

Managing the Chemical Reactivity Hazards associated with Hazardous Waste

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Hazardous waste can introduce chemical reactivity hazards during its handling, storage, treatment and disposal. This paper will present an overview of the current definitions of hazardous waste in various regulatory settings (e.g., UK/EU, and US). Subsequently, two hazardous waste/chemical reactivity incidents are presented through the lens of chemical reactivity hazard management. In each incident, an unintended chemical reaction led to adverse consequences, and sufficient information existed or could have been obtained to identify the hazards in advance.

Introduction

In addition to toxic hazards and environmental pollution, hazardous waste can introduce chemical reactivity hazards during its handling, storage, treatment and disposal. The fact that there are hazards associated with these activities is implicit to the very term “hazardous waste”. The word “hazard” clearly conveys that there is some danger associated with the waste; however, as it relates to regulatory requirements, the term “hazardous waste” has a specific definition, typically associated with potential environmental and health hazards. The governmental agencies charged with enforcing the management of hazardous waste are similarly focused on human health and the environment: in the UK, the Environment Agency, and in the US, the Environmental Protection Agency. As a result, hazardous waste generators, carriers, and disposal facilities typically have sophisticated and robust systems for managing the environmental and health hazards associated with these wastes. However, in order to adequately manage the chemical reactivity hazards of hazardous waste, and achieve a satisfactory level of risk, the generators of the hazardous waste and those charged with its transport and disposal may need to take actions that exceed the minimum regulatory standard for environmental protection.

Both environmental agencies in the UK and US, along with the Center for Chemical Process Safety (US), have been active in communicating chemical reactivity hazards to the regulated community. However, the history of process safety incidents associated with reactive hazardous wastes suggests that greater awareness can be achieved. The objective of this study is to examine how chemical reactivity factors into the definition of hazardous waste, and then examine some of the unique chemical reactivity challenges posed by hazardous waste and the activities associated with it.

First is a review of the definitions of hazardous waste in various regulatory settings (e.g., UK/EU, and US). Subsequently, a series of hazardous waste/chemical reactivity incidents is presented through the lens of chemical reactivity hazard management. In each incident, an unintended chemical reaction led to adverse consequences, and sufficient information existed or could have been obtained to identify the hazards in advance.

Review of regional regulatory definitions and regulations regarding hazardous waste

In the European Union (EU) the legislative framework for the handling of wastes is laid out in the Waste Directive 2008/98/EC, whereas in the United States, hazardous waste is defined by Resource Conservation and Recovery Act (RCRA) regulations (Title 40 of the Code of Federal Regulations). These definitions are reviewed in the following sections.

European Union and United Kingdom

In the European Union (EU) the legislative framework for the handling of wastes is laid out in the Waste Directive 2008/98/EC. This Directive defines the key concepts such as waste, recovery and disposal and puts in place the essential requirements and obligations for the management of waste. It establishes such principles such as the obligation to handle waste in way that does not have a negative impact on the environment or human health and a requirement that the costs of waste disposal must be borne by the holder, previous holders or producer of the waste.

Waste must be assessed in accordance with the Directive, and is based on;

- The List of Waste decision (2000/532/EC)
- Annex III of the Waste Directive (2008/98/EC)

Until recently, these in turn relied on the classifications derived from the chemical legislation Dangerous Substances Directive 67/548/EC and the Dangerous Preparations Directive 1999/45/EC. However, from the 1st June 2015, these were replaced by the Classification, Labelling and Packaging Regulation (CLP) (2008/1272/EC). This introduced a system of chemical classification for mixtures based on hazard classes, categories and statement codes (rather than risk phrases and categories of danger). As a consequence, Annex III of the Directive has been revised to amend the hazardous properties to align with the CLP and to provide hazardous waste criteria based on hazard statement codes.¹

A waste producer must therefore classify waste produced and identify its hazardous properties before it is moved, disposed of or recovered. The producer must identify the appropriate code or codes from the List of Waste, which may require some form of assessment related to the properties of the waste. The waste may be classified as hazardous on the basis of its physical properties, such as explosive, oxidising, flammable or corrosive, and/or by the presence of substances at concentrations that may cause a hazard to human health, such as skin irritation, carcinogenicity or acute toxicity. A substance may also be classified as hazardous waste due to the presence of substances representing environmental hazards such as hazardous to the aquatic environment or the ozone layer. The presence of individual substances within the waste does not necessarily render the waste hazardous, rather an assessment of the concentrations of one or more the substances present in the waste is required, to determine whether concentration limits for a specific hazard has been reached. Extensive guidance on the relevant approach to assessment is set out in the Waste Classification and Assessment – Technical Guidance WM3, provided by the Environment Agencies of the United Kingdom.²

