

# Potential Fire Suppression Agents for Metal Hydride Fires

## *White Paper Prepared by the Hydrogen Safety Panel*

### **Abstract**

Sodium chloride and four or five other particulate materials have been used successfully as fire suppression agents for specific combustible metal fires. The certification testing and National Fire Protection Association recommendations for using these suppression agents are summarized here. The sodium chloride based agent and ordinary sand have also been used in some sodium hydride fires, and in a sodium hydride fire test series. However, there is a need to explore chemical compatibility and fire suppression effectiveness for these and other agents against the wide assortment of candidate metal hydrides being considered for hydrogen storage applications. A three-task research program to determine the compatibility and effectiveness of these agents is recommended for DOE funding.

### **Introduction**

Numerous metal hydrides are currently being synthesized and tested extensively as part of hydrogen energy storage research programs around the world. A recent review article by Sakintuna et al. [1] categorizes the potentially viable metal hydrides for hydrogen storage applications into the following groups: magnesium based hydrides, sodium alanates, lithium and potassium alanates, lithium nitrides, lithium boro- and beryllium hydrides, and intermetallic compounds composed of a metal forming a stable hydride and a metal forming an unstable hydride. According to Latroche [2], stable hydrides are formed from alkali metals, early transition metals such as zirconium, titanium, and magnesium, and rare earth metals, whereas unstable hydrides are formed from late transition metals such as chromium, iron, and nickel. Sakintuna et al. describe the use of catalysts and ball milling of these metal hydrides to improve desorption kinetics for vehicle refueling applications.

Intermetallic compounds containing nickel, such as  $\text{LaNi}_5$ -type compounds, are also widely used as negative electrodes in nickel-metal hydride batteries [2]. Simpler metal hydrides, such as sodium hydride, are also used as chemical intermediaries in pharmaceutical production, and in other chemical manufacturing operations.

Most metal hydrides exhibit varying degrees of pyrophoricity depending on their particle size and surface characteristics. This pyrophoric property has led to fire incidents in laboratory and production facilities, and in hydride tank test facilities, with some examples given under Metal Hydride Fire Incidents. Some of these metal hydride fires involve persistent white-hot flames such as shown in Figure 1. Other hydride fires can be in the form of almost invisible hydrogen flames or glowing, smoldering particles, as illustrated in the section of the paper on metal hydride fire incidents.



**Figure 1 Controlled Sodium Hydride Fire (from Fluegeman et al, 2005)**

Metal hydride fires can present a formidable fire suppression challenge. Since almost all the hydrides are water reactive, aqueous suppression agents are inappropriate. Similarly halogenated agents and carbon dioxide can react violently with many hydrides so they should generally not be used. The most logical candidate agents are those that have proven effective on combustible metal fires, i.e. the Class D fire suppression agents. The following section of the paper provides a brief description of these Class D agents.

## **Combustible Metal Fire Suppression Agents**

Nelson's NFPA Handbook chapter [3] groups the combustible metal fire suppression agent into four categories: Listed (Certified) Agents, Other Proprietary Agents, Non-proprietary Agents, and Miscellaneous Agents. All the listed Class D agents are dry powders with compositions that include materials to promote fire extinguishment, long-term storage without deterioration, and rapid discharge from the agent container. They also have carefully controlled particle size distributions. However the agent listings can change from year-to-year as manufacturers change agents and as listing requirements evolve.

The most well-known listed agent in the U.S. is called Met-L-X<sup>TM</sup>, which is composed of sodium chloride and a thermoplastic polymer to bind the NaCl particles into a cohesive mass as it covers the burning metal. As indicated in Table 1, sodium chloride based agents have been found effective and listed for use on sodium, potassium, and magnesium fires, and Met-L-X<sup>TM</sup> in particular has been reported to be effective to powdered aluminum and titanium fires. The Met-L-X<sup>TM</sup> Underwriters Laboratories Inc. listing includes 30-lb hand portable, and 150 lb and 350 lb wheeled and stationary extinguishers.

There are two other manufacturers with sodium chloride based agents that have been either FM approved or U.L. listed as Class D fire extinguishers per UL Standard 711 [4]. These other listed/approved agents are also available in 30-lb capacity portable extinguishers and in 150 lb capacity wheeled units. The portable extinguisher with hose and nozzle has an agent application range of 8 to 10 ft.

