

## HANDLING OF REACTIVE CHEMICAL WASTES – A REVIEW

J C Etchells, H James, M Jones, and A J Summerfield  
Health and Safety Executive

© Crown Copyright 2008. This article is published with the permission of the Controller of HMSO and the Queen's Printer for Scotland

A study has been made of 142 incidents reported to HSE, caused by unintentional or inadequately planned mixing of incompatible waste chemicals, or the decomposition of thermally unstable wastes. 62% of the incidents occurred at waste producer sites, the remainder occurring during waste treatment and transit. The immediate effects of such incidents included fires, explosions, chemical releases and drums rocketing off-site. In some cases employees were killed or injured. Five common reaction types accounted for over 68% of incidents where the chemistry was known. In most cases these reactions could be linked to specific industry types, in particular the chemical industry and engineering/metal treatment.

This paper reviews the incidents and their causes, many of which were failures to take simple precautions, such as properly characterising, packaging and labelling the waste, particularly during "bulking up" into storage containers. The guidance available to prevent such incidents has been identified and, where gaps were found, suggestions to take matters forward with industry are made. A particular issue is the screening procedures required before waste chemicals are mixed, particularly in large tanks and reaction vessels, both at waste producer and waste-treatment sites. An ongoing research project on scale-up, being carried out for HSE by HSL is described. The Environment Agency (EA) is taking an active interest in this project.

### INTRODUCTION

A number of incidents have been reported to HSE which occurred during the storage, handling and transport of chemical waste, caused by unintentional or inadequately planned mixing of incompatible chemicals, or in some cases by the decomposition of thermally unstable substances. The incidents occurred, in particular, at waste producer sites (such as the chemical industry), and also at waste-treatment sites and during transport. Concern amongst HSE inspectors led to the formation of a small HSE working group to review the causes of these incidents and identify where further action is needed, including the need for guidance. This paper discusses the main findings of the WG and how HSE is taking matters forward in collaboration with the Environment Agency (EA). The need to minimise the amount of waste produced in order to avoid/minimise the impact of such incidents is outside the scope of this paper, although it clearly should be considered.

**Table 1.** Number of incidents by location

|                           |     |     |
|---------------------------|-----|-----|
| Waste producer            | 100 | 62% |
| Waste treatment company   | 40  | 25% |
| Transport                 | 14  | 8%  |
| Information not available | 9   | 5%  |

## ENFORCEMENT AGENCIES

HSE and EA/SEPA (Scottish Environment Protection Agency) both have roles for regulating the supply, handling and transport of hazardous wastes. HSE take the lead on safety issues. The role of EA/SEPA includes enforcing pollution prevention and control legislation (PPC), regulating hazardous waste movements and licencing and inspecting waste storage/treatment sites, including those at the waste producer. There are memorandums of understanding between HSE and EA/SEPA defining the arrangements for liaison and co-operation between the agencies.

## INCIDENT HISTORY

A review of incidents reported to HSE was carried out, to provide information on key technical areas and industries involved. 142 incidents involving reactive wastes were identified for the period 1989 to 2005. The average number of incidents per year (over the 11 years where data was most reliable) was approximately ten.

The incidents ranged from relatively minor explosions in drums to major releases of hazardous chemicals. The effects included fires, explosions, chemical releases and drums rocketing off-site. In some cases employees were killed, in others large numbers of people were evacuated from the surrounding area and the incidents led to environmental effects, such as contamination of the watercourse.

A breakdown of the number of incidents by location is given in Table 2. The majority of incidents (62%) occurred at waste producer sites, and typically involved unintended mixing/reaction in drums and containers, which occurred for example as a result of mixing incompatible chemicals together (often termed “bulking up”). The main industries involved (other than waste-treatment) were chemical manufacture and supply (41%), and engineering and metal treatment (22%). Smaller incidents at schools, colleges, universities, hospital teaching labs accounted for 20% of the incidents. Other industries involved included printing, ceramics, nuclear, electronics and leather processing. Poor control of intentional mixing of chemicals for treatment was involved in 15% of incidents at waste producer sites.

