}$). The calculation is displayed in Equation I.

$$HC_{Dewar} = (\text{Heat injected from heater}) - (\text{Heat absorbed by the liquid})$$

$$HC_{Dewar} = [(Q \cdot t) - (m \cdot Cp_{AV} \cdot \Delta T)]/\Delta T \qquad \text{(Equation I)}$$

The heat capacity of most standard glass Dewar vessels in the 500 ml to 1000 ml scale is typically 50 to 200 $J \cdot K^{-1}$ depending on the inserts present in the vessel. For stainless steel Dewar flasks, the value is somewhat higher (normally in the range of 200 to 300 $J \cdot K^{-1}$). The use of large inserts (for example, heater, stirrer, temperature probe) in the vessel will compromise its heat capacity and hence the size of inserts should be minimised wherever possible.

To compare the heat capacity of vessels of different size, the phi factor can be calculated. This describes the extent to which the heat generated by a reaction is maintained within the reaction mixture compared with that which is used to heat the vessel up to the same temperature. The phi factor is calculated from Equation II.

$$\text{Phi Factor } (\Phi) = [(m_{Dewar} \cdot Cp_{Dewar}) + (m_{sample} \cdot Cp_{sample})]/(m_{sample} \cdot Cp_{sample})$$

$$= [(HC_{Dewar}) + (m_{sample} \cdot Cp_{sample})]/(m_{sample} \cdot Cp_{sample}) \qquad \text{(Equation II)}$$

Heat Loss Determination

From the cool-down section of the calibration test, the heat loss coefficient of the vessel can also be determined. At a specific temperature, the rate of cooling (dT/dt) is calculated from the cooling data along with the temperature

Table 1. Indicative heat loss coefficients for a simplified range of plant storage vessels (uninsulated)

Vessel details	Wind speed ($km \cdot h^{-1}$)	HLC ($W \cdot kg^{-1} \cdot K^{-1}$) aqueous	HLC ($W \cdot kg^{-1} \cdot K^{-1}$) light organic oil
5 m^3 horizontal vessel, 1.5 m diameter,	0	0.043	0.041
2.83 m long dished ends, saddle	16	0.099	0.093
mounted	24	0.113	0.106
25 m^3 horizontal vessel, 3 m diameter,	0	0.025	0.024
3.54 m long dished ends, saddle	16	0.057	0.053
mounted	24	0.065	0.061
100 m^3 vertical vessel, 6 m diameter,	0	0.012	0.011
3.54 m long flat ends, ground	16	0.027	0.025
supported	24	0.030	0.029
500 m^3 vertical vessel, 12 m diameter,	0	0.007	0.007
4.42 m long flat ends, ground	16	0.016	0.015
supported	24	0.018	0.017

difference (ΔT) between the calculation temperature and the ambient temperature. The heat loss coefficient (HLC) can then be calculated from Equation III.

$$\mathrm{HLC_{Dewar}} = (\mathrm{d}T/\mathrm{d}t \cdot Cp_{\mathrm{AV}})/\Delta T \qquad \text{(Equation III)}$$

CALIBRATING THE HEAT LOSSES AND PHI FACTOR OF PLANT VESSELS

Bulking up operations in waste treatment occur at a variety of scales ranging from 2.5 L laboratory Winchester bottles up to large scale tanks with volumes of tens to hundreds of cubic metres. Bulking vessels are typically not provided with any facility for heat removal. Any incipient exothermic reaction will therefore be reliant on atmospheric heat losses only to moderate the temperature rise. Predicting, or measuring, the heat loss of a plant vessel is not an easy assignment. However, it is critical for assessing the "scalability" of laboratory test data.

The data in Table 1 illustrates the effect of scale on the heat loss coefficient of a range plant vessels (for three different environmental wind speeds). If the vessels are insulated, the heat loss coefficient can be reduced by an order of magnitude or more. Evaluating the heat transfer coefficient of the plant vessel is the most demanding element of the calculation. This can be determined through plant scale heat loss testing – although this is rather impractical – but can be estimated by utilising commercially available heat transfer software (as was done to collect the data in Table 1). The heat loss coefficient is derived from the overall heat transfer coefficient (U), the surface area (A) for heat transfer from the tank and the mass of material in the tank as in Equation IV.

$$\mathrm{HLC_{vessel}} = (U \cdot A)/m \qquad \text{(Equation IV)}$$

The heat capacity of the plant scale vessel can be estimated form Equation II knowing the mass and heat capacity of the vessel.

IS THE TEST VALID?

If the HLC and phi factor of the Dewar are less than the corresponding values calculated for the plant situation, the test is providing a realistic simulation of the plant scale and the data can be used directly. Mathematical correction of invalid simulation can be made to account for the HLC and phi factor deficiency of the test but such correction should only be applied where the differences in phi factor and HLC are modest. Correcting from large differences in HLC or phi factor will yield increasingly questionable results. In this case, more stringent temperature rise criteria are applied when assessing the reaction.

In cases of particularly large vessels with very low HLC's, consideration should be given to the conduct of adiabatic Dewar tests where the heat loss of the test is reduced to zero. This is the only realistic option for providing valid simulation results for large-scale vessels. The flowchart in Figure 5 indicates the decision-making process and criteria when assessing the acceptability of a proposed bulking operation following testing.

GOOD PRACTICES IN WASTE BULKING AND TREATMENT

The potential for adverse reactions can be minimised by adopting a number of simple principles in site operation.

