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Preventing chemical product failure

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PREVENTING CHEMICAL PRODUCT FAILURE

by

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ABSTRACT

The purpose of this thesis is to demonstrate a research methodology to prevent chemical product failures. This methodology extends the risk in early design (RED) method for prevention of failure in electromechanical products to include products with chemical subsystems. Inclusion of this domain is demanded by the ever-growing semiconductor and energy industries. The RED method was extended by first identifying principal chemical failure modes and adding them to the failure mode taxonomy. The RED database was then augmented with historical failures of products that included chemical subsystems. Finally, the extension was validated with a case study of a fuel cell.

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TABLE OF CONTENTS

LIST OF TABLES

1. INTRODUCTION

This research presents a methodology to analyze risk during the conceptual design stage for products with substantial chemical components. This work is motivated by the continuing growth of the semiconductor and energy industries.

Safety, performance, and reliability are principal concerns of any industry. These concerns are particularly important to industries that rely on chemicals or chemical processes because most chemical-human interaction is undesirable. Most process chemicals have a negative impact on the human biochemical system, and many are documented carcinogens or toxins; therefore, accidents involving these products are particularly deadly. The Bhopal disaster is a dramatic example. This incident took place at a Union Carbide pesticide plant in the Indian city of Bhopal, Madhya Pradesh, on December 3rd, 1984. The plant released an estimated 42 tons of toxic methyl isocyanate (MIC) gas, exposing more than 500,000 people to MIC and other chemicals. The first official death toll was 2,259. The government of Madhya Pradesh later confirmed that total of 8,000 to 10,000 died within 72 hours, and 25,000 have since died from gas-related diseases (Broughton, 2005). To address these concerns, the industry is currently pushing to include safety and risk assessment in the early stages of conceptual design (Uder, Stone and Tumer, 2004). Performance and safety problems can be eliminated with a thorough understanding of potential failure modes and their causes. Such an understanding can be gained from an understanding of prior product failures.

Past failures involving chemicals or chemical processes can be efficiently cataloged using the RED method. Relevant information includes a description of the failure, as well as its causes and effects. Such information is available from a variety of sources such as academic journals (e.g. Physical Chemistry Chemical Physics journal, American Physical Society, and Journal of Power Sources), The Mary K. O'Connor Process Safety Center, and the Sandia National Laboratories web page.

To make use of the information available from historical failures during conceptual product design, the RED method links failures need to product function (Grantham Lough, Stone and Tumer, 2009).The use of function models improves the ability to explore potential risk early in the conceptual design, independent of form and specific solutions. Once the information has been stored in the RED knowledge base, a risk analysis can be performed quickly, and without great expense, even by inexperienced designers.

A standard taxonomy is necessary to catalogue historical failures and to prevent ambiguity in describing them. Such a taxonomy provides designers with a repeatable and reusable vocabulary to work with (Tumer and Stone, 2003). The failure mode taxonomy developed by Tumer and Stone does not presently account for chemical failure modes. This research has developed a chemical failure mode addendum to the present failure mode taxonomy. This modification will allow novice designers and engineers to quickly generate chemical design risk by linking historical product failures to functionality.

2. RELATED WORK

2.1. CURRENT PRACTICES FOR RISK INVOLVING CHEMICAL FAILURE

Current techniques to evaluate the potential for chemical failure include failure modes and effects analysis (FMEA), fault tree analysis (FTA) and hazard and operability studies (HAZOPS).

FMEA is a specific methodology to evaluate a system, design, process, or service for possible failure mechanisms (Price, 1996). It is particularly suited for analyzing potential reliability problems early in the development cycle where such issues are more easily overcome. There are several types of FMEAs; some are used much more often than others. System FMEA focuses on global system functions; design FMEA focuses on components and subsystems, and process FMEA focuses on manufacturing and assembly processes.

One benefit of FMEA is early identification and elimination of potential product and process failure modes. This method prioritizes product and process deficiencies and captures engineering and organization knowledge. FMEA emphasizes problem prevention and documents risks and the actions taken to mitigate them (Price, 1996).

Unfortunately, FMEAs are cumbersome and time consuming. Bluvband and Zilberberg (1998) have pointed out that FMEAs identify too many relationships between failure modes, effects, causes, current controls, and recommended actions. According to Montgomery et al. (1996), the several entries in the FMEA worksheet make FMEA reports difficult to understand, produce, and maintain. In addition, FMEAs require detailed knowledge of products and processes, and thus, the novice engineer cannot easily use them. Another shortcoming of FMEAs is that they require engineers and designers to estimates occurrence, severity, and detection based on experience. Montgomery (1996) noted that the brainstorming process for FMEA is lengthy, time consuming, and, prone error.

FTA is a logical, structured process that can identify potential causes of system failure before the failures actually occur. Fault trees are powerful design tools that can help ensure that product performance objectives are met. (Fault Tree Analysis, 2009)

FTA permits identification of possible system reliability or safety problems at design time. FTA can assess system reliability or safety during operation and improve understanding of a system. It identifies components that may require testing or more rigorous scrutiny for quality assurance. They help identify root causes of equipment failures (Henley and Kumamoto, 1981).

Although fault trees may reveal human error, they do little to determine the underlying cause. FTA requires detailed knowledge of system design, construction and operation. They are not suitable for assessing normal operations and may become very large and complex (Henley and Kumamoto, 1981). Significant training and experience are necessary to use this technique properly, and even once the technique has been mastered, application remains time consuming. FTA is not practical for systems with many safety-critical failures.