Failing to take simple precautions was the most common factor involved in incidents at waste-producer sites, for example checking the label for compatibility with other chemicals (particularly during bulking up), appreciating the composition of the waste and its hazardous properties, and contamination or the addition of an incompatible chemical.

**Table 2.** Business activities at waste-producer sites where incidents occurred

Of the incidents at waste producer companies, 85 involved companies whose main activity could be readily identified:

| Main business activity of waste producer company  | Number of incidents | Percentage |
|---|---------------------|------------|
| Chemical manufacture and supply (including solvents, lubricants, fertilisers, paints and varnishes, plastics, rubber chemicals) | 35                  | 41         |
| Engineering, metal plating, metal finishing, motor vehicle repair   | 19                  | 22         |
| Schools, colleges, universities, hospital teaching labs   | 17                  | 20         |
| Printing, reprographics   | 3                   | 4          |
| Ceramics products and services  | 2                   | 3          |
| Nuclear   | 1                   | 1          |
| Contact lens manufacture  | 1                   | 1          |
| Electronics manufacture   | 1                   | 1          |
| Geologists  | 1                   | 1          |
| Leather processing  | 1                   | 1          |
| Textile coating   | 1                   | 1          |
| Packaging manufacture   | 1                   | 1          |
| Total   | 85                  | 100        |

### CHEMICALS INVOLVED

The types of chemical reaction involved in the incidents, and the associated industries involved, have been reviewed. It was found that 6 reaction types accounted for 68% of the incidents, and 87% of incidents where the chemistry was known. These are summarised in Table 3. 22% of the incident records had insufficient information to deduce what reaction had been involved, and it is a matter of concern that the contents of the waste does not appear to have been sufficiently known by the waste handlers.

A significant number of the incidents, perhaps not surprisingly, involved strong acids, particularly nitric and sulphuric acids, reactive metals, sodium hypochlorite and reactive monomers.

Although most industries appear to show a fairly uniform distribution of reaction scales from small containers to bulk tanks and vessels, in the plastics industry most incidents occurred in drums. There is evidence to suggest that the practice of “reacting off” some “waste” monomers in drums is occurring at some sites.

The main issues are discussed below.

**Table 3.** Chemical reactions involved in the accidents

| Chemical reaction  | % of Total |
|--|------------|
| Reactions involving potentially reactive metals, n.b aluminium, magnesium, sodium, with water and acids to produce hydrogen. | 19%        |
| Nitric acid in combination with various solvents and acids to produce unexpected unstable nitrations.                        | 14%        |
| Reaction of hypohalites, e.g. sodium hypochlorite (often in bleach), with acids to produce chlorine                          | 10%        |
| Unstable monomers reacting together in runaway polymerisations   | 9%         |
| Sulphuric acid and metals producing hydrogen   | 8%         |
| Acid/base neutralisations  | 8%         |
| Unknown Chemistry  | 22%        |
| Other  | 10%        |
| Total  | 68%        |

## WASTE CHARACTERISATION

Waste streams need to be characterised sufficiently to ensure that they can be safely handled and stored, for example to prevent them being inadvertently mixed with incompatible chemicals, and so that they can be safely treated. A number of incidents occurred due to failures to adequately characterise the waste, both at waste producers and during subsequent handling and treatment.

Guidance on characterisation is given in reference 1, published by the EA. Although primarily aimed at waste-treatment operators, it also contains useful guidance for waste producers. Properties requiring characterisation include:

- Quantity;
- Chemical analysis (individual constituents and their percentages, as a minimum, are usually required);
- Form (solid, liquid, sludge, viscosity etc.);
- Hazardous properties, e.g. flammability, toxicity, corrosiveness, reactivity, thermal stability, etc;
- The specific process from which the waste is derived

The type of analysis required should be part of a risk-based approach. This can require the exercise of considerable professional judgment. Some guidance on this is given in references 2 and 3. However most of the factors that need to be considered are standard good chemical engineering practice, including:

- The need to identify the critical components of the waste stream, e.g. heavy metal concentrations in wash waters, acid concentration, etc. These play an important role in defining storage requirements, and ultimately any treatment routes;

- The physical nature and uniformity of the waste, for example the number of phases present;
- The variability (and potential variability) of the processes that have produced the waste. For example, waste from trial runs and batch processes are likely to be more variable than that from established and continuous processes;
- The treatment process or handling regime to be used, and its sensitivity to variations in waste characteristics. “Off spec” product is a particular risk, for example, if it contains unreacted or thermally unstable material, and procedures to deal with this should be in place where necessary.
- the need to record the results of the characterisation tests systematically.