United States

In the United States, hazardous waste is defined by Resource Conservation and Recovery Act (RCRA) regulations (Title 40 of the Code of Federal Regulations).³ RCRA defines hazardous waste as belonging to one of two groups: listed wastes and characteristic wastes. Listed hazardous wastes are defined and tabulated in the regulations, and generally they are associated with a specific manufacturing process or specific chemical.

There are four categories of hazardous characteristics: corrosivity, ignitability, toxicity, and reactivity. Three of these characteristics—corrosivity, ignitability, and toxicity—are determined by a specific test method. However, the reactivity characteristic is loosely defined; it is defined by a narrative description, and not by a specific test method or measurement. A waste is deemed reactive if it satisfies one of the following four criteria:

1. it can explode or violently react when exposed to water, when heated, or under normal handling conditions;
2. it can create toxic fumes or gases when exposed to water or under normal handling conditions;
3. it meets the criteria for classification as an explosive under US Department of Transportation rules; or
4. it generates toxic levels of sulfide or cyanide gas when exposed to a pH range of 2 through 12.5.

Within the United States, the Environment Protection Agency (US-EPA) definition for waste reactivity represents a minimum regulatory requirement but the definition may not be an appropriate basis to address process safety concerns. To achieve a satisfactory level of process safety, responsible parties must consider the hazardous properties of the waste and may need to take actions that exceed the minimum regulatory standard for environmental protection.

Within the United States, both the waste generator and the treatment, storage, and disposal facility (TSDF) have responsibility to satisfy the applicable environmental regulations as well as safely manage the waste. This requires that the generator of the hazardous waste must be able to identify the chemical constituents in the waste and to communicate this information to the TSDF. Subsequently, the TSDF should evaluate the reactivity characteristics of the waste and consider reactivity hazards that may be introduced as part of the disposal process. Due to the fact that a chemical reactivity hazard is often a function of the concentrations of constituents within the waste, which may vary from load to load, the TSDF should carefully consider the degree to which chemical constituent concentrations may be an important factor in the safe handling, treatment, and disposal of the waste.

A more detailed discussion on the US-EPA treatment of chemical reactivity hazards is presented a prior publication by Cox et. al.⁴

Case Studies

The following sections will present two case studies of incidents involving hazardous waste. The incidents can be summarised in two words each: inadvertent heating and inadvertent mixing. Both represent circumstances where a lack of information about hazardous waste resulted in a negative outcome, underscoring the importance of clear communication and documentation between industry partners in the first case, and workplace colleagues in the latter.

Case Study 1: Inadvertent Heating: Instability during stabilisation

Solidification and stabilisation (S/S) processes are a wide range of treatment methodologies that typically involve mixing inorganic cementitious binders (e.g., Portland cement) into waste or soil.⁵ In the EU and UK, stabilisation “means processes which change the hazardousness of the constituents in the waste and transform hazardous waste into non-hazardous waste” whereas solidification “means processes which only change the physical state of the waste by using additives without changing the chemical properties of the waste.”⁶ In practice, S/S processes are designed to accomplish one or more of the following results: improve the handling and physical characteristics of hazardous waste, decrease the surface area of the waste across which transfer or loss of contaminants can occur, and/or limit the solubility of any hazardous constituents of the waste.⁷ In the US, S/S is one of the most frequently selected treatment technologies for waste generated at abandoned or uncontrolled hazardous waste (“Superfund”) sites.⁸ In the UK and Europe, S/S processes have not seen the same prevalence due to a number of barriers, but its proposed applications include the remediation of brownfield sites.^{9,10,11}