Two different U.S. manufacturers have agents listed/approved for use on lithium fires. One is a graphite based agent, while the other is a copper powder. According to Nelson [3], the graphite powder with additives works by a combination of partial air exclusion and heat conduction to cool the burning lithium. The copper powder agent was developed by the Naval

Sea Systems Command, and seems to form a copper-lithium alloy on the surface of the burning molten lithium. The alloy excludes air to extinguish the lithium fire and prevent re-ignition [3]. It is available in both portable and large (250 lb) capacity wheeled extinguishers.

Table 1. Class D Fire Suppression Agent Effectiveness Matrix  
(based on references 3 & 5)

	Sodium Chloride	Graphite	Copper Powder	Sodium Carbonate	Dry Sand
Aluminum	Yes [3,5]	No [5]	Yes [3], No[5]	Yes [5]	Yes [5]
Lithium	No [5]	Yes [3,5]	Yes [3]	Yes [5]	Yes [5]
Magnesium	Yes [3,5]	Yes [3], No [5]	Yes [3], No [5]	Yes [5]	Yes [5]
Potassium	Yes [3,5]	Yes [5]	Yes [5]	Yes [3,5]	Yes [5]
Sodium	Yes [3,5]	Yes [3,5]	Yes [5]	Yes [3,5]	Yes [5]
Tantalum	Yes [5]	No [5]	No [5]	No [5]	Yes [5]
Titanium	Yes [3, 5]	No [5]	No [5]	Yes [5]	Yes [5]

Nelson’s non-proprietary metal fire extinguishing agents include sodium carbonate, also known as soda ash, and sand. According to Nelson, the soda ash extinguishing mechanism is similar to that of sodium chloride [3]. At least one Japanese manufacturer (Nippon Dry-Chemical) produces a portable extinguisher with sodium carbonate agent for use on most metal fires. The same manufacturer also produces a portable extinguisher with a calcium chloride agent for use on lithium fires and magnesium fires, as well as many other metals.

Table A.13.3.3 of NFPA 484 [5] has an extensive effectiveness matrix of specific metals and extinguishing agents, and some of that data is included in Table 1 above. NFPA 484 Chapter 13 has the following admonition about agent application technique. “Application of dry extinguishing agent shall be conducted in such a manner as to avoid any disturbance of the combustible-metal dust, which could cause a dust cloud. The use of pressurized extinguishing agents shall not be permitted on a combustible-metal powder fire or chip fire, unless applied carefully so as not to disturb or spread the combustible-metal powder or chip fire.” It goes on to say that these agents are effective for small and incipient fires, but not for large fires. Therefore NFPA 484 recommends inert gases such as argon and helium for large fires in an enclosure or room.

NFPA 484 [5] recommends using dry, fine sand with grains small enough to pass through a 20 mesh sieve. Paragraph A.13.3.3.10.1 of NFPA 484 states that the sand should be stored in closed containers situated near the combustible metals, and that long-handled shovels should be stored next to the containers. It further states that the sand should be deposited around the perimeter of the burning metal, rather than thrown directly onto the burning metal.

Agent application limitations associated with sand and other solid particulate agents have motivated the research and development of certain liquid agents for combustible metal fires. For example, the Air Force sponsored the development of a trimethoxyborane,  $(\text{CH}_3\text{O})_3\text{B}$ , based agent called Boralon for magnesium fires on aircraft [6, 7]. The final formulation of Boralon included 30% Halon 1211, which is no longer being produced because of regulations on stratospheric ozone depleting chemicals. A new proprietary formulation liquid agent called FEM-12 and based on an aqueous solution of inorganic chemicals has recently been developed and tested by the Federal Aviation Administration (FAA) and the Air Force for use on aircraft combustible metal fires [8]. Test results are summarized below.

## Certification Testing for Combustible Metal Suppression Agents

UL 711 describes in detail the fire suppression tests that Class D agents must pass in order to receive UL listing. There are separate test series for magnesium fires and for alkali metal fires. The magnesium fire tests are conducted in a 4 ft<sup>2</sup> test pan with the magnesium in the forms and quantities shown in Table 2. The magnesium is ignited by a torch, and the extinguisher is discharged from a distance of 8 ft.

Table 2. UL 711 Fire Tests with Magnesium

Form of Mg	Amount (lb)	Depth (inch)
0.25 mm chip	40	4.5
0.05 mm chip	40	4.5
Dust	25	1

Figure 2 shows the results of a slightly modified version of the UL 711 magnesium fire test after a sodium chloride based agent was applied to 26 lb of burning magnesium castings and turnings. The sodium chloride agent formed an approximately 0.5 inch deep hard crust over the burning magnesium that smothered the fire. As long as the crust remained undisturbed, the magnesium would not reignite into a flame.