### **SAMPLING**

Where the contents of a waste container/stream are not already known, a suitable sampling regime is needed to ensure that the samples obtained are truly representative. The development of the sampling regime should form part of the technical assessment and take particular account of the variability of the waste, arising from:

- the normal process;
- foreseeable deviations;
- variability within the container such as settling and multiple phases.

The analysis required will depend on the nature of the waste, the treatment process to be used and what is already known about the waste. In particular, the following checks should be made:

- A check on the constituents;
- Determination of all relevant hazardous characteristics, for example pH, flashpoint;
- Further analysis relevant to the waste stream or treatment method, for example cyanide or chloride content.

It is important that the technique selected produces a representative sample, for example by taking a core sample to the base of the container, or by producing a composite sample from several individual samples taken at different points in the container. The most suitable sampling technique will depend on:

- the physical and chemical characteristics of the waste;
- the type of container to be sampled; and
- any special circumstances, such as highly corrosive or toxic properties, the presence of multiple phases or volatile constituents.

A wide variety of sampling techniques are available, both for on-line sampling, e.g. from continuous waste streams, and for sampling of containers, such as drums and tankers. Information on sampling of hazardous wastes is given in References 4 to 18. Until recently, most of these were not specific to waste materials. However CEN/TR 15310, parts 1–5<sup>14–18</sup>

were published recently and give useful information on waste sampling criteria, techniques, field sampling, packaging and transport and developing sampling plans.

Open sampling tubes are often used by the industry. Reference 8 specifies that one end should be narrow, so that the thumb can easily close it (the standard is not specific to hazardous waste and consideration of personal exposure during sampling must be included in the risk assessment). The other end is drawn to an orifice diameter that is specified for the viscosity of the material to be sampled. Reference 8 also states that open sampling tubes are not suitable for sampling very viscous liquids because of the difficulty in getting a representative sample and retaining it in the tube.

### **BULKING OF BATCHES**

Bulking is the placing of smaller quantities of what should be similar materials for storage and/or transport into larger containers. It does not include the intentional mixing of chemicals for treatment, which is discussed later. Bulking up of chemicals accounts for the approximately 70% of incidents at waste producer sites, due to:

- Inadvertent mixing of incompatible chemicals;
- The use of contaminated/inadequately cleaned or emptied storage containers;
- Contaminated waste, e.g. waste containing reactive materials such as peroxides;
- Self-reactive materials or mixtures (e.g. monomers) being placed in the container either too hot, or for too long, or with insufficient inhibitor;
- Water leaking into waste containers (mainly drums) and reacting.

### **EXAMPLES INCLUDED:**

*An operator was injured after being in the vicinity of an exploding IBC. It had contained alkaline solution and was wrongly identified as being suitable for disposal of dilute acid. It exploded six hours after the dilute acid was added.*

*An operator decanted sulphuric acid into a drum containing waste chlorinated solvents for disposal. The subsequent reaction resulted in chemical burns to his face, neck and arm.*

*Scrap resin in a number of 200 litre drums in a warehouse started to react. Fumes issued from one, and others showed signs of pressurisation. The drums were cooled and the bungs removed. The next day, one drum was found 9–12 m away.*

In some cases incidents also occurred in road tankers, due to bulking up of incompatible chemicals.

