HSE   Environment Agency

Testing waste stream compatibility before further processing

Interim guidance

Purpose

1 This interim guidance is aimed at dutyholders ('operators') in the hazardous waste management industry. It provides guidance on the standards of laboratory testing that waste sites should adopt to avoid adverse chemical reactions in bulking up chemical wastes in storage vessels. This document is not intended for treatment operations, which are otherwise covered in sector guidance note S5.06[1] and HSE guidance HSG143.[2]

Introduction

2 It is common practice in the waste management industry for waste streams to be bulked up with other waste streams for storage. In order to assess the compatibility of the wastes being mixed, an assessment should be carried out to determine whether an adverse chemical reaction is possible. For the purposes of this guidance, an adverse chemical reaction is one that can generate sufficient heat and/or gas to result in a harmful release either to people or to the environment.

3 In the past, reliance has been placed on relatively basic laboratory tests in a variety of equipment, including test tubes, small glass beakers and, occasionally, Dewar flasks. The tests involve just the mixing of wastes and the measurement of temperature increases over a 5–10 minute period.

4 However, a number of unexpected, adverse chemical reactions have occurred in the industry recently during bulking operations, resulting in the release of toxic and/or flammable gases.[3] In view of this, HSE and the Environment Agency have reviewed[4] the adequacy of current waste industry practices for assessing compatibilities and detecting the risk of adverse chemical reactions.

5 The review showed that these basic tests cannot be relied on to detect the risk of adverse chemical reactions in all cases, and especially where wastes are mixed in large vessels. This is because larger vessels heat up much more quickly due to a number of scale-up effects (see Annex 1 for further information). These effects are well known in the chemical industry.[5-7] In view of this, further work is planned, in conjunction with the waste industry, to establish what revisions to the procedures are now required. This work is unlikely to be completed until 2010.

Case study: A waste management company was bulking up acids in a storage tank. Prior to bulking up, a compatibility test of the different acids was carried out in a beaker, and the mixture was observed over a few minutes for any signs of reaction. As no reaction was seen in the beaker (until much later) the company proceeded to mix the acids in the storage tank. Some one to two hours later, staff working in the treatment plant noticed an odour and orange/brown fumes leaking from the tank. The gases were caused by an increasingly vigorous reaction in the acid storage tank. As the temperature in the tank increased, PVC ducting in the extraction system began to melt, causing the release to increase. It continued well into the next day. Four staff were overcome by the fumes and detained in hospital overnight. A number of people in the surrounding area were also affected. The plant was shut down for almost two months. Subsequent tests by HSE indicated that a suitable test in an insulated Dewar test flask would have predicted the hazardous chemical reaction much sooner.

6 In view of these incidents and with concerns over the shortcomings of current practices, interim guidance on the measures that operators should take to assess waste types prior to subjecting them to any bulking-up operation, is set out below. This includes guidance on the circumstances when it is necessary to carry out such tests as part of an overall risk-based approach. The basic testing referred to above does not meet the requirements of S5.06,[1] specifically section 2.1.3 BAT points 31, 32, 33, 39 and 43 and section 2.1.4 BAT point 6 and would not deliver permit compliance. Failing to meet a published standard would be an important shortcoming in sustaining a breach of health and safety legislation.

7 The measures below do not replace the need for companies to carry out their own individual risk assessments (eg DSEAR risk assessments[8] and COSHH assessments[9]), which may indicate that further measures are needed.

Assessing waste compatibility before any mixing, bulking up or blending operations

8 The first step in assessing compatibility should be a desktop assessment of the potential reactions that may occur, including an assessment of any gases likely to be evolved (both volume and identity) and any expected temperature and pressure increases within the mixing tank. Information on the type of calculations and assessments that can be carried out are given in references 6 and 7. In order to do this you should know the chemical composition of all the wastes you are bulking.

9 The desktop study may be assisted by analytical techniques such as pH measurement, Redox potential, GLC and/or titration measurements as appropriate. The following should also be considered:

- the accuracy of the sampling techniques used to identify the chemical composition;
- for a repeat load, the consistency of the waste from the producer on previous occasions;
- the likelihood of contamination/impurities; and
- the concentration of chemicals in the waste.

10 If your desktop study indicates that mixing cannot be carried out safely, the wastes should not be mixed.

11 If your desktop assessment demonstrates that the wastes will not react in an adverse manner once bulked, you may then proceed to bulk up your wastes without extending the risk assessment to laboratory scale testing.