Figure 2 Results of sodium chloride based agent application to burning magnesium (from reference 8)

In the case of agents to be listed for alkali metal fires, the sodium or potassium is first melted by first pre-heating the metal to 510°C in an inert atmosphere. The metal in the test pan

is then exposed to air and auto-ignites. The test pans and alkali metal quantities shown in Table 3 are used.

Table 3. UL 711 Fire Tests with Alkali Metals

Pan Size (ft <sup>2</sup> ) Amount of Metal (lb)	
4	3
2.5	7
2.5	35

As with the magnesium fire tests, the alkali metal fire suppression agents are applied manually to the pans and metal quantities are shown in Table 3. The fire extinguishment time and agent throw distance are recorded and reported as part of the listing.

### Other Fire Suppression Tests for Combustible Metals

The UL 711 listing/certification tests described above involve direct agent application to stationary burning metal in a pan. Other tests have been conducted to investigate the effectiveness of suppression agent application to other fire configurations. For example, Wilson et al. [9] described the results of tests with various agents applied to burning magnesium flowing down a vertical screen and then indirectly to burning magnesium partially obstructed in a pan under the screen. They report that Met-L-X<sup>TM</sup> was very effective on the vertical flowing magnesium fire, but allowed re-ignition of the magnesium fire that was not directly accessible by the agent. Another fire scenario tested by Wilson et al. [6] involved magnesium turnings in an aircraft engine cowling, such that agent application was obstructed by the cowling and the magnesium eventually flowed out of the open cowling onto the floor below. The Met-L-X<sup>TM</sup> application was only partially effective for this obstructed and eventually displaced fire configuration.

The FAA Fire Research Group conducted magnesium fire extinguishment tests using the 10 lb combination of magnesium printing plates and oil-coated turnings shown in Figure 3. After a free burn that allowed the printing plates to become fully involved, fire suppression agents were applied from various portable extinguishers, using a sodium chloride based agent and using the new FEM liquid agent [8]. The sodium chloride based agent successfully coated and seemed to smother the magnesium fire, but smoke continued to be emitted from the pile. When the coating was disturbed with a pole, flames reappeared from the still burning magnesium under the coating. Thus, the sodium chloride smothered the fire without cooling the magnesium to prevent re-ignition. When the FEM liquid agent was applied, the fire flared up and burning embers were propelled out of the burning magnesium as shown in Figure 3. Eventually the FEM-12 did cool and extinguish the fire.



Figure 3. Application of liquid agent FEM-12 to burning magnesium (from ref 8).

## Metal Hydride Fire Incidents

Anecdotal descriptions of metal hydride fire incidents illustrate both the nature of hydride fires and the varying success achieved in using fire suppression agents. For example, the sodium hydride fire shown in Figure 1 occurred in a pharmaceutical plant dispensing room as the sodium hydride was dispensing the hydride from a drum [10]. The operator and/or emergency responders, equipped with proper personal protective equipment, successfully extinguished the fire with Met-L-X<sup>TM</sup> agent. Figure 4 shows the deposits of Met-L-X<sup>TM</sup> on the floor of the dispensing room. The photo shown as Figure 1 was taken after the emergency responders deliberately disturbed the smothered fire in order to gradually burn off and dispose of the sodium hydride [10].