Reference 1 gives guidance for bulking of batches at waste treatment sites. This requires such operations to take place under the “direct instruction and supervision of a suitable manager/chemist and should be under local exhaust ventilation in appropriate cases”. There does not appear to be equivalent guidance for waste producer sites, many of which may not employ chemists (e.g. printers and metal treatment works) and HSE are planning to prepare a short information sheet which will be available on the web-site. This

will stress the need for operators to consider in advance the likely range of operations to be undertaken, so that appropriate instructions can be given to their operating personnel.

### USE OF COMPATIBILITY CHARTS AND TOOLS

Where chemicals are to be mixed or bulked a number of tools have been developed to assist in assessing their compatibility, such as matrices and computer tools. These are useful aids, but they should be interpreted by a competent person and not relied on in isolation. For example they may not take account of concentration effects and may only be able to consider binary mixtures, so the effects of impurities, reaction intermediates and catalysts may not be accounted for. Matrices may also assume a homogeneous reaction mixture, which is known not to be the case with many waste streams. In addition they do not always take account of temperature effects. One of the models failed to predict incidents from the HSE data where heating occurred, for example, when steam entered a tank of waste containing dinitrochlorobenzene.

One approach that has been adopted in the USA is based on work conducted by the US Environment Protection Agency<sup>19</sup>. This uses a matrix to define a generic compatibility look up table to identify potential incompatibilities. Comparison of the model with the HSE accident data showed a good performance in predicting most of the incidents that occurred. However it is important that the matrix is not relied upon in isolation for the reasons mentioned above.

A Chemical Reactivity Worksheet<sup>20</sup> is available free of charge from the US Environmental protection Association (EPA) and National Oceanic and Atmospheric Administration (NOAA). It includes a database of reactivity information and a way of virtually “mixing” chemicals to find out what dangers could arise from accidental mixing. The EPA/ NOAA website does warn that, whilst they believe it can accurately predict whether or not a reaction will occur between two chemicals, there are difficulties in predicting more complex mixtures.

### STORAGE, PACKAGING & LABELLING

Poor standards of storage (particularly segregation), packaging and labelling can initiate and contribute greatly to the speed of escalation and severity of incidents involving chemical wastes.

Problems with labelling were found to include lack of labelling, incorrect or inadequate labelling and multi-labelling.

- *Chlorine evolved due to inadvertent mixing of hydrochloric acid and sodium hypochlorite residues from carboys being emptied for cleaning. Both carboys were labelled “hypochlorite waste”.*

Guidance on labelling of waste for transport to transfer or treatment stations is given in reference 1. In cases where the waste is to be transferred for supply purposes, e.g. for blending into cement kiln fuel (cemfuel), then CHIP classifications<sup>21</sup> may be required.

Where waste is to be treated on site, no specific guidance was found, although the transport classifications form a good basis. For reactive wastes there is also a need to consider chemical compatibilities within the transport classes, for example using the EPA compatibility tables.

Packaging, considerations should include the integrity of the packaging and its compatibility with its contents, or any previous contents.

- *A wooden pallet containing three drums of chlorate waste caught fire whilst being moved prior to loading onto a vehicle, possibly due to the pallet reacting with spilt chlorate.*

Most container manufacturers should provide guidance on the compatibility of their products. However, manufacturers' guidance does not normally include any consideration of compatibilities for re-use.

With regard to storage, management issues include storage area design, segregation, separation, housekeeping, fire prevention and emergency response.

EA, in collaboration with HSE, has recently redrafted its guidance on the storage of hazardous wastes<sup>22</sup> and relevant findings from the HSE study have been incorporated.

## **WASTE TREATMENT (MIXING)**

There are a number of options for the treatment of hazardous wastes, e.g. incineration, biological treatment. This paper discusses the mixing of incompatible wastes as part of their treatment, e.g. acid-base neutralizations, cyanide destruction by hypochlorite.