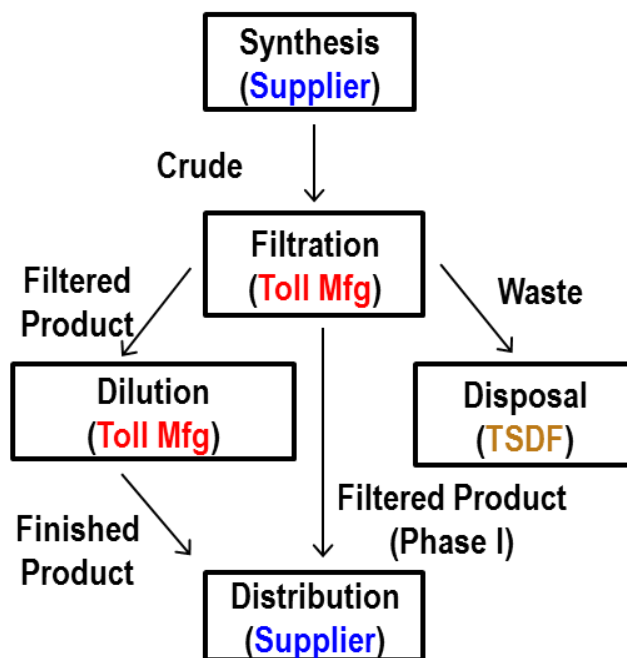


Figure 1. Flow diagram of material from synthesis to distribution/disposal.

Regardless of regulatory environment, many S/S processes involve chemical reactions, many of which are exothermic, meaning heat is released as a result of the reaction. The temperature of the waste may increase as a result. Whether this temperature increase is significant depends on many factors, but can result in a chemical release or fire. An example discussed below involves the treatment of hazardous waste generated by a toll manufacturer.

A raw material (crude) was produced by the supplier and then shipped by tanker truck to a toll manufacturer contracted to filter the suspended solids that remained after the synthesis process. This process is represented by a sketch in Figure 1. Initially (during Phase I), the filtered product was sent back to the supplier without dilution, but for subsequent batches, the toll manufacturer was asked to begin diluting the filtered product to its final, finished form. The finished product was then shipped back to the supplier or directly on to distribution.

The material was filtered through a hydraulic filter press (see Figure 2). The filter press was operated by circulating crude from a bulk tank, through the filter medium that consisted of filter paper and diatomaceous earth (“filter aid”), until the clarity within the bulk tank indicated that sufficient suspended solids had been removed. Upon completion of a batch, or when process conditions dictated, the filter press was opened and excess liquid was captured in a drip pan and stored in totes until project completion. The drip pan was then removed, and the remaining contents of the filter press were captured in a roll-off box. This waste consisted primarily of the solid sediment removed from the product, the filter paper used to capture the sediment, diatomaceous earth used to aid in the filtration process, and some entrained product. Because of trace levels of arsenic in the crude, the material in the roll-off boxes was designated hazardous waste, and was sent to a waste treatment, storage, and disposal facility (TSDf) for treatment and disposal. The material was not considered “reactive” per the regional hazardous waste regulations.



Figure 2. (left) Filter press building, adjacent bulk supply tank, and roll-off box for waste. (right) Close-up of similar filter press.

The first three roll-off boxes were stabilized with a commercially available fly ash material without any reported issues; however, the fourth roll-off box began “steaming” and emitting unwanted gases after treatment. Since three prior roll-off boxes were treated without incident, the investigation focused on determining differences in the generation, handling and treatment of the fourth roll-off box.

A post-incident review of product literature revealed that, while stable at normal temperatures, the primary ingredient of the product could become unstable at elevated temperatures. This information was presented on the product safety data sheet (SDS), but no such SDS existed for the crude material, and the SDS for the finished product (filtered and diluted) was neither asked for by the TSDF nor provided by the toll manufacturer. The TSDF did not inquire whether the material was stable at elevated temperatures, and the waste generator was unaware that the treatment methodology would involve an exothermic process. Thus, a focus of the investigation was whether the fourth roll-off box contained a larger quantity of entrained product than previous shipments. A detailed mass balance across the entire filtration process revealed that, if anything, less entrained product was expected per pound of waste in the fourth shipment than the previous three. Contamination and other changes to the waste composition, including the change of procedure from Phase I to Phase II, were investigated, but ruled out. However, further investigation revealed differences in the treatment process at the TSDF.