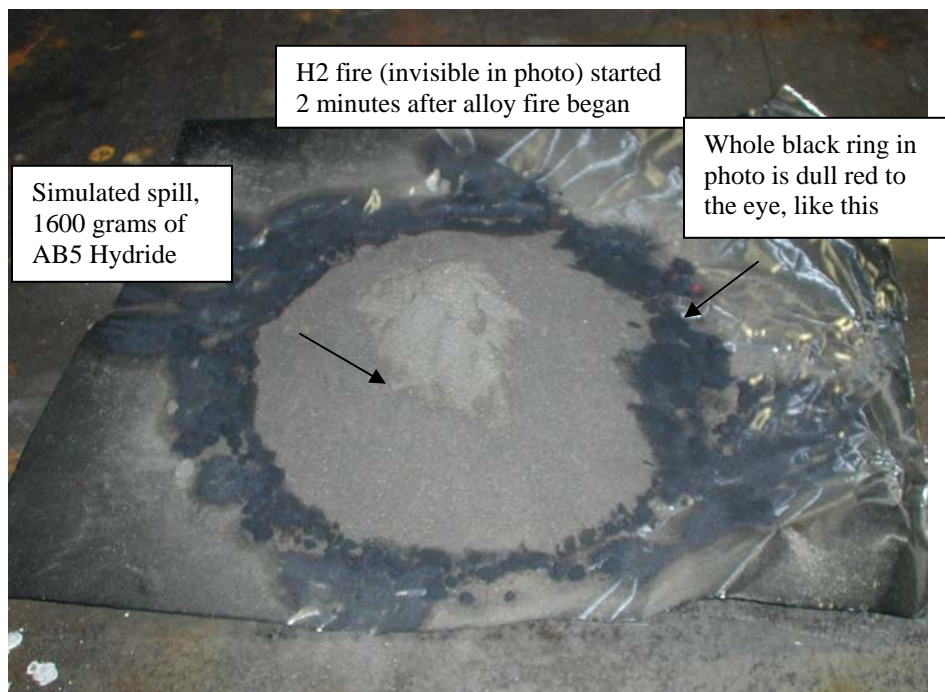
Figure 4 Sodium hydride fire extinguished with Met-L-X<sup>TM</sup> (from Fluegeman et al., 2005)

Figure 5 shows a different type of hydride fire simulating a spill of an AB<sub>5</sub> hydride (partially substituted LaN<sub>5</sub> hydride) that resulted from a breach in a hydride storage canister. As suggested by the notes in the photo and reference 11, this fire actually consists of two separate fires, i.e. a hydrogen fire and a smoldering AB<sub>5</sub> powdered metal fire. This illustrates the issue



that the fire can occur before the hydrogen is fully absorbed by the metal. Therefore, it is important that extinguishing agents be effective for the powdered metal fire as well as the metal hydride fire.

The UK Chemical Reactions Hazard Forum compilation of incidents includes a fire, <http://www.crhf.org.uk/incident41.html>, that occurred at a chemical plant when a 5 kg bag of sodium hydride was being dispensed into an inerted vessel. A powder extinguisher was used which initially put the fire out, but secondary fires started due to the force of the fire extinguisher. Dry sand was successfully used on these secondary fires. The sodium hydride contamination was extensive.



**Figure 5 AB<sub>5</sub> metal hydride spill fire (from F. Lynch, 2005).**

The American Industrial Hygiene Association Health and Safety Committee Web site includes an incident of a lithium aluminum hydride (LAH) fire in a laboratory fume hood. A small amount of LAH leaked from a small hole in a bag, onto the surface of the hood and burst into flames, startling the worker and causing him to drop the remainder of the bag (8-10 grams of LAH) onto the fire. The fire was not successfully extinguished and had to burn out by itself in the fume hood, but not before burning a lab coat in the hood. The Committee Web site reports that a Met-L-X™ has now been mounted in the fume hood, and a container of sand is now on the floor near the fume hood. However, Met-L-X™ is a sodium chloride based agent that is not certified for lithium based metal fires, as indicated in Table 1.

There have been two recent metal hydride fires in Department of Energy laboratory facilities [12]. An August 2005 fire occurred when about 200 mg of sodium hydride was being

weighed and reacted with moisture in the ambient air. The student working in the lab first tried unsuccessfully to extinguish the fire with his lab coat before getting a portable fire extinguisher with unspecified agent to extinguish it successfully. A January 2006 fire occurred when a mill used to grind metal hydride particles was removed from an argon-inerted glove box. Although the mill had been wiped down several times prior to removal from the glove box, some metal hydride particles remained in the mill bolt holes. The residual hydride subsequently reacted with air and isopropyl alcohol used to clean the mill. The fire was extinguished with MET-L-X™, but not before the flash fire caused first and second degree burns to the face, head, and hand of one of the workers.

## Hydride Chemical Reactivity Screening

Before attempting to use any fire suppression agent on a metal hydride, it is crucial to anticipate any adverse chemical reactions between the hydride and the agent. One convenient tool for screening for chemical reactivity hazards is the Chemical Reactivity Worksheet developed by the National Oceanic and Atmospheric Administration (NOAA) and available free for downloading from a NOAA Web site. The Chemical Reactivity Worksheet has over 6,000 chemicals in its database, including many metal hydrides.