HAZOPS have been used over approximately four decades for identifying potential hazards and operability problems caused by deviations from the design intent of both new and existing process plants (Tyler, Crawley and Preston, 2008). The HAZOPS procedure requires a full description of a process and systematic questioning of every part of the system to determine how deviations from the design intent can arise. Once deviations are identified, an assessment is made to determine whether the deviations and their consequences can have a negative effect on the safe and efficient operation of the plant. If necessary, action is then taken to remedy the situation. This is the method followed by the Mary Kay O'Connor Process Safety Center (Mary Kay O'Connor Process Safety Center, 2009).

The HAZOPS process is a systematic examination and therefore very thorough. The team approach to HAZOPS makes the process multidisciplinary; allowing an in-depth study of risk (Kletz, 2006) The HAZOPS team relies on operational experience and historical performance. The process covers safety as well as operations and may indicate solutions to the problems identified. HAZOPS consider operational procedures and human errors.

A disadvantage of HAZOPS is their focus on single events rather than combinations of possible events. Their reliance on guide words allows HAZOPS to overlook some hazards not related to those words. From an engineering standpoint, HAZOPS are qualitative; they do not attempt to quantify either the occurrence or severity of hazards (Neogy, et al., 1996). In addition, extensive training is essential for optimum results, especially for the facilitator. HAZOPS are typically time consuming and thus expensive.

All the methods currently available have three drawbacks: First they require experienced designers or engineers. Second, they are time consuming. Third, their results rely on the assumptions of designers and engineers regarding severity and occurrence. The methodology presented here addresses these issues by allowing the novice engineers and designers to quickly and repeatedly analyze risk for new product or process involving chemical components by drawing from historical failure data and using consistent terminology. This method is based on RED method developed by Grantham Lough (Grantham Lough, Stone and Tumer, 2009).

2.2 THE RISK IN EARLY DESIGN (RED) METHOD

The RED method maps a product's functions to potential failures and determines the likelihood, and consequence of failure based on relevant cataloged historical failure information. Table 2.1 shows the consequence and likelihood calculations used in RED. Equation 1 yields the function-failure mode matrix using cataloged historical failure modes:

$$\mathbf{EC \times CF = EF\ (1)} \qquad \text{Equation (1)}$$

Where EC represents the function-component matrix, CF represents the component-failure matrix and EF is the function-failure matrix.

Efforts to examine multiple electromechanical products led to the development of some basic heuristics that assume a fully populated database of related historical failures. The categories in the RED heuristics are described below (Grantham Lough, Stone and Tumer, 2009)

System Level: A stage of design that considers the product as a whole.

Subsystem Level: A stage of design that considers subsystems or smaller pieces of the product.

Human centric product: Product requiring human input for its operation.

Unmanned product: Product requiring no direct human interaction during operation.

The summary of the heuristics is presented in Table 2.2.

RED uses a matrix-based risk assessment to identify specific function-failure mode combinations that have occurred historically and to quantify that information into consequence and likelihood (Grantham Lough, Stone and Tumer, 2009). Since this method employs documented historical function-failure combinations, novice designers and engineers can implement it to ascertain potential risks. Also, the historical failures catalogued in RED remove personal bias by providing a database with which to determine consequence and likelihood values. (Grantham Lough, Stone and Tumer, 2009). RED can even be applied in the early conceptual phases of product design. Avoiding risks at this early stage is less costly because the physical form has not yet been determined

RED manipulates risks so that the risks are compatible with the risk fever chart (Office of the Under Secretary of Defense, 1999). The RED method is maps risks so that both consequence and likelihood have integer values ranging from one to five. The risk fever chart plots consequence values against the likelihood of values. It is easy to decipher because risk elements are classified into three categories: high-risk, moderate-risk, and low-risk, each represented by a different color. The fever chart is populated with risk data produced by the RED method and plotted according to values for consequence and likelihood taken from the appropriate mapping matrices (Grantham Lough, Stone and Tumer, 2009).

Table 2.1. RED Likelihood and Consequence Mapping Summary (Grantham Lough, Stone and Tumer, 2009)

	L1-Prod	L2-Agg	C1-Max	C2-Ave Aug
	$l_{ij} = \text{int}\left\{5\frac{ef_{prod_{ij}}}{\max\limits_{\substack{1\le i\le n\\ 1\le j\le m}}(ef_{prod_{ij}})}\right\}$ (2)	$l_{ij} = \text{int}\left\{5\frac{ef_{prod_{ij}}}{\max\limits_{\substack{1\le i\le n\\ 1\le j\le m}}(ef_{agg_{ij}})}\right\}$ (3)	$c_{ik} = \max\limits_{1\le j\le m}(ec_{ij}cf'_{jk})$ (4)	$c_{ik} = \text{int}\left(\frac{1}{h}\sum\limits_{1\le j\le m} ec_{ij}cf'_{jk}\right)$ (5)
Pros	▪ Provides hierarchy of probable product specific risks ▪ Conservative estimate of risk probability ▪ Reduced dependency on data concentration of failure database	▪ Risk likelihoods are relative to all recorded failure occurrences ▪ Does not overestimate risk likelihood for low occurrence failures in database	▪ Conservative risk estimate ▪ Focuses designer's attention directly to severe failures	▪ Average risk estimate ▪ Not dependent on a single severe failure occurrence ▪ Considers only relevant function-component-failure combinations
Cons	▪ May provide too much attention to a low occurrence failure	▪ Can downplay risks with low failure occurrence in database ▪ Risk likelihood is directly related to the number and distribution of all recorded failures in the database	▪ A single severe failure will dominate the risk analysis regardless of occurrences of lesser severity ▪ Single severity value dependence prevents risk value from representing all recorded failures	▪ Severity of a failure can be diminished with many occurrences of a less severe case ▪ Highly dependent on the combination of number of recorded failures and their severity values