Upon receipt of the waste, the TSDF performed laboratory testing to establish a recipe that was sufficient to stabilize the waste relative to the hazardous component. A bench-scale test was then performed using the recipe to determine whether the ratio of flyash, water and waste could be safely mixed by monitoring the temperature rise in the material. Once a recipe was issued, treatment was performed, and the load was transferred to a holding shed. Samples were collected and sent to the laboratory to determine whether the waste had been successfully stabilized and could be landfilled, or if further treatment was necessary. This process is shown in schematic form in Figure 3. A temperature rise of 5°C was observed, the waste was approved for treatment and a recipe was issued for the first roll-off box. An identical recipe was issued for the second roll-off box; however, no recipe was issued for the third or fourth roll-off boxes, and process documentation revealed significant discrepancies in the treatment of these roll-off boxes. Based on truck scale tickets, over 4,000 kg (9,000 lbs) of unaccounted for material was added to the fourth waste load during treatment. A calculation of the adiabatic reaction temperature showed that, if this additional mass was the TSDF’s normal mixture of flyash and water, the temperature could have been risen much higher during treatment of this load than the first two.

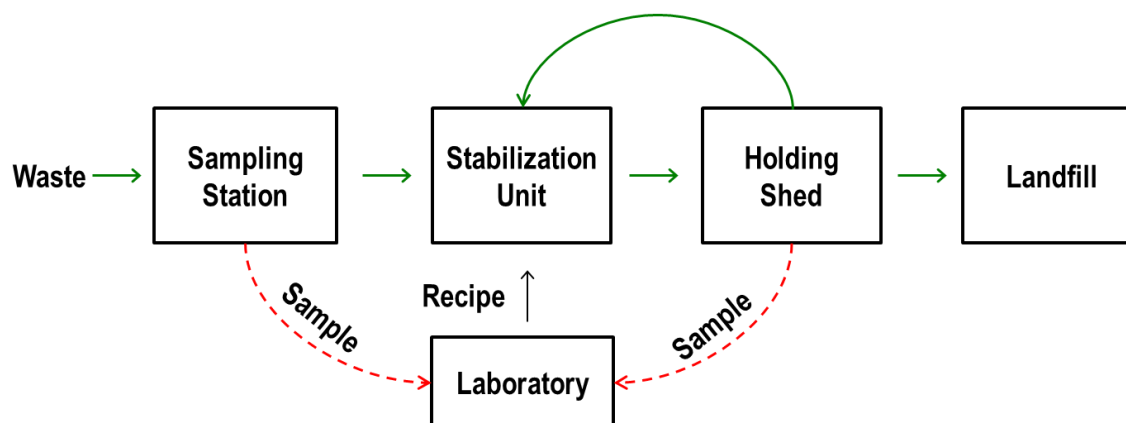


Figure 3. Schematic representation of material handling at the hazardous waste transportation, disposal and storage facility (TSDF).

Further investigation revealed that, in practice, the operators did not monitor or record the quantity of water added from the wash-out of roll-off boxes, and that flyash was added “as needed” to solidify any remaining liquid at the operator’s discretion. Interviews revealed that the TSDF operators were unaware that the flyash and water reacted with one another. Yet, in the US, stabilisation is defined as “[a process that] involves the use of the following reagents (or waste reagents): (1) Portland cement; or (2) lime/pozzolans (e.g., fly ash and cement kiln dust)...”¹² These chemicals typically contain calcium oxide (CaO), which reacts with water to form calcium hydroxide (Ca(OH)₂). The literature suggests that very active fly ashes “generate a large exotherm and very rapidly, due to the presence of substantial quantities of CaO that can hydrate violently.”¹³ Furthermore, “the low heat transfer rate from a large mass of treated waste while curing can drive the internal temperature to unacceptable levels, even though the laboratory test did not indicate a potential problem”.

Literature studies of flyash similar to that used at this TSDF indicated that the “hydration process is dominated by direct hydration of the CaO component”.¹⁴ Bretherick’s Handbook of Chemical Reactivity Hazards cites incidents with powdered CaO where temperatures have reached 150-300°C (302-572°F) and “may ignite combustible material.”¹⁵ Bretherick’s continues that “occasionally 800-900°C (1472-1652°F) has been attained.” The US-EPA has recognized that the exothermic nature of stabilisation can lead to serious safety problems including the possibility of gas releases and fires, citing a 1983 fire after lime was added to a sludge pit.¹⁶ The US-EPA also provided an example of a fire that occurred on December 8, 1992, after Portland cement was added to a hazardous waste containing arsenic and benzene.^{17,18}

The most probable explanation for the odour release was inadvertent heating due to the exothermic reaction during treatment. While there were clear deficiencies at the TSDF, better communication between the generator and the TSDF may have prevented this incident. To avoid similar events, communication between the TSDF and the waste generator may need to exceed the regulatory minimum to properly characterize the hazards associated with each waste treatment decision.