As an example, one of the metal hydrides in the Chemical Reactivity Worksheet is lithium aluminum hydride, also called lithium tetrahydroaluminate (CAS number 16853-85-3) or lithium alanate. According to the Reactivity Worksheet, this hydride is both air reactive and violently water reactive, thus ruling out any aqueous suppression agent. The Reactivity Worksheet has also been used to determine whether there would be any adverse chemical reaction if the four generic metal fire suppression agents listed in Table 1 were mixed with lithium alanate. The results indicated that three of the agents could undergo an exothermic reaction with these hydrides and produce gaseous reaction products that could pressurize an enclosure. The agent that does not cause any reaction is sodium chloride. The same result was obtained with sodium hydride, sodium alanate, lithium borohydride and additions of the four generic suppression agents, i.e. only sodium chloride produced no reaction at all. None of the agents appeared to produce violent reactions with these metal hydrides.

It would be useful and easy to do similar reactivity screening evaluations for the various other metal hydrides of interest to the hydrogen storage program. It would also be convenient to use the Chemical Reactivity Worksheet or a similar screening tool to determine any possible adverse reactions that might be associated with new candidate suppression agents, and with the additives to the existing Class D suppression agents.

## Sodium Hydride Fire Suppression Tests

Fluegeman et al. [10] describe a sodium hydride fire test program conducted to assess the relative effectiveness of five suppression agents in both extinguishing the fire and preventing reignitions upon disturbing the resulting pile of agent and hydride. The five agents tested were potassium bicarbonate (Purple K™), potassium carbonate, calcium carbonate, Met-L-X™, and damp sand. The authors state that Lith-X™ (the graphite based agent certified for lithium based metal fires) was not used in the fire testing because preliminary tests indicated that the graphite application procedure was “very messy” and excess agent “contaminated everything within a fair radius of the experiment.”



It is interesting to note that only one of the five agents in the full testing (sodium chloride based Met-L-X<sup>TM</sup>) is included in the table of agents for alkali metal fires in NFPA 484 and in Table 1 here. NFPA 484 emphasizes the need to use dry sand, rather than the damp sand used by Fluegeman et al.

The sodium hydride fire tests were conducted with 25 to 500 grams of hydride in a 3 liter steel bowl. Thermocouples were used to record the temperature in the center and on the surface of the hydride as it burned. The fires were ignited by remotely adding water to the hydride in the bowl. After several minutes of free burning, the suppression agent was dispensed into the bowl to an approximate depth of 1 inch. After the fire was suppressed, the bed was disturbed to determine if it would re-ignite.

According to the Fluegeman et al. paper [10], all five suppression agents successfully extinguished the sodium hydride fires. Upon disturbing the agent-hydride mix, re-ignition occurred with all five agents. This re-ignition demonstrates that the agents function primarily by oxygen exclusion from the hydride. After the fires re-ignited, Fluegeman et al. applied liquid nitrogen to the fire bed. The liquid nitrogen application extinguished the second fire and prevented further re-ignition with Met-L-X<sup>TM</sup> and damp sand, but not with the other three agents.

Based on these tests, Fluegeman et al. developed a Detailed Action Plan for responding to any more sodium hydride fires in Eli Lilly and Company production facilities. The Plan specifies that the sodium hydride spill/fire be contained or smothered by application of damp fill sand (4 to 6% moisture content). The smothered fire is then to be cooled with liquid nitrogen while the interior of the pile temperature is monitored. The smothered and nitrogen cooled hydride is then to be transferred into a metal drum that is further inerted with additional liquid nitrogen. The authors conclude their paper by stating that use of damp sand is being explored for other metal fires, such as magnesium. Since this proposed use of damp sand to extinguish certain metal and hydride fires is not consistent with established recommendations in the fire protection community, its use should only be adapted after extensive testing to verify its effective and safe implementation.

## **Recommended Reactivity and Fire Test Program**

In view of the wide variety of metal hydrides being evaluated for hydrogen storage applications, and the wide assortment of potential fire suppression agents, additional material compatibility screening and fire testing are needed. The Hydrogen Safety Panel recommends the following three-task research program be funded. The general objective of the program would be to determine effective fire suppression agents for the various chemical groups of metal hydrides being considered for hydrogen storage applications, i.e. for representative magnesium based hydrides, sodium alanates, lithium and potassium alanates, lithium nitrides, lithium boro- and beryllium hydrides, and intermetallic compounds forming a combination of a stable hydride and an unstable hydride [1].