Table 2.2. RED Heuristics (Grantham Lough, Stone and Tumer, 2009)

		Product Type	
		Human Centric	Unmanned
Design Level	System Level	L2, C1	L2, C2
	Subsystem Level	L1, C1	L1, C2

Grantham Lough, Stone, and Tumer (2009) illustrate RED risk assessment performed on a functional model of a thermal control subsystem. Thousands of anomaly reports for various missions and subsystems are contained in the problem/failure reporting (P/FR) database at Jet Propulsion Laboratory (Grantham Lough, Stone and Tumer, 2009). A Thermal Control Subsystem is among these. From the functional model of the subsystem, the functions were collected and used to select entries in the EC matrix. Using this EC matrix thus formed, the product-specific function-failure (EFprod) matrix was determined. EFprod lists only function-failure pairings that are relevant to the particular product. Next, the risk likelihood and consequence calculations were performed using the equations as shown in Table 2.1.using EC matrix and component-failure severity (CF') matrix. The L1 likelihood mapping is used as a risk assessment in the subsystem design level, whereas L2 mapping is used at the system design level. The C1 consequence mapping is used in risk assessments that involve human related products, whereas C2 mapping is better suited for unmanned products (Grantham Lough, Stone and Tumer, 2009).The pros and cons for each of these mappings are shown in Table 2.1. The risk fever chart from the four RED risk assessments performed on thermal control subsystem risk assessments are shown in Table 2.3. All the risk assessments produced 73 risk elements. Some sample risk elements from Thermal Control Subsystem RED risk assessments are shown in Table 2.4. The risk elements contain specific functions at risk for a specific failure mode, with a consequence and likelihood combination.

Table 2.3. Thermal Control Subsystem RED Risk Assessments (Grantham Lough, Stone and Tumer, 2009)

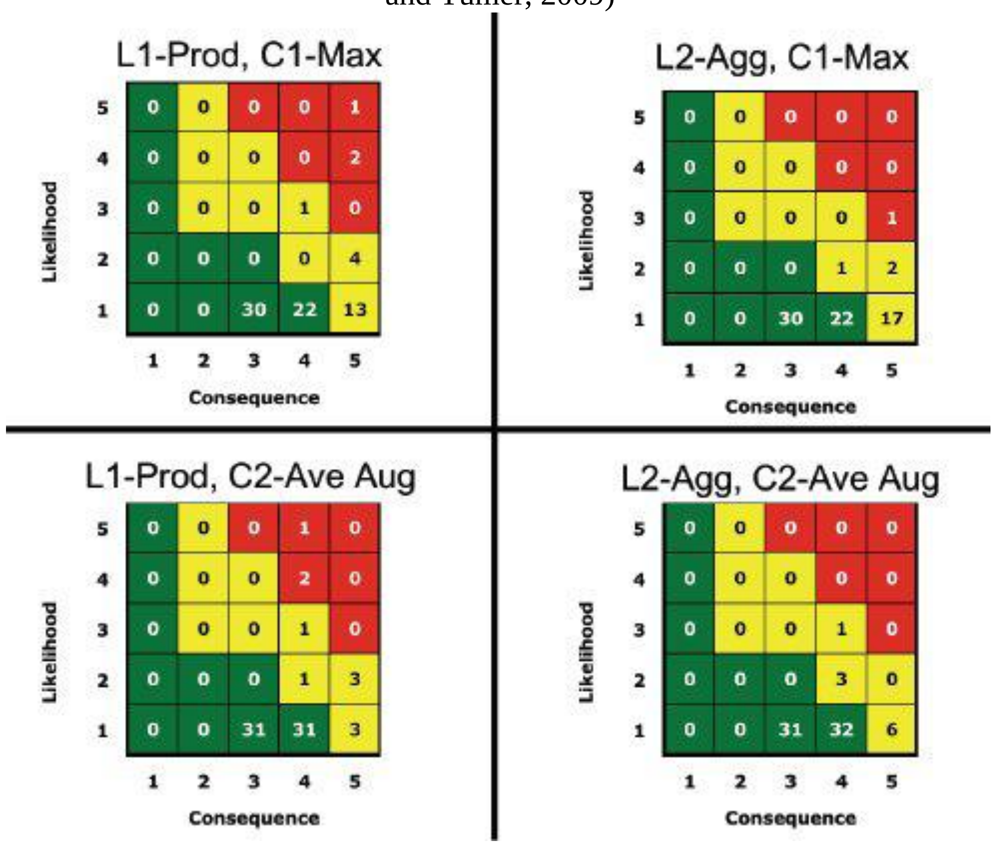


Table 2.4. Sample Risk Elements from Thermal Control Subsystem RED Risk Assessments (Grantham Lough, Stone and Tumer, 2009)

Risk Element Statement	(C1,L1)	(C1,L2)	(C2,L1)	(C2,L2)
Export thermal energy fails due to high cycle fatigue	(5,5)	(5,3)	(4,5)	(4,3)
Export thermal energy fails due to yielding	(4,3)	(4,2)	(4,3)	(4,2)
Guide gas fails due to thermal fatigue	(5,2)	(5,1)	(5,2)	(5,1)

This work used the principle of the RED method to analyze chemical risk for product with chemical subsystems. The following chapter describes the methodology.