Case Study 2: Inadvertent Mixing: One of these things is not like the others

On April 25, 2002, a chemical waste-mixing incident occurred at a sign manufacturer (anonymised to ABC Company for the purposes of this write-up) located in the United States. The result was an explosion that injured more than 30 persons and caused significant damage to the building. ABC Company manufactured architectural metal signs and letters using primarily stainless steel, aluminium, and brass using methods that included metal treating, etching, silk screening, polishing, and coating. Part of the production process of the graphics and lettering employed a photo-resistant masking material and a chemical etching process which involved the use of an aqueous solution of ferric chloride and hydrochloric acid. The final stages of production products were polished and coated with paints, lacquers, and inks.

Based on review of the business permits filed with the municipality, ABC Company held a permit for the use and storage of up to 3,785 L (1,000 US gal) of paint and lacquer and up to 2,082 L (550 US gal) of flammable solvents which were primarily alcohol and lacquer thinner (a mixture of primarily acetone and toluene). During the course of normal operations, ABC Company generated hazardous waste as a result of the chemical products employed in the production process. Purportedly the majority of the hazardous waste was spent etching solution which was an aqueous mixture of ferric chloride, ferrous chloride, hydrochloric acid, and solubilized metals classified as hazardous due to corrosiveness. Although smaller in quantity, paint waste and solvent, classified as hazardous due to ignitability, were also generated. To dispose of this chemical hazardous waste, ABC Company contracted with a licensed hazardous waste firm to transport the accumulated waste to an authorized treatment facility.

ABC Company typically accumulated waste chemicals onsite and arranged for them to be picked up every few months by a hazardous waste disposal contractor. Although the waste was stored in 55-gallon drums (208 L) and 15-gallon carboys (57 L) the hazardous waste was shipped from the facility exclusively in 55-gallon drums. On the day of the incident explosion, employees reported that one of the 15-gallon carboys was leaking. As a result, the production foreman instructed two employees to transfer the contents of the leaking carboy into a 55-gallon drum.

The workers, using a pump, transferred the contents of the leaking carboy, along with approximately 10 other carboys, into a plastic 55-gallon drum (incident drum). Upon completion of the pumping, the lead worker advised the helper to seal the drum and then took the pump to rinse it with water. The helper, intending to seal the drums later, left the area. Shortly after leaving the immediate area of the incident drum, other workers reported hearing hissing sounds emanating from the waste consolidation area. Within a short period of time the hissing sound increased in ferocity and liquid was observed being ejected upward from the drum opening. Seconds later, the explosion occurred.

The blast dislodged portions of the basement ceiling and inside walls, blew out windows up to the fifth floor, and caused a stairwell within the building to collapse. Following the blast, a fire was ignited in an area adjacent to where the workers had been transferring waste into the incident drum. Following the explosion and subsequent fire, the Chemical Safety Board (CSB) of the United States was called upon to perform the incident investigation.

CSB investigators found two 55-gallon drums, one plastic and one metal, in the area they determined to be origin of the explosion that demonstrated evidence of overpressure. The plastic drum, believed to be the incident drum in which the workers were combining the contents of the various carboys, was found to have ruptured along the drum axis and the bottom had blown out as illustrated in Figure 4. The vendor label, still visible on the drum, indicated the original contents of the drum were an aqueous ferric chloride solution. It is unclear what quantity, if any, or residual ferric chloride solution remained in the incident drum at the time that workers began consolidating the approximately 10 waste carboys.



Figure 4. Ruptured 55-gallon plastic drum found in the area of origin.

It is believed that after the wastes were mixed in the drum, a chemical reaction occurred which resulted in the rapid generation of an unknown gas and, as a result of the small opening in the top of the drum, the gas could not escape the drum at a rate greater than or equal to the rate of generation. Thus, pressure began to build within the drum until the drum failed which resulted in the explosion.

Investigators observed numerous carboys in the vicinity of the incident drum which was consistent with the workers' description of the area immediately preceding the explosion. An analysis of the residuals within these carboys indicated that several of the carboys contained dissolved metals and lacquer thinner which was consistent with the spent acidic etching solution. Workers stated to the CSB investigators that the last carboy transferred into the incident 55-gallon drum was of metal construction and therefore unique from all of the previously transferred plastic carboys. An analysis of the residuals within the metal carboy found in the area revealed that it likely contained a concentrated nitric acid solution. Although the CSB investigators were not able to identify the exact chemistry that led to the internal overpressurization of the incident drum, it is known that if lacquer thinner is combined with nitric acid, an exothermic reaction generating gas can occur.