Task 1 of the proposed program would be chemical compatibility screening using both reactivity hazard literature and software, such as the NOAA Chemical Reactivity Worksheet. The screening would involve one or more hydrides and un-hydrated metals from each of the candidate chemical groups in combination with each of the combustible metal fire suppression agents shown in Table 1 (plus additives identified in agent supplier Material Safety Data Sheets) and the accompanying discussion above. Results would indicate which combinations of metal hydrides and suppression agents/additives are known to be compatible, which combinations produce potentially dangerous reactions, and which combinations have unknown reactivity.

Task 2 would be devoted to the specific agent-metal hydride combinations for which the Task 1 chemical compatibility screening produces inconclusive or ambiguous results. Laboratory reactivity hazard tests should be implemented for these combinations. The particular reactivity hazard tests include Differential Scanning Calorimetry and other special tests described in Center for Chemical Process Safety (CCPS) guideline publications on reactivity screening and testing [13, 14]. Other tests that characterize reactivity kinetics and associated hazards should also be considered including any pertinent recent developments from the CCPS Reactivity Management Forum.

Task 3 would entail fire suppression testing with representative combinations of suppression agents and metal hydrides that appear to be compatible per the results of Tasks 1 and 2. The particular hydrides to be tested in Task 3 will also depend on which hydrides appear to be most promising in achieving DOE Hydrogen Storage Program goals. The Task 3 tests should also include the use of dry and damp sand as non-commercial suppression agents since sand is almost omnipresent in chemical laboratories handling metal hydrides. Fire testing with compatible agents should start with small-scale, carefully controlled, laboratory tests with less than 1 kg of the hydride and the particulate metal itself. Successful candidate agents should then be tested in larger scale, probably on a scale currently used for certification testing [4]. However, the pyrophoric nature and chemical reactivity of the metal hydrides, as well as the results of the small-scale tests, need to be considered before deciding upon large-scale fire test procedures and equipment.

## References

1. Sakintuna B, Lamari-Darkrim, F., Hirscher, M., and Dogan, B., "Metal hydride materials for solid hydrogen storage: A review," *Int J Hydrogen Energy* (2006), doi: 10.1016/j.ijhydene.2006.11.022
2. Latroche, M., "Structural and thermodynamic properties of metallic hydrides used for energy storage," *Journal of Physics and Chemistry of Solids*, v. 65, pp. 517–522, (2004).
3. Nelson, R., "Extinguishing Agents and Application Techniques for Combustible Metal Fires," *NFPA Handbook*, Chapter 11-7, National Fire Protection Association, 2003.
4. U.L. 711, "Rating and Testing of Fire Extinguishers," Underwriters Laboratories, Inc. 6<sup>th</sup> Edition, 2002.
5. NFPA 484, "Standard for Combustible Metals," National Fire Protection Association, 2006.
6. Wilson, C., Tapscott, R., and Zallen, D., "Extinguishing Agent for Magnesium Fire: Phase II – Reformulation and Origination of Extinguishing Agents," New Mexico Engineering and Research Institute Report TA3-20 prepared for Air Force Engineering and Services Center, Tyndall Air Force Base, 1985.
7. Lee, M., and Tapscott, R., "Handheld Delivery System for Modified Boron-Type Fire Extinguishing Agent," Air Force Engineering and Services Center Engineering Services Laboratory Report ESL-TR-88-46, 1993.
8. "Evaluation of a New Liquid Fire-Extinguishing Agent for Combustible Metal Fires," Federal Aviation Administration Report DOT/FAA/AR/TN06-26, November 2006.

9. Wilson, C., Plugge, M., and Zallen, D., "Extinguishing Agent for Magnesium Fire: Phase 1 – Evaluation of Existing Agents," New Mexico Engineering and Research Institute Report prepared for Air Force Engineering and Services Center, Tyndall Air Force Base, 1983.
10. Fluegeman, C., Hilton, T., Moder, K., and Stankovich, R. "Development of Detailed Action Plans in the Event of a Sodium Hydride Spill/Fire," Process Safety Progress, vol 24, pp. 86-90, 2005.
11. Lynch, F., Memo to ISO TC 197 WG10 Hydride Working Group, January 2005.
12. "Operating Experience Summary," Department of Energy Office of Environmental Health and Safety OE Summary 2006-3, April 2006.
13. Guidelines for Safe Storage and Handling of Reactive Materials, Center for Chemical Process Safety, AIChE, 1995.
14. Johnson, R., Rudy, S., and Unwin, S., Essential Practices for Managing Chemical Reactivity Hazards, Center for Chemical Process Safety, AIChE, 2003.

Respectfully submitted,

Robert G. Zalosh (principal author)