3. CHEMICAL RED METHOD

Chemical RED methodology relies on the concept of RED (Grantham Lough, Stone and Tumer, 2009) to asses risks associated with chemical components or subsystems. In addition, it uses function and the components of the functional basis, and adds chemical failure modes to the failure mode taxonomy. The taxonomies permit efficient communication of the potential risks in the early phases of product development. These risks are then mapped to the risk fever chart, which shows the high-risk, moderate-risk and low-risk elements using numerical and colored codes. This chapter describes the chemical failure modes developed for addition to the electrochemical failure mode taxonomy and the steps of the methodology

3.1 FAILURE MODE

Failure mode is defined as the link between failure cause and failure effect, (Collins, 1993). Failure modes are the physical, chemical, electrical, mechanical, electromagnetic, structural, thermal, or atomic processes that lead to failure. Previous work has produced an extensive list of electromechanical failure modes (Uder, Stone and Tumer, 2004). Literature review and the definition of failure mode were combined to ascertain the causes, failure modes, and effects that describe how chemical components or subsystems fail at the elemental, physics-based level. Table 3.1 presents the resulting chemical failure mode taxonomy as an addendum to the electromechanical taxonomy.

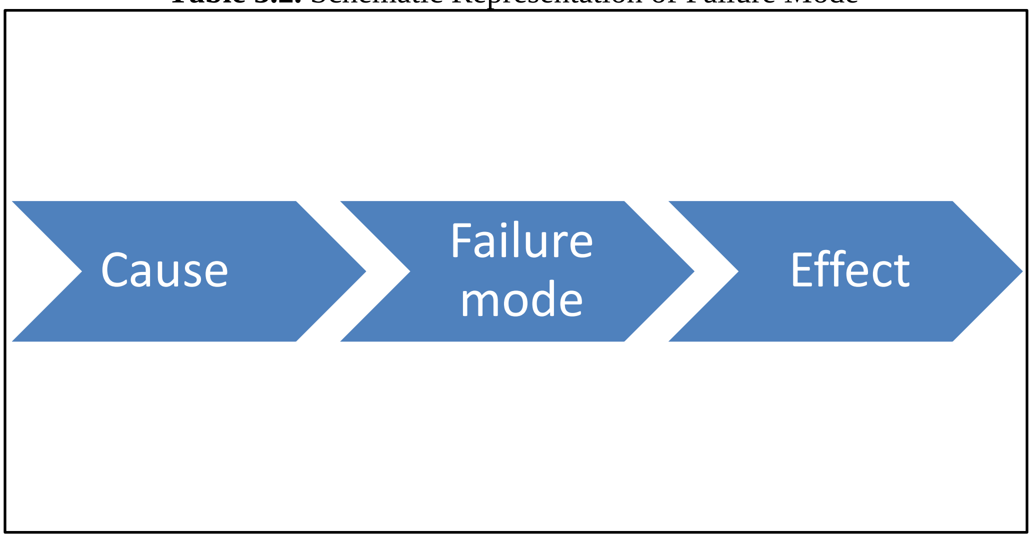
Table 3.1. Chemical Failure Modes

Failure mode	Example of device	Failure effect
Catalytic effect	Microchip	Nonpredictable behavior
Charge imbalance	Light-emiting diode	Reduced intensity of light
Diffusion	Microbarrier	Discoloration
Free radical formation	Polymer barrier	Reduced voltage

The chemical taxonomy formulation process sought to identify failure modes that can be described in terms of the elemental chemistry. New terms added to the taxonomy had to be mutually exclusive to prevent overlapping among terms.

A review of the literature permitted identification of failure effects with chemical significance. The failure cause was identified, and the link (the failure mode) derived from this relationship. Table 3.2 is a schematic representation of this relationship.

Table 3.2. Schematic Representation of Failure Mode



If a term overlapped to some degree with an existing term, then the following categorization algorithm developed by Uder et al. (2004)was employed:

1) The new term might be a superset of the existing term it overlaps with, in which case the new term might be used as a primary identifier.
2) The new term might be similar enough to an existing term that it might be categorized as a comparable term (synonym) rather than entering it into the basis as a new item.
3) The new term and the term which it overlaps may need to be combined or replaced by a slightly broader term.
4) The new term and/or the term which it overlaps may need to be replaced by a more specific term that provides mutual exclusivity.

Applying these algorithms, this work identified four chemical failure modes to be added to the taxonomy. This section briefly defines the chemical failure modes presenting the alphabetically by primary identifier in the same order in which they appear in the chemical failure mode taxonomy addendum in Table 3.1. Although electrical failure modes result in a short or open circuit, chemical failure modes lead to an undesirable chemical reaction or process that manifests as degraded performance or a total malfunction of device or subsystem. Some electrical failure modes, such as electron migration, may also be classified as chemical failure modes because they lead to undesirable chemical reactions that degrade performance.

Some possible failure modes identified by the literature review but eliminated by the algorithm include interface failure and microdrop debonding. In the case of interface failure, localized bonding of polymer-to-metal and polymer-to-glass have been successfully achieved with transmission laser joining technique for the assembly and packaging of polymer-based microsystems. Sultana (2007) performed failure mode analysis of these bonds by optical microscopy, scanning electron microscopy and atomic force microscopy. His work showed that interface failure is dominant in weak joints and material failure is predominant in strong joints. Chemical analysis in the joint region, performed by x-ray photoelectron spectroscopy, showed that interface failure as a mechanism and diffusion as the failure mode in the perceived failure effect (a discolored and weak joint). Although Polyvinylidene Fluoride. is a relatively stable polymer, it forms comparatively good joint by chemical bonding with titanium and forms titanium fluoride and titanium carbide type bonds as titanium diffuses across the bond. (Sultana, 2007). Therefore diffusion is the failure mode, and interface failure was not included as a failure mode.

Microdrop debonding was noted on silicon carbide-coated carbon fibers in aluminum matrix composites. One of the major problems associated with these systems is the formation of aluminum carbide at the fiber/matrix interface, which promotes the degradation of the fiber’s mechanical properties Both water and oxygen act as catalysts in the reaction between aluminum and either carbon or silicon carbide to form aluminum carbide in the fiber/matrix interphase region. The microdrop debonding is actually a failure effect of the failure mode catalytic effect and therefore was not included in the addendum to the failure mode taxonomy.

