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Development of Performance-Based Protection Standards from Recent Research on the Hazards of Silane Releases

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Abstract

Factory Mutual Research (FMR) is an FM Global affiliate charged with providing advanced property loss prevention research and engineering support for the benefit of the customers of FM Global and the public at large. This goal is achieved through a combination of internally-sponsored activities and contract work for industrial or government clients. Targeted research is undertaken when available knowledge is found to be inadequate to satisfactorily address the situation for which protection needs to be devised. This was perceived to be the case of hazards from accidental silane leaks encountered in semiconductor manufacturing and other industries. In particular, existing design recommendations for the protection of ventilated enclosures were found to set requirements based on outdated and, in some instances, misinterpreted data. Extensive research was carried out by FMR (under partial support from SEMATECH) to develop improved protection guidelines for silane handling systems through enhanced understanding of the behavior of releases of this pyrophoric gas. The work has addressed and generated new information on three aspects of the problem: the prompt ignition behavior of silane; the reactivity characteristics of quiescent silane/air mixtures; and the rates of reaction of silane leaked into enclosures with and without explosion venting, in the presence of ventilation air flow. After developing correlations and generalizations of the test data with the assistance of models, this new knowledge was used as the foundation for a set of performance-based protection guidelines for implementation by FM Global loss prevention consultants worldwide. Because of their departure from rigid prescriptions, these guidelines provide the designer with the ability to evaluate different protection solutions and select the one that is most appropriate for the particular situation of interest.

Organizational Background

In its role as an FM Global affiliate, Factory Mutual Research (FMR) is charged with the mission "to develop technical tools and information in the area of property loss control based on sound, validated, fundamental and applied scientific research and advanced engineering applications". This is done through research, third-party equipment testing and standards development activities. Solutions to specific protection problems are usually devised for the immediate benefit of customers of FM Global. More generally applicable results are made available to the public at large through several vehicles, which include publications in technical journals, meeting presentations, and participation in consensus standard committees. The overall goal of advancing loss prevention technology is achieved by combining internally-sponsored projects with contract work for industrial or government clients.

Technical activities in the FMR Research Division* cover a broad range, which includes:

- Fire protection: Sprinklers and fine sprays, foams, detection systems, commodity classification.
- Materials behavior: Flammability issues, explosions, smoke production, corrosion/aging.
- Structural response: Dynamic response, structural loads (wind, fire, flood, seismic…), probabilistic impact studies.
- Risk engineering: Industrial risk exposure, engineering systems reliability, electrical ignition safeguards.

Specific areas are chosen as suitable targets for research if the available knowledge is judged to be insufficient to satisfactorily address the situation for which protection is needed. Depending on the circumstances, an assessment of inadequacy of existing guidelines can be triggered by loss history or by considerations based on business exposure. While it is often a difficult task, improvements in FM Global protection standards are also sought proactively by identifying those changes in industrial practice and processes that have a potentially negative impact on safety. The typical technical approach involves a combination of experimentation, often at realistic scales, and modeling, with the latter generally being used to extrapolate the experimental results to conditions that are different from those of the tests.

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* The Research Division is one of three units in which Factory Mutual Research is organized. The other two are the Approvals and the Standards Divisions. They are respectively involved in third-party testing of equipment and in the development of the FM Global Property Loss Prevention Data Sheets.

Advances from FMR Explosion Research

A detailed review of the advances made by FMR in the area of property loss control is well beyond the scope of this paper, whose main emphasis is intended to be on the silane work. However, the progress made in two other explosion problems is also discussed briefly, as an illustration of the range covered in this technical area. The examples used are: dust explosion vent sizing and explosion hazard from flammable liquid spills.

Dust Explosion Vent Sizing

In terms of accomplishments, the work done on dust explosions represents one of the more mature demonstrations of FMR's involvement in this type of protection issues. The results of several years of research have led to the development of improved vent sizing guidelines for use by FM Global loss prevention consultants[1]. In recognition of the advances that this FMR technology offers compared to alternative methods, the NFPA 68 Committee has recently voted to adopt it as the basis for the revision of the part of the guideline[2] which deals with dusts. This is an example of a situation where judicious use of modeling concepts (developed at FMR) was combined with available data (mostly generated outside FMR) to yield significant advances in several different aspects of dust explosion protection.