- Separation of waste streams in dedicated tanks wherever possible.
- For particularly hazardous materials, direct transfer into treatment without bulking is a beneficial approach.
- Separation of offloading location for incompatible fluids.
- Arrange site operations into liquid flow streams with minimum crossover options.
- Avoid large storage tanks. Large tanks will inevitably receive many different loads of potentially variable composition and will also exhibit very low HLC's (making them difficult to simulate experimentally).

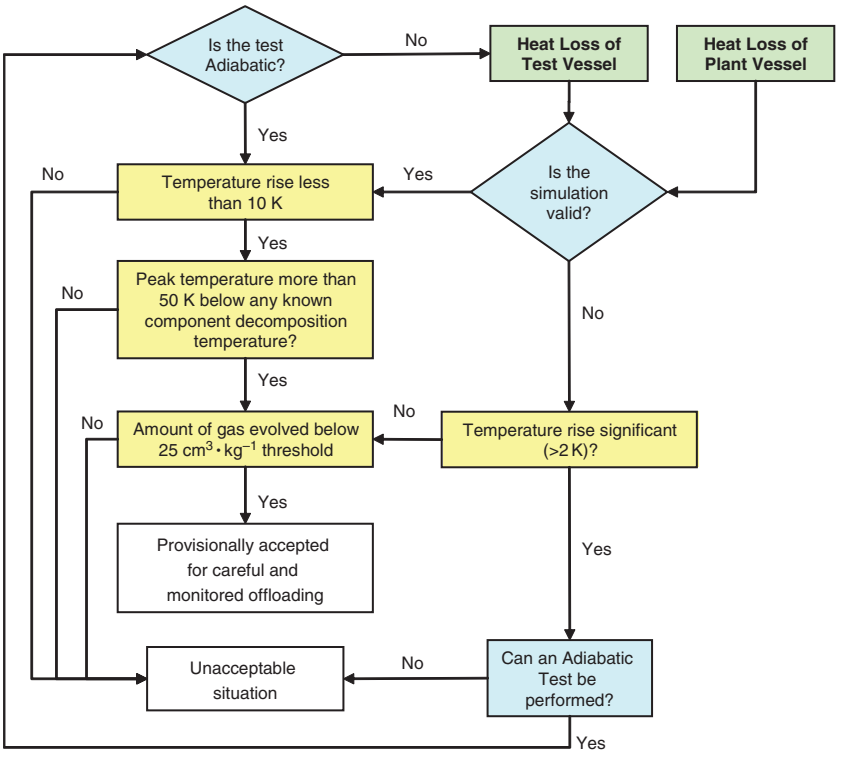

Figure 5. Flowchart for evaluating dewar test results

- Provide mixing facilities on storage tanks to ensure uniformity and avoid "hot spots".
- Provide sufficient instrumentation to allow adverse reactions to be detected.
- Provide sampling facilities on storage tanks capable of delivering a representative sample.
- Institute an inspection and cleanout routine for all tanks.
- Robust procedures should be available to cover waste receipt, testing, tanker offloading tank supervision, and waste treatment operations. These procedures should cover normal operation and abnormal/emergency conditions. Operating staff should be trained in these procedures.
- Documentation (load sheets, laboratory test results, etc) should be archived for at least two years. Lessons learned from testing routines should be accumulated within site compatibility charts.
- Tank drainage systems should be designed to allow complete discharge from vessels.

CONCLUSIONS

Any waste treatment site where exothermic or gas generating adverse reactions could potentially occur owing to delivery or treatment upset, should be considered to be a chemical site and subjected to the same considerations. In particular, risk assessment of the potential for adverse reactions needs to be comprehensive and focused, both for general site operation and for each individual waste, and for normal and abnormal operations.

A key defence for the avoidance of adverse reactions in the storage tanks used for "bulking-up" is laboratory compatibility assessment and testing. In order that any test results may be considered a valid simulation of plant behaviour, the heat losses from the laboratory test apparatus should be similar to, or less than, those of the plant equipment. This means that ideally, an adiabatic calorimeter should be used for the test, but at least a low heat loss Dewar arrangement should be used, calibrated and its efficacy compared with the plant. A more complete discussion of the strategy and methods for compatibility testing is provided in the guidance (Environment Agency, 2010).

NOMENCLATURE

HC_{vessel}	the heat capacity of the vessel (the energy required to increase the (empty) vessel temperature by 1°C) ($J \cdot K^{-1}$).
$Q \cdot t$	the heater power, Q (voltage × current for DC power supply units) and time, t (seconds) during activation of the heater. This is the overall energy entering the system from the calibration heater (J)
m	mass (kg)
Cp_{AV}	the average heat capacity of the liquid in the vessel ($J \cdot kg^{-1} \cdot K^{-1}$).

ΔT	the temperature rise/drop measured in the vessel during a heat step or cool-down step (K).
dT/dt	Rate of heating or cooling ($K \cdot s^{-1}$)
HLC	Heat loss coefficient of the vessel ($W \cdot kg^{-1} \cdot K^{-1}$)
U	Overall heat transfer coefficient ($W \cdot m^{-2} \cdot K^{-1}$)
A	Surface area for heat loss (m^2)

SUBSCRIPTS

Dewar	Experimental Dewar flask
Vessel	Large scale tank
Sample	The calibration liquid or waste liquid

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