12 You should record the result of the desktop risk assessment. The record should show that you have assessed the wastes for incompatibility and the decision that has been made. The record should clearly state which competent chemist has made the decision and how that decision was made.

13 Where companies are either: uncertain of the chemical composition of a waste stream for any reason; or unable to demonstrate that mixing will not result in an adverse chemical reaction, representative samples of the individual waste streams proposed to be bulked should be taken and tested for compatibility before any plant scale work is done. In cases where some variation of the waste stream may occur, additional samples should be taken for testing. The record should show that you have assessed that the bulking operation cannot be understood using only a desktop risk assessment, that a decision has been made that testing is required and which competent chemist has made the decision.

Compatibility tests

14 Only qualified chemists (HNC minimum standard), with training and practical experience in chemical reaction hazards, should carry out compatibility tests. Information on suitable training courses is available from the Institution of Chemical Engineers.

15 Testing carried out by mixing samples of wastes in test tubes, beakers or other receptacles and comparing any temperature increase against some arbitrary yardstick (eg 5°C over ten minutes) is not a reliable basis for assessing potential incompatibilities and should not be used.

16 There are a number of commercial and non-commercial calorimeters available that can be used for the tests, including adiabatic and non-adiabatic Dewar flasks. Information on the use of calorimeters is described in some of the references.[4, 6, 7, 10-13] These references also contain information on the use of Dewar flasks to obtain basic screening information on chemical reactivity. However, it is important that the results of such tests are not scaled up beyond their limits of applicability. Advice on this can be obtained from individual calorimeter suppliers. Some information on the use of Dewar flasks is given below.

17 Any laboratory compatibility testing should include the collection of data on both temperature and gas generation, from which an assessment of the ability of the proposed treatment plant to handle the proposed reaction should be carried out. This data should include the:

- total temperature rise;
- total volume of gas generated;
- rate of gas generation; and
- identification of any gases evolved (if bulking up is to proceed).

18 Samples should normally be tested at the operating temperatures of the bulk materials (this is because reactions are temperature sensitive). They should not be mixed before they are placed in the calorimeter/Dewar flask.

19 The initial assessment criterion should be no temperature rise over a minimum period of 30 minutes. In cases of uncertainty, (for example where the consistency or reactivity of a material is uncertain) this period should be extended to at least an hour. If either the desktop study or the calorimetric test indicate that there may be exothermic or gas-generating reactions between the different waste streams, mixing should not be carried out until further testing has been done to evaluate the effects of the total temperature rise and/or gases generated. Under these circumstances, the test should be continued until there is no further increase in

temperature or gas generation. Once the reaction is complete, results from this second stage of Dewar testing should be used for scale-up and assessment purposes.

Procedures and records

20 Operators should provide and follow operating procedures for the use of Dewar flasks or calorimeters.

21 Up-to-date records should be kept of the hazard assessment and any data required by paragraph 17, along with the name of the chemist and the start and finish time of the test.

Use of Dewar flasks or calorimeters

22 Always consider the potential for generation of toxic/flammable/reactive gases prior to carrying out tests in a Dewar. It is recommended that a smaller sample should be mixed together first and a check made for any gassing before filling the Dewar. This should be done in a suitably extracted fume cupboard and not the open lab.

23 The flask should be provided with a stirrer, which must be used during testing, and equipped with accurate temperature measurement equipment capable of measuring at least 0.3°C intervals. An electric thermocouple capable of being read and logged remotely is considered to be the 'best available technique'.

24 The flask should be loosely closed with a bung of insulating material (eg cork), which can be released easily in the event of the test vessel being overpressurised. Screw tops should not be used. A suitable gas bleed (normally at least 6 mm diameter) should be connected to a volumetric gas-measuring device, such as a manometer or gas burette, in order to provide an estimate of gas flow. Information on methods for the measurement of gas generation is given in *Chemical Reaction Hazards*.[7] In selecting a suitable method, the company should consider the hazards of the gases generated and their reactivity with any fluids used in the test (this can affect the accuracy of the test method).

25 Test results from a Dewar flask should only be used for assessment if it can be shown that the specific heat losses from the Dewar are similar to those from the proposed reaction vessel. If the specific heat losses in the Dewar are higher, the results cannot be used for scale up and the proposed mixing should not take place in this vessel unless a more accurate test method (such as adiabatic calorimetry) can be used. Remember that even the more accurate calorimetric methods have scale-up limitations.