The progress made falls in three general categories:

- Generalized vent sizing curve – The correlation is based on the prediction of a model, validated by comparison with experimental data. Unlike numerical fits, use of a curve and correlation parameters that are theoretically based allows for vent sizing beyond the range of conditions of the underlying experiments.
- Correction of errors in existing guidelines – Examples in this category are: the treatment of the effect of vent ducts, scaling of vent area requirements in partial volume deflagrations (PVDs), and correlation for the duration of a vented explosion.
- Solutions for problems not previously addressed – Effects of vent panel inertia, venting of equipment inside buildings, flame reach into clean connecting ductwork.

Explosion Hazard from Flammable Liquid Spills

Existing standards lack guidelines to deal with the situation where the explosive mixture occupies only a fraction of the available volume. This situation arises, for example, in the case where the explosive mixture is formed by the vaporization of a flammable liquid spilled on the ground, or by the slow and localized leak of a heavy gas. While the expectations is that venting requirements should be less than those of the corresponding full-volume case, the outstanding engineering question is by how much. This problem is the object of an FMR project currently in progress. Testing has already been completed to determine the venting requirements of stratified mixtures[3]. These experiments have provided new information on the mechanism by which the portion of the fuel layer with concentrations above the upper explosive limit (UEL) reacts in a convective mode behind the traditional premixed flame. Interpretation of these results has required the modification of an existing explosion model, which can simulate this dual mode combustion.

This work is now being supplemented by the development of a calculation method to predict the evolution of vapors from the spill and their dispersion above the ground. Coupling of this solution to the already developed explosion model will allow for a fully predictive method, which will be able to take into account the details of the postulated accidental spill. Scenario-specific evaluations are not done by existing methods, which define varying degrees of severity of the hazard based on the size of the spill and on certain properties of the spilled material.

Silane Leaks in Ventilated Enclosures

Present Regulatory Requirements

Silane is a gas used in semiconductor manufacturing and other industries (liquid crystal displays, glass making). Its pyrophoric nature presents safety issues in the case of accidental releases. Protection guidelines applicable to the case of indoor storage and dispensing of silane in ventilated enclosures can be found in articles 51 and 80 of the Uniform Fire Code[4] and in UFC Standard 80-1[5]. These documents include provisions for ventilation inside the enclosures, as well as for the control of the silane flow in the event of a supply line rupture.

The ventilation requirements are presented in terms of an average velocity of not less than 200 lfpm (1 m/s) across access ports and unwelded fittings and connections of the piping system, with a minimum velocity of 150 lfpm (0.75 m/s) at any point with external access. Flow control requirements include the use at the gas cylinder of restrictive flow orifices (RFOs) not exceeding 0.010 in. (0.25 mm) in diameter. In addition, the standard requires excess flow control valves downstream of the RFO, to limit the outflow of gas in the event of a line rupture. These design criteria are applied to any enclosure, regardless of its size, and do not take into account the supply line size and pressure.

While the development of these recommendations is only partially documented, it appears to have been based on empirical interpretations of tests carried out in volumes of the order of that of three-cylinder gas cabinets. Furthermore, the prescription of the minimum ventilation level as a velocity has been justified, at least in part, by the argument that the presence of air motion is required to promote prompt ignition of the release. An additional unstated goal, even though not quantifiable in terms of a value for the ventilation velocity, is to prevent any significant build-up of silane in the enclosure.

These prescriptive requirements for both ventilation and flow control have also appeared as recommendations for silane gas cabinets in earlier issues of the FM Global's loss prevention guideline on semiconductor fabrication facilities. The current edition of this guideline[6], however, fully incorporates the conclusions reached after the recent FMR studies, which have been documented in reports[7,8] and publications[9,10]. The cited reports also contain evaluations and analyses of the data from work performed by organizations other than FMR. The interested reader is referred to those documents for the details.