3.1.1. Failure Mode Identified as Catalytic Effect. Catalytic effect is the increased or decreased in the rate of a chemical reaction by means of a chemical substance known as a catalyst (Jencks, 1969). A catalyst is not consumed by the reaction itself but may participate in multiple chemical transformations. Catalysts generally react with one or more reactants to form intermediates that subsequently yield the final reaction product. Catalytic effect may cause an unintended reaction, which results in the reduced performance of a product. An example of this type of failure is in the oxidation of silicone. Silicone device fabrication requires the oxidation of silicon. The presence of cesium atoms promoted localized oxidation (Ernst and Yu, 1990). This localized oxidation leads to failure of these devices

3.1.2. Failure Mode Identified as Charge Imbalance. Charge imbalance is a loss of electrons (which creates a positive charge) or a gain of electrons (producing a negative charge). Electrons are added and removed under the influence of elements electro negativity. The imbalance charge creates a more reactive chemical species; which when such species react successfully it can cause failure in some characteristic of the product. For example, in the manufacture of organic light emitting diodes (OLEDs) there is a growing consensus that one factor leading to the chemical failure is an imbalance of charge carriers in one of the transport layers composing the device. Experiments carried out by Knox et al.(2006).suggest that for Tris (8-hydroxyquinoline)aluminum(III) (AlQ3)-based devices, degradation is related to an imbalance of charge on the AlQ3 side of the heterojunction, resulting in the build-up of cationic AlQ3 species which may be less stable and more reactive than the pristine material. Cationic AlQ3 may be more susceptible to chemical reactions such as the hydrolysis failure. The luminosity of affected OLED's is compromised. Types of chemical chosen, operating temperature and electromagnetic field have an effect on charge imbalance.

3.1.3. Failure Mode Identified as Diffusion. Diffusion refers to the process by which molecules intermingle as a result of their kinetic energy of random motion (Zumdahl, 2006). It is a net transport of molecules from a region of higher concentration to one of lower concentration by random molecular motion. Fundamentally, two types of diffusion occur: Tracer diffusion a spontaneous mixing of molecules taking place in the absence of concentration or chemical potential. Gradient and chemical diffusion occurs in the presence of concentration or chemical potential gradient and it results in net transport of mass, (Brogioli and Vailat, 2001). Diffusion may bring reactive species closer, facilitating an unintended chemical reaction that leads to performance degradation in device or subsystem. In the semiconductor industry, tin nitride has been popularly used as a diffusion barrier between aluminum and silicone to prevent ‘‘spiking.’’ Spiking has, been reported to occurs through tin nitride at temperatures higher than 500 °C. The investigation of Al/TiN/Si showed that before spiking occurs, aluminum accumulates at the bottom of tin nitride. Silicone also diffuses through tin nitride and dissolves into aluminum. The aluminum accumulation at the bottom of tin nitride results in an interfacial reaction between aluminum and tin nitride. This produces Al3Ti as a spike.

3.1.4 Failure Mode Identified as Free Radical Formation. Free radicals are atoms, molecules, or ions with unpaired electrons on an otherwise open shell configuration. These unpaired electrons are usually highly reactive, so radicals are likely to take part in chemical reactions (Housecroft and Sharp, 1999). The formation of radicals may involve the breaking of covalent bonds either homolytically, a process that requires significant amounts of energy, or by single electron oxidation or reduction of an atom or molecule. In a typical fuel cell, hydrogen is delivered to the anode side of the cell that contains a catalyst, such as platinum. The platinum splits the hydrogen molecules into hydrogen ions and electrons. With a proton exchange membrane in the middle, only hydrogen ions can travel through the membrane to the cathode. Electrons travel on a different path through the electrical circuit to the cathode, creating an electrical current. Fuller’s research shows that the membrane, commonly made of a synthetic polymer, is prone to attack by free radicals that create holes in the barrier. The free radicals are formed by the decomposition of hydrogen peroxide, a strong oxidizing chemical that can form near the membrane (Bi and Fuller, 2008)

3.1.5 Database Generation. The quality of the outputs of the methodology depends largely on the quality of the historical failure data captured. A strong failure knowledge-base is essential for the generation of reliable estimates of chemical risks. The present work investigated 22 failures of a chemical device or subsystem and catalogued the failure information. It included failure of microchips, diodes, fuel cells, polymer membranes, nanofibers, adhesive bonds, implanted devices, microelectromechanical machines, anodes, packing material, photo voltaic cells, and microbarriers. This small database was used for the proof of concept of the method. The data thus extracted was combined to build a failure knowledge-base by populating EC CF and CF' matrices to obtain the EF matrix, as described in Equation (1). This method uses RED equations exactly. Table 3.3, 3.4, 3.5 and 3.6 show the matrices. The CF' matrix uses the failure severity values shown in Table 3.7 to map severity. The impact of the failure modes on the devices is either explicitly stated in the text or can be inferred from the failure effects noted in the case studies.