A search of the incidents occurring at waste producer sites found 15% to be due to intentional mixing over the 25-year period. Examples included:

*Runaway reaction during de-odourisation of chemical waste containing hydrogen peroxide. Probably caused by over-addition of caustic soda. Explosion and resulting fire caused widespread damage. One person killed, two injured, more than 500 evacuated.*

*Chemist sprayed with corrosive mix when neutralising an acid copper solution using caustic soda pellets. Too much added at once.*

EA Document S5.06<sup>1</sup> gives guidance on waste treatment. It specifies that any waste should be adequately characterised prior to treatment and the need for compatibility testing. Where chemical reaction hazards exist it refers to HSE's guidance "Designing and Operating Safe Chemical Reaction Processes"<sup>23</sup> for further guidance. However problems arise where companies may not subject such processes to the same rigour as they would for planned chemical reactions. HSE and EA are considering the way forward on this issue.

## **INCIDENTS AT WASTE-TREATMENT SITES**

A number of serious incidents also occurred at waste treatment sites, particularly during bulking up and waste treatment. Several of these resulted in serious off-site consequences and damage to the environment, for example pollution of watercourses. In addition, several



incidents caused substantial local disruption and public concern, and led to prosecutions by EA and/or HSE.

Following such incidents, the industry has been required to improve its screening procedures, including compatibility checks, sampling and laboratory tests. It has responded by using simple Dewar flasks to pre-screen their samples of material for compatibility before mixing them on the large scale, both for storage and treatment. Temperature rises of between 6–10°C in the Dewar vessel over a period of 10 minutes have been suggested by the industry to indicate an exothermic reaction of concern, with gas bubblers being used to measure any gas generation. Whilst this approach may be valid for smaller volumes, HSE has questioned the validity of these test methods for scale up to large volumes. Comparisons of the heat losses between Dewar flasks and large-scale vessels are given in the literature, for example references 23–26.

As a result of these concerns, HSE have asked HSL to review existing data/literature on cooling rates and heat losses data for various pieces of calorimetric equipment, including Dewar vessels, and examine further the scale up limitations with particular reference to the waste treatment industry. Whilst it would be expected that individual occupiers would justify this approach for their own individual installations, such information would provide useful information for inspectors and should be of wider interest to the industry. This Work is being reported separately<sup>27</sup>.

## **ENSURING WASTE SAFE FOR TRANSPORT**

Nine incidents involving transport were recorded. The most common cause was inadequate cleaning of tankers between loads. This led to unplanned reactions that resulted in explosions, loss of containment and fires. Examples included:

- *A runaway reaction occurred in a tanker collecting caustic waste, due to metallic aluminium in the tanker.*
- *Hypochlorite solution in a tanker reacted with methanol that had previously been transported.*
- *An exothermic reaction in a road tanker containing tallow oil. The tank had not been cleaned out following a previous load of nitric acid sludge.*

HSE are planning targeted guidance on the specific issue of tanker cleaning in the form of a short information sheet.

## **CONCLUSIONS**

A large number of incidents are reported to HSE involving the storage, handling and transport of chemical waste, most of which are caused by unintentional or inadequately planned mixing of incompatible chemicals.

Of the incidents analysed, 62% occurred at waste producer sites. Of these, 70% occurred during bulking-up. EA Guidance on this is available for waste treatment sites,

and this could usefully be applied at waste-producer sites. HSE are planning to produce a short information note on this topic.

An analysis of the chemical incompatibilities that have caused the incidents showed that six common reaction types accounted for 87% of incidents where the chemistry was known. In most cases these could be identified with particular industry types.

The incident analysis indicated that many companies had failed to adequately characterise their waste products, and hence establish a suitable disposal route. Guidance on the characterisation of such wastes has been identified. Most of the factors that should be considered are standard good chemical engineering practice. Poor standards of storage, packaging and labelling also contributed to the speed of escalation and the severity of incidents. Joint EA/HSE guidance on this topic has been prepared.

Poor control of intentional mixing was involved in 15% of the incidents at waste producer sites. Although the total number is not large, their potential consequences can be severe and it is important that these operations are subjected to rigorous risk assessments, as for any chemical operations.

25% of incidents occurred at waste treatment sites, including many of the more serious accidents, both during mixing and storage. EA and HSE are active in inspecting waste treatment sites and a research project on the issue of compatibility testing is underway. The incidents also illustrate the importance of adequately controlling and characterising the wastes, including upstream at waste-producer sites and during transfer.