FMR Research on Silane

Motivation for the Research

The problem with the prescriptions in the UFC standard is that they have been based on limited understanding of silane. Furthermore, the form chosen for the presentation of the recommendations is strongly suggestive that their applicability is at best limited to systems whose geometry is very similar to that of the facilities used for the experiments. This presents an obvious difficulty, if changing conditions in the storage, distribution and utilization of silane by industry require the evaluation of significantly different systems. It became apparent that effort should be expended to better understand the fundamental behavior of silane leaks, with the ultimate goal to develop improved design guidelines based on such understanding.

The approach taken in the FMR work has been to plan and carry out tests that would address the individual aspects of the phenomenology of silane releases. More specifically, the ignition characteristics were investigated separately from the rate of energy production by the material as it reacted with air. Full details on the results of this work are provided in the cited references[7-10]. The following sections will present an overview of the main conclusions.

Possible Ignition Types

Ignition behavior represents one of the main questions arising in connection with the release of a pyrophoric material. The fact that a substance is labeled as pyrophoric means that its autoignition temperature is lower than that of the ambient. In practice, however, prompt ignition of the release is not always guaranteed. In the case of silane, instances have been reported in the literature of situations in which a release has remained initially unreacted, only to undergo a delayed ignition with catastrophic consequences, several seconds after interruption of the release. Events of this type have been taken by some as evidence of the "random" and "unpredictable" behavior of silane. The fact is that careful studies can clarify the reasons for the apparent randomness. Such clarification has been one of the outcomes of FMR's research on the problem.

The research carried out at FMR has identified five possible ignition modes:

- Prompt ignition;
- Ignition during flow decay;
- Ignition at shutoff;
- Piloted ignition; and
- Bulk autoignition.

Prompt ignition represents the expected and, from a safety perspective, the most desirable manifestation of the pyrophoric nature of the material. The most destructive case, to be avoided at all cost, is the one involving bulk autoignition. This situation can arise if the release remains initially unreacted and the concentration of the resulting mixture of silane with air exceeds a certain value, making the mixture metastable. This is the most likely scenario to have been involved in the catastrophic events observed in some of the testing reported in the literature.

Despite much effort devoted to this aspect of the problem, attempts at defining the conditions for prompt ignition of silane releases from the sudden failure of a pressurized line have been largely unsuccessful. In general, prompt ignition is found to be more likely when the initial pressure of the line is low (50 psi [3.4 bar] or less) and the line diameter is not too small. Unfortunately, the ignition characteristics display a statistical behavior over much of the range of conditions of practical interest, preventing the establishment of clear regimes where one type of behavior can be assured. In terms of safety assessment procedures, this result has led to the conclusion that accidental release scenarios should be evaluated, and confirmed to lead to acceptable consequences, under all possible ignitions conditions. In practice, prompt ignition and ignition and shutoff are the two scenarios that are relevant to safety evaluations.

Reactivity of Silane/Air Mixtures

The characterization of the reactivity of silane/air mixtures probably represents the most significant result from the research carried out at FMR. Previous work had failed to explore this important aspect, probably because of the experimental difficulties associated with the generation of unreacted silane/air mixtures. This was overcome by developing a technique that allowed for the reliable blending of silane and air in a laboratory-scale vessel in all desired proportions. Through this method, which uses high-speed jets and nitrogen pads to prevent ignition either at the start or at the end of the injection process, it was possible to generate mixtures with silane concentrations up to 35% (by volume).

The details of this work have been reported in previous publications[9,10]. Only selected highlights of the conclusions are repeated here. There are three possibilities regarding the reactivity of silane/air mixtures at ambient (pressure and temperature) conditions. They depend on the concentration of silane, X_f, as follows:

- $X_f < 1.4\%$ Non-flammable mixtures;
- $1.4\% < X_f < \sim 4.1\%$ Flammable and stable mixtures; and
- $X_f > \sim 4.5\%$ Metastable mixtures.