Table 3.3. EC Matrix

	diode	micro chip	laser bond	packing	implant device	Photo voltaic cell	carbon fibers	proton exchange membrane	mems	micro barrier
Guide solid	0	0	0	0	1	0	0		1	
convert energy	1	1	0	0	0	1	0	0	1	0
guide energy	1	1	0	0	0	1	1	0	0	1
guide liquid	0	0	0	0	0	0	0	1	0	0
guide gas	0	0	0	0	0	0	0	1	0	1
store liquid	0	0	0	0	0	0	0	0	0	0
store gas	0	0	0	0	0	0	0	0	0	0
mix liquid	0	0	0	0	0	0	0	0	0	0
separate solid	0	0	1	1	0	0	0	0	0	1
separate liquid	0	0	0	1	0	0	0	1	0	1
separate gas	0	0	0	0	0	0	0	1	0	1
store energy	1	1	0	0	0	0	0	0	1	1

The rows of the EC matrix consists of functions from the functional basis (Hirtz et al., 2002), and the column lists components from component taxonomy (Greer, et al., 2003). The binary entries in this matrix indicate that the functionality has been solved (1) or not (0) by the corresponding component. The numbers are either 0 or 1. 0 indicates that the function (for instance guide solid) was not carried out by the component (diode, micro chip, photovoltaic cell, etc) in the historical catalogued case studies. 1 indicates that the function (for instance guide energy) was indeed carried out by the component in the catalogue of historical failures (diode, micro chip, photovoltaic cell, carbon fibers, and micro barrier). This matrix is used to calculate the EF matrix, as shown in Equation (1), the risk likelihood as shown in Equations (2) and (3), and risk consequence as shown in Equations (4) and (5).

Table 3.4. CF Matrix

	catalytic effect	charge Imbalance	diffusion	free radical
diode	1	1	0	0
microchip	1	2	4	0
laser bond	0	0	1	0
packing	1	0	0	0
Implant device	1	2	0	0
Photo voltaic cell	0	0	1	0
carbon fiber	0	1	0	0
proton exchange membrane	0	0	1	3
mems	1	1	1	0
micro barrier	0	0	3	0

The CF matrix of the chemical RED method lists components in rows and failure modes (from the taxonomy addendum. It is also used in Equations (2) and (3) to calculate risk likelihood. The numerical matrix values indicate how many times the component has exhibited a failure mode in the 22 cases investigated. For instance, microchips failed four times by diffusion, two times by charge imbalance, one time by catalytic effect. They never failed by free radical failure modes. This matrix is used to formulate the function-failure mode EF matrix, as seen in Equation (1). The numerical entries correspond to how many times the function has exhibited the corresponding failure mode in the cases that were investigated. For instance, store liquid has exhibited the failure mode catalytic effect once.

Table 3.5. EF Matrix

test	catalytic effect	charge imbalance	diffusion	free radical formation
Guide solid	0	2	0	0
convert energy	1	3	3	0
guide energy	4	2	6	1
guide liquid	2	0	1	3
guide gas	1	0	1	3
store liquid	1	0	0	0
store gas	0	0	0	0
mix liquid	0	0	0	0
separate solid	2	2	4	0
separate liquid	2	0	3	3
separate gas	1	0	2	1
store energy	3	5	7	0

The rows and columns of the CF' is identical to the CF matrix, however, the numerical entries represent the severity of the failure as displayed in the severity mapping in Table 3.7, and range from 0 to 5. For example**,** for the implanted device, the severity of the failure was at 5 for both catalytic effect and charge imbalance. This level of severity indicates that failure of the device may cause harm to humans.

Table 3.6. CF' Matrix

	catalytic effect	charge imbalance	diffusion	free radical
diode	2	3	0	0
Photo voltaic cell	0	0	3	0
microchip	3	2	4	0
mems	2	3	3	0
packing	5	0	0	0
laser	0	0	3	0
Implant device	5	5	0	0
Anode	2	0	0	2
carbon fiber	0	1	0	0
proton exchange membrane	0	0	3	5
micro barrier	0	0	3	0

Table 3.7. Failure Severity Value Mapping (Wang and Roush, 2002)

Failure Severity Values				
1	2	3	4	5
Unreasonable to expect the customer to notice very minor failure	Low severity – only slight customer annoyance	Moderate – failure causing some customer dissatisfaction. Customer annoyed.	High –degree of failure resulting in the product not working and customer angry.	Very High – this indicates that the customer is at risk. Safety regulations are being infringed

In the case of AlQ3-based OLEDs, Knox et al. (2006) notes that diodes failed by charge imbalance. This information is entered in the CF matrix. Knox et al observed reduced intensity of the light emitting diodes, which would correspond to severity value of 3 from Failure severity value mapping shown in Table 3.7. This value is entered into the CF' matrix. The diodes functional model is then derived (Stone, Tumer and Van Wie, 2004). The function failure matrix entry for the failure effect (charge imbalance) and the corresponding functions (guide energy) is then provided a value indicating the number of times guide energy has failed by charge imbalance.

3.2 APPLYING THE CHEMICAL RED METHOD

As in the RED method developed by Grantham Lough et al., in the chemical RED method feeds the functional requirements into the failure knowledge base to generate a list of potential risks. This list helps the novice designer forecast high-risk functions or find ways to mitigate specific failures early in the design process. The steps involved in are as follows.

Step 0: Database Population

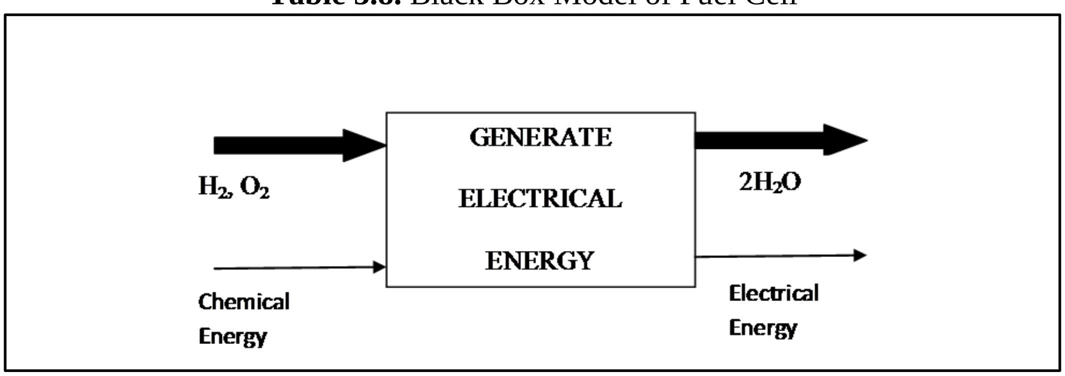
An essential requirement of the method is to have a database of historical failure data to include chemical failure modes. To generate such a database, a considerable number of failures with chemical components or subsystems must be examined. Failure severity is assigned to the failure modes based on impact to system or device performance on a 1 to 5 scale, with 5 bearing most severe impact with device posing harm to humans.