## REFERENCES

1. EA Sector Guidance Note IPPC S5.06 Guidance for the Recovery and Disposal of Hazardous and Non Hazardous Waste, available on the Environment Agency website
2. "Design and development of a hazardous waste reactivity testing protocol", Wolbach CD, Whitney RR and U Spannagel, report no. EPA-600/2-84-057, US Environmental Protection Agency, February 1984
3. Management of Process Industry Waste, Bahu, R., Crittenden, B., & O'Hara, J., IChemE, ISBN 0-85295-324-0
4. "Methods for sampling chemical products - Part 1: Introduction and general principles", BS 5309-1, 1976
5. "Sampling procedures for inspection by attributes – Part 0: Introduction to the BS 6001 attribute sampling system", BS 6001-0, 1996 (ISO 2859-0, 1995)
6. "Encyclopaedia of Chemical Technology", Kirk-Othmer, 4<sup>th</sup> edition, 1997, Vol. 21 pp.626–650
7. "Waste analysis at facilities that generate, treat, store and dispose of hazardous wastes", A Guidance Manual, 1994, available on the US EPA web-site
8. "Methods for sampling chemical products Part 3: Sampling of liquids", BS 5309-3, 1976
9. "Methods for sampling chemical products Part 4: Sampling of solids", BS 5309-4, 1976

10. "RCRA Waste sampling draft technical guidance – planning, implementation and assessment", US Environmental Protection Agency, EPA530-D-02-002, August 2002, available from the US EPA web-site
11. "A practitioner's guide to testing waste for onward reuse, treatment or disposal acceptance", Environmental Services Association Research Trust (ESART), WRc Ref: UC6656, July 2004
12. "Guidance on sampling and testing of wastes to meet landfill waste acceptance procedures", Environment Agency, Version 1, April 2005: available from the EA web-site
13. "Characterization of waste - sampling of waste materials - framework for the preparation and application of a sampling plan", EN 14899, CEN, 2005
14. prCEN/TR 15310-1 "Characterization of waste - sampling of waste materials - Part 1: guidance on selection and application of criteria for sampling under various conditions"
15. prCEN/TR 15310-2 "Characterization of waste - sampling of waste materials - Part 2: guidance on sampling techniques"
16. prCEN/TR 15310-3 "Characterization of waste - sampling of waste materials - Part 3: guidance on procedures for sub-sampling in the field"
17. prCEN/TR 15310-4 "Characterization of waste - sampling of waste materials - Part 4: guidance on procedures for sample packaging, storage, preservation, transport and delivery"
18. prCEN/TR 15310-5 "Characterization of waste - sampling of waste materials - Part 5: guidance on the process of defining the sampling plan"
19. A Method for determining the compatibility of hazardous wastes, H.K.Hatayama, J.J.Chen, E.R. de Vera, R.D. Stephens, D.L.Storm, EPA Paper – 600/2-80-076. 1980
20. Chemical Reactivity Worksheet, available from the US Office of Response and Restoration web-site
21. CHIP for Everyone, HSE Guidance Booklet, HS(G)228, ISBN 0-7176-2370-X, HSE Books
22. Proposed EA, SEPA, NI EHS and HSE Joint Guidance on the Storage of Hazardous Wastes, downloadable from the EA web-site
23. *Designing and Operating Safe Chemical Reaction Processes*, HSE Guidance Booklet, HS(G) 143, ISBN 0-7176-1051, HSE Books
24. Wright, TK & Rogers, RL, Adiabatic Dewar Calorimeter, IChemE Symposium Series No. 97, 121–132, 1986
25. J A Barton & R L Rogers (editors), 1997, *Chemical Reaction Hazards*, 2nd edn., ISBN 0 85295 341 0, IChemE, Rugby
26. Singh, J, Safe Scale-up of Chemical Reactions, Chemical Engineering, May 1997
27. Dewar Scale Up for Reactive Chemical Waste Handling, L Vechot, J Hare, hazards XX, 2008