While the identification of a lower explosive limit (LEL) of about 1.4% confirms a result already available in the literature, the other two sets of conditions represent a new finding. In the case of stable flammable mixtures, measurements of the fundamental burning velocity yielded values as high as 5 m/s (16.4 ft/s) at a silane concentration just over 4%. A point of perspective for the level of reactivity implied by this figure can be gained by noting that the burning velocity of a worst-case (near stoichiometric) hydrogen/air mixture is 3 m/s (9.8 ft/s). Furthermore, this level of silane reactivity is reached at a fuel/air ratio which, for most other systems, corresponds to the LEL (the stoichiometric concentration of silane in air is 9.5%).

At concentrations of about 4.5% or greater, the mixtures were found to be metastable in that they ignited spontaneously after a certain delay. The delay is shorter, the higher the concentration of silane. For these ignition events, a burning velocity could not be defined, as the mixture appeared to undergo ignition in bulk throughout the volume. Experimentally, this manifested itself with the achievement of the full explosion pressure in the 5.1-liter (0.18-ft^3) vessel used for the tests in a fraction of a millisecond. In an actual accident, this event should be expected to be extremely destructive and one against which the protection provided by venting would be totally ineffective.

Rate of Reaction of Silane Releases

As already indicated, situations that can lead to the generation of a significant volume of unreacted flammable mixture are to be avoided, due to the high reactivity of the resulting system. In terms of the evaluation of the consequences from accidental releases, cases involving piloted ignition and ignition at shutoff are the ones which are practically relevant. The severity of the accident is a function of the rate at which energy is generated during these transient events. This rate of energy release was measured under both ignition scenarios and correlations were developed to extend these results to conditions different from those of the tests. The interpretation of the data was carried out with the assistance of models of explosions and other analytical techniques, resulting in a methodology to predict the pressure development produced by the release in a ventilated enclosure.

Improved FM Global Guidelines

Having learned from the research how to estimate the consequences of different accident scenarios, the next logical step was to develop design guidelines that would ensure that the consequences would not exceed an acceptable level for the conditions of the situation of interest. As a result, ventilation requirements and sizing of RFOs become a function of the characteristics of the system and are no longer prescribed *a priori*. The recommendations currently implemented by FM Global loss prevention consultants address the following concerns:

- Bulk Autoignition Hazard from Initial Release -- Limit the maximum average concentration in the enclosure, resulting from the release of the silane inventory, to a value of 1%. This means that the estimated standard volume of the silane inventory should be less than 1:100 times the volume of the enclosed space. A higher value for this critical volume ratio is allowed by a recently developed correlation for the discharge time of pressurized lines. When combined with an analysis of the mixing in the enclosure, it provides a more accurate estimate of the average silane concentration than the assumption of instantaneous mixing.
- Minimum Ventilation Requirement -- The average silane concentration resulting from the mixing of the RFO-controlled flow with the ventilation air should not exceed 0.4%. The air ventilation rate should be set at least equal to 250 times the silane release rate produced by the supply pressure/RFO size combination.
- Pressure Development -- Sufficient vent area should be provided to prevent the maximum pressure developed by silane reaction, either for prompt ignition or for ignition at shutoff, from

exceeding the maximum value allowed for the enclosure. In the absence of other information, a value of 1 psig (70 mbar) is recommended.

- Ventilation Design -- The ventilation air flow should be arranged in such a way to prevent the formation of dead zones near likely leakage sites.

The basic philosophy behind these recommendations is that their implementation will not completely eliminate physical damage in the case of an accidental silane release. An ignition event, for example, could still be sufficiently strong to cause the doors of a gas cabinet to blow open, requiring replacement of the cabinet. Compliance with the recommended guidelines, however, will keep the physical damage localized and prevent the occurrence of the violent ignitions which have occurred in some accidents.

Conclusions

The data and analytical generalizations, developed in the course of the research on silane carried out at FMR, have greatly increased our level of understanding of the quantitative behavior of reactive systems involving this pyrophoric material. As a result, sufficient knowledge has become available to support a new method for the evaluation of the potential hazards from silane releases that takes into account the details of the system involved. This assessment method replaces existing guidelines that failed to capture the essence of the hazard and were, at best, adequate to deal only with a narrow range of situations. The approach taken in addressing this question is similar to that followed in dealing with other explosion problems, in that the solution of technical issues with safety implication has been escalated to the level that is necessary to develop sound engineering answers.

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