26 Advice on the calibration of Dewar flasks is available.[3,10] As a rough guide, a 1 litre capacity Dewar flask is unlikely to be suitable for assessing the risks from mixing waste in vessels larger than 10 m^3 capacity. For viscous mixtures and slurries, this limit is likely to be much lower.

Preventing injury to operators

27 The requirement to carry out risk assessments (paragraph 7) includes the need to ensure that a risk assessment of any laboratory operation is carried out prior to laboratory testing in order to prevent injury to operators. Particular points requiring attention are outlined below.

28 It is important that the company considers the potential effects of failure of any testing vessel under pressure, and provides suitable screening of the operators from the effects of missiles. Small, shatterproof safety screens are available from chemical apparatus suppliers, which can be placed between the apparatus and the (closed) fume cupboard front. In addition, there are (flexible) plastic mesh tubes that can be used to sleeve the vacuum flask.

29 The Dewar should be placed in a fume cupboard provided with a shatterproof screen. Even so, operators should not stand in front of it when an experiment is underway.

30 If there is a possibility that flammable gases, vapours or dusts may be released into the fume cupboard then the company will need to ensure that potential ignition sources are not present. This includes the need to provide suitably protected electrical equipment.[8]

Annex 1: Scale-up effects

There are a number of scale-up effects, which mean that tests in small, uninsulated vessels, such as test tubes and beakers, will not simulate mixing in larger vessels such as tanks. The main ones are shown below.

- **Surface area to volume ratio.** The larger the vessel the lower the volume to surface area ratio becomes (typically 100 to 1000 times lower). They heat up much more quickly because they cannot lose heat quickly enough through their surface.
- **Heat capacity.** The smaller the vessel, the more heat is lost proportionately to the walls of the retaining vessel. Again, this means that a tank will heat up more quickly.
- **Heat and gas losses through the top of the vessel.** Test tubes and beakers are open vessels so any gas generated is lost through the top of the vessel and may not be detected. Heat can also be lost by vaporisation to the surrounding atmosphere much more quickly.
- **Stirring.** If the contents of the tank are not stirred or agitated, this will reduce the amount of heat loss compared to an agitated vessel such as a shaken test tube or beaker.
- **Sampling.** It is also much harder to obtain representative samples when the mixture being tested is small.

References

1 *IPPC S5.06: Guidance For The Recovery And Disposal Of Hazardous And Non-Hazardous Waste* www.environment-agency.gov.uk/business/sectors/39737.aspx

2 *Designing and operating safe chemical reaction processes* HSG143 HSE Books 2000 ISBN 978 0 7176 1051 8

3 *Review Of Incidents At Hazardous Waste Management Facilities* (2009) www.environment-agency.gov.uk/business/sectors/34862.aspx

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5 *Chemical reaction hazards and the risk of thermal runaway* Leaflet INDG254 HSE Books 1997 (single copy free or priced packs of 15 ISBN 978 0 7176 1404 2) www.hse.gov.uk/pubns/indg254.htm

6 *Designing and Operating Safe Chemical Reaction Processes* HSG143 HSE Books 2000 ISBN 978 0 7176 1051 8

7 *John Barton and Richard Rogers Chemical Reaction Hazards* IChemE 1997 Second edition ISBN 978 08529 5464 5

8 *Fire and explosion: How safe is your workplace? A short guide to the Dangerous Substances and Explosive Atmospheres Regulations* Leaflet INDG370 HSE Books 2002 (single copy free or priced packs of 5 ISBN 978 0 7176 2589 5) www.hse.gov.uk/pubns/indg370.pdf7

9 *COSHH a brief guide to the Regulations: What you need to know about the Control of Substances Hazardous to Health Regulations 2002 (COSHH)* Leaflet INDG136(rev3) HSE Books 2005 www.hse.gov.uk/pubns/indg136.pdf

10 *Rogers RL Plant/Operations Progress: The Advantages and Limitations of Adiabatic Dewar Calorimetry in Chemical Hazard Testing* 1989 Volume 8 Issue 2

11 *N Maddison Isothermal and adiabatic Dewar calorimetry – a simple approach to reactor heat loss simulation under emergency conditions*, IBC Conference 24/10/2000

12 United Nations *Recommendations on the Transport of Dangerous Goods Manual of Tests and Criteria 2003* Fourth edition ISBN 978 92113 9087 2

13 HarsNet *Thematic Network on Hazard Assessment of Highly Reactive Systems* www.harsnet.net/harsbook/6.Adiabatic%20calorimetry.pdf

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