The EC and CF matrices, their product (the EF matrix), and the CF' matrix created using the chemical failure cases as described in Section 3.1.5. These matrices represent the repository based on chemical failure information and will be used to analyze a fuel cell case study.

Step 1: Determine functions of product under investigation

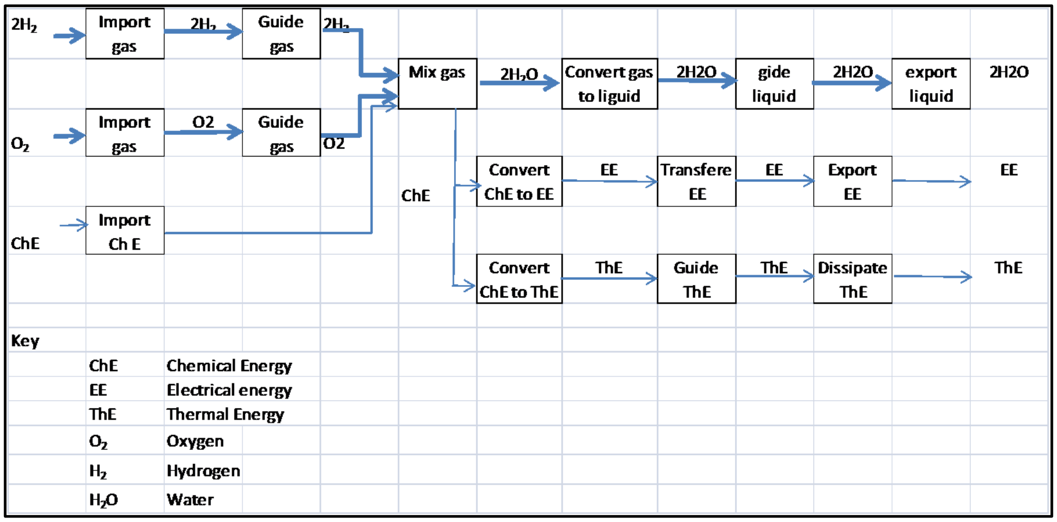
To develop a function model of the new design or subsystem, a black box model must first be created. The functional model is then derived from the black box model according to the methodology of Stone et al. (2004). The functions are used to generate the EF matrix as a part of the method, as described in Equation (1). The functionalities are expressed in the form of function and flow by using the functional basis function taxonomy. For the case study of the fuel cell, the black box model is shown in Table 3.8, and in Table 3.9 as the functional model.

Table 3.8. Black Box Model of Fuel Cell



A fuel cell is an electrochemical conversion device. It produces electricity from fuel (on the anode side) and an oxidant (on the cathode side), which react in the presence of an electrolyte. This case study analyzes a proton exchange membrane (PEM) fuel cell that failed (Stamenkovic and Markovic 2007). The Black Box model shows the overall system requirement to generate electric energy. From the black box model, a functional model is derived following Functions Failure Design method (Stone, Tumer and Van Wie, 2004).

Table 3.9. Functional Model of Fuel Cell



The functions derived are in the boxes, and are in a verb (for example export) object (electrical energy) form. For the Fuel Cell case study, the functions are presented as Table 3.10.

Table 3.10. Fuel Cell Functions

import gas	export liquid
guide gas	convert chemical energy
mix gas	transfer electrical energy
convert gas to liquid	export electrical energy
guide liquid	

Step 2: Risk Calculations

The next step is to map the consequence and likelihood mapping. Normally, the formulations provided in Equations (2) through (5) are used to attach likelihood and consequence data to the potential failures and thus arrive at identifiable risks.

For the fuel cell case study, only Equations (3) and (4) are used for this purpose. Table 3.11 below shows, how Equations (3) and (4) are used in RED and why they are used in the fuel cell case study. Given these three elements (EF, C1, and L2), combined risk items are identified and quantified. The L2 equation is chosen as devices under study will be considered systems. Since these devices require human inputs, the C1 equation is used.

Table 3.11. Mapping Equations L2 and C1

	RED	THE METHOD
L2 = $l_{ij} = \text{int}\left\{5\frac{ef_{pred_{ij}}}{\max\limits_{\substack{1\le i\le n\\1\le j\le m}}(ef_{agg_{ij}})}\right\}$	Used at system design level	Devices under sudy will be considered systems
C1 = $c_{ik} = \max\limits_{1\le j\le m}(ec_{ij}cf'_{jk})$	Used for risk assessment which involve human related products	These systems require human inputs

The entries in the C1 matrix indicate the consequence of a particular function-failure combination, and the entries in the L2 matrix indicate the likelihood that a particular function will fail by a specific failure mode. By matching data from each of these entries, risk statements can then be constructed. Table 3.12 shows the resulting risk statement.

Guide gas fails by the failure mode diffusion with a consequence of 3 and a likelihood of 1.