As a result of the identification of a concentrated nitric acid solution on site, CSB investigators reviewed company purchase records but found none for nitric acid. Additionally, no material safety data sheet (MSDS) for the nitric acid was found in company records. This, in conjunction with workers never recalling using nitric acid in the manufacturing process, led CSB investigators to conclude that the nitric acid was likely used at one time and since forgotten, and the workers were likely unaware of their contents. The CSB found shortcomings relative to numerous regulatory requirements, including worker training and hazard communication.

While this case study was riddled with errors in risk management and regulatory compliance, lessons can be learned for even the most sophisticated company that manages their own waste or waste generated by others. Training workers to recognize important distinctions and inconsistencies can aid with hazard identification and mitigation. This is especially relevant during waste transfer and mixing operations that may involve multiple waste streams.

Concluding Remarks

Both case studies represent avoidable incidents had sufficient information been shared between involved parties. In each incident, an unintended chemical reaction led to adverse consequences, and sufficient information existed or could have been obtained to identify the hazards in advance. Both cases represent circumstances where a lack of information resulted in a negative outcome, underscoring the importance of clear communication and documentation between industry partners in the first case, and workplace colleagues in the latter. This communication may need to go beyond that required to maintain regulatory compliance, as demonstrated in the first case study, where the obligatory information sharing left neither the waste generator nor the TSDf with sufficient information to avoid the incident.

¹ <http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32014R1357>

² https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/427077/LIT_10121.pdf

³ Resource Conservation and Recovery Act, Title 40 of the Code of Federal Regulations, 1976, Parts 239–282.

⁴ B.Cox, A. Carpenter, R. Ogle, Lessons Learned from case studies of Hazardous Waste/Chemical Reactivity Incidents, *Process Safety Progress*, (33), 4, 395-398, DOI 10.1002/prs.11698.

⁵ Al-Tabbaa, A. et al. “UK stabilization/solidification treatment and remediation – Part I: binders, technologies, testing and research.” *Land Contamination and Remediation*, 14 (1), 2006.

⁶ LIT 10121. Guidance on the classification and assessment of Waste. 1st Edition (2015). Technical Guidance WM3, Environment Agency, UK, p. A8

⁷ USEPA, Handbook for Stabilization/Solidification of Hazardous Waste, EPA/540/2-86/001, June 1986.

⁸ Bates, E. and Collins, C. *Stabilization and Solidification of Contaminated Soil and Waste: A Manual of Practice*. September 2015.

⁹ *Stabilisation/Solidification for the Treatment of Contaminated Soil*. CL:AIRE (Contaminated Land: Applications in Real Environments). GB 1. November 2005.

¹⁰ Environment Agency (UK), Guidance on the use of Stabilisation/Solidification for the Treatment of Contaminated Soil. Science Report: SC980003/SR1, 2004.

¹¹ Al-Tabbaa, A. et al. “UK stabilization/solidification treatment and remediation – Part I: binders, technologies, testing and research.” *Land Contamination and Remediation*, 14 (1), 2006.

¹² USEPA, Handbook for Stabilization/Solidification of Hazardous Waste, EPA/540/2-86/001, June 1986.

¹³ Conner, JR, *Chemical Fixation and Solidification of Hazardous Wastes*, Van Nostrand Reinhold (1990).

¹⁴ Anthony, EJ, Jia, L, Wu, Y, and Caris, M, “CFBC Ash Hydration Studies”, 2003 International Ash Utilization Symposium, Center for Applied Energy Research, University of Kentucky, Paper #8, (2003).

¹⁵ Bretherick’s Handbook of Chemical Reactivity Hazards, 6th Edition, Vol. 1, p. 1326 (1999).

¹⁶ USEPA, Handbook for Stabilization/Solidification of Hazardous Waste, EPA/540/2-86/001, June 1986.

¹⁷ USEPA, Report on Emergency Incidents at Hazardous Waste Combustion Facilities and Other Treatment, Storage, and Disposal Facilities (TSDFs), EPA 530-R-99-014, June 1999.

¹⁸ Resource Conservation and Recovery Act, Title 40 of the Code of Federal Regulations, Parts 239-282.