Table 3.12. Risk Statement

guide gas fails due to diffusion, (3, 1)
guide gas fails due to free radical, (5, 2)
guide liquid fails due to diffusion, (3, 1)
guide liquid fails due to free radical, (5, 2)
convert energy fails due to diffusion, (3, 2)
transfer energy fails due to diffusion, (3, 3)
export electrical energy fails due to diffusion, (3, 2)

Step 3**:** Risk Result Communication

The chemical RED method performs risk analysis that yields important information for designers, such as the specific failure mode, likelihood, and consequence for each function. These three elements must be properly communicated among design team members. Visual representation is appealing to engineers, so they are plotted on a risk fever chart (Office of the Under Secretary of Defense, 1999). The chart allows risk statements to be condensed into low-risk; medium-risk; and high-risk elements by plotting each of the risk statements according to the coordinates given by C and L matrices. In this case the C1 and L2 matrices. The results indicate the overall risk. This method was followed to produce the fever chart shown in Table 3.13**.**

Table 3.13. Risk Fever Chart for Fuel Cell

Likelihood					
5	0	0	0	0	0
4	0	0	0	0	0
3	0	0	1	0	0
2	0	0	2	0	2
1	0	0	2	0	0
	1	2	3	4	5
	Consequence				

The fuel cell studied here showed three moderate-risk items, and four low-risk items. The moderate risk items were transfer energy fails due to diffusion, guide liquid fails due to free radical, and guide gas fails due to free radical.

The purpose of this case study was to validate that the chemical Red method identifies failure in an actual case. The fuel cell under study was a hydrogen fuel cell with a Nafion polymer proton exchange membrane. Chemical changes in the Nafion membranes were analyzed by X-ray photoelectron spectroscopy (XPS) and clear evidence of polymer degradation was observed. Exposure of the membrane to two hours of X-ray radiation did not affect the chemical structure of the membrane. However, treatment with various Fenton's reagents indicated that the $(CF_2)_n$ polymer backbone had decomposed due to free radical formation. Fluorine and sulfur XPS peak intensity decreases were consistent with the detection of fluoride and sulfate ions during test of the fuel-cell. The increase in oxygen atom concentration suggests that oxygen-rich moieties formed in the membrane after long-term operation. This case study demonstrated that the fuel cell indeed failed due to free radical formation failure mode in the Nafion polymer proton exchange membrane whose function is to guide liquid and gas in the fuel cell (Stamenkovic and Markovic, 2007).

The chemical RED method indicates that free radical formation is a moderate risk, and in the fuel cell case study showed that this was the primary failure mode. It also indicated that diffusion due to transfer energy was a moderate risk. In the case study, diffusion was identified for a secondary failure mode of a chemical attack of the CF_2 backbone. Fourier transform infrared spectroscopy (FTIR) spectra showed the formation of oxygen moieties in the degraded membrane. Two degradation schemes consistent with the results observed have been proposed by Stamenkovic and Markovic (2007). Under the same experimental conditions, no detectable changes in XPS spectra were found between a fresh membrane electrode assembly (MEA) and an MEA after long-term operation. These results suggest that degradation occurred mainly within the membrane or at the membrane-electrode interface due to diffusion of oxygen-rich moieties. Therefore as predicted the fuel cell membrane failed by diffusion, however, this was not the main failure.

The medium-risk items predicted by the chemical RED method were both evident in the actual fuel cell case. The chemical RED method was therefore validated as a useful risk analysis tool.

4. CONCLUSIONS AND FUTURE WORK

The purpose of this paper was to demonstrate a method for assessing the risk posed by chemical subsystems. During the early phase of product or process design, there are many opportunities to avert risks by making changes to the functions, with minimal impact on budget and schedule. The chemical RED method is effective when applied early in the preliminary design phase, as demonstrated by the case study. Chemical RED predicted that free radical formation and diffusion would present a moderate risk of failure. Both were present in the fuel cell case studied, which identified free radical formation as a primary failure mode. Four chemical failure modes were identified and added to the electrochemical failure mode taxonomy. Potential areas of risk introduced by chemical subsystems were determined using historical chemical failure data. The current database was developed through the investigation of 22 chemical subsystem failure case studies. This small database is used for proof of concept of the method. Many more cases must be added to the database to ensure the effectiveness of this methods risk assessment. This paper presents the procedure to apply the method to analyze chemical or chemical subsystem risk. No prior knowledge of chemical failures is required to use this method; one need only be familiar with the functions of the device or product under study. This method, proved to be an efficient tool for novice engineers and designers to determine chemical risks in the early design stages by identifying potential failures based on catalogued historical data.

Future work on this topic will involve analysis and validation of the current database and developing the database to include many more chemical failure case studies. Such work will help form a more complete database and thus improve effectiveness of this method in risk assessments. In addition, more chemical failure modes need to be added as new material and processes come into existence.

APPENDIX

POTENTIAL FAILURE MODES THAT WERE DISCARDED

Potential failure mode	Reason for being discarded	Source
Electron migration	Already in electrochemical taxonomy	1
Coating failure	Failure effect	2
Micro drop debonding	Failure effect	2
Interface failure	Failure effect	3
Material failure	Failure effect	3
Electrode delamination	Failure effect	4
Hydrolysis	Charge imbalance is primary identifier	5
Cathode Catalysis	Catalytic effect is primary identifier	5
Loss of mass transfer rate	Diffusion is primary identifier	6
Increased diffusion gradient	Diffusion is primary identifier	7
Resistivity increase	Failure effect	8
Fiber breakage	Failure effect	2
Cathode oxidation	Charge imbalance is primary identifier	9
Moisture contamination	Is a failure cause	10
Loss of conductivity	Failure effect	6
Gate oxide failure	Already in electrochemical taxonomy	1

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