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International Physical Protection Self-Assessment Tool for Chemical Facilities

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Prepared by
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Abstract

This report is the final report for Laboratory Directed Research and Development (LDRD) Project #130746, *International Physical Protection Self-Assessment Tool for Chemical Facilities*. The goal of the project was to develop an exportable, low-cost, computer-based risk assessment tool for small to medium size chemical facilities. The tool would assist facilities in improving their physical protection posture, while protecting their proprietary information. In FY2009, the project team proposed a comprehensive evaluation of safety and security regulations in the target geographical area, Southeast Asia. This approach was later modified and the team worked instead on developing a methodology for identifying potential targets at chemical facilities. Milestones proposed for FY2010 included characterizing the international/regional regulatory framework, finalizing the target identification and consequence analysis methodology, and developing, reviewing, and piloting the software tool. The project team accomplished the initial goal of developing potential target categories for chemical facilities; however, the additional milestones proposed for FY2010 were not pursued and the LDRD funding therefore was redirected.

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NOMENCLATURE

ACC	American Chemistry Council
CFATS	Chemical Facilities Antiterrorism Standards
CWC	Chemical Weapons Convention
DHS	Department of Homeland Security
DOD	Department of Defense
DOE	Department of Energy
FY	Fiscal Year
ICCA	International Council of Chemical Associations
LC50	The median lethal concentration
LD50	The median lethal dose
LDRD	Laboratory Directed Research and Development
NFPA	National Fire Protection Association
NIOSH	National Institute of Occupational Safety and Health
OSHA	Occupational Safety and Health Administration
RAM-CF	Risk Assessment Methodology for Chemical Facilities
Sandia	Sandia National Laboratories
UN	United Nations
UNCETDG	The United Nations Committee on Experts on the Transport of Dangerous Goods
US	United States
WHO	World Health Organization
WMD	Weapons of Mass Destruction

1. INTRODUCTION AND BACKGROUND

Intentional attacks against domestic or international chemical facilities can cause widespread death, injuries, and damage to the environment as well as chemical industry infrastructure. These effects, in turn, may also lead to civil unrest and political and economic destabilization. International efforts to prevent the malicious use of chemicals have focused on verifying the destruction of declared chemical weapons through member states compliance with the Chemical Weapons Convention (CWC), or regulating the export of dual-use chemicals and technologies. However, no international standards or guidance exist for determining the appropriate level of physical protection for facilities manufacturing, distributing, or handling hazardous chemicals, or for preventing sabotage or theft of these hazardous chemicals. In the United States (US), the Department of Homeland Security (DHS) issued the Chemical Facilities Antiterrorism Standards (CFATS) Interim Final Rule (June 8, 2007) which imposes comprehensive federal security regulations for high-risk chemical facilities. Prior to the CFATS standards, Sandia National Laboratories (Sandia) developed a Risk Assessment Methodology for Chemical Facilities (RAM-CF) tool which was approved by the American Chemistry Council (ACC). The RAM-CF tool has been made available to over twenty companies who have received commercial licenses. However, the RAM-CF is export-controlled and best-suited for large facilities with rigorous safety standards and operational analysis procedures. Proprietary information generated from risk assessments in the US is generally protected from release into the public domain. Not surprisingly, the chemical industry worldwide demands similar protection for their proprietary information.

The purpose of this project was to develop an exportable, computer-based risk assessment tool for small to medium size chemical facilities. The tool would enable these facilities to improve physical protection of their assets, while maintaining control of their sensitive information. In addition, successful development and deployment of the tool would promote Sandia’s reputation as the "place to go" for chemical facility risk assessment, which in turn would allow Sandia to expand work for government agencies that have international outreach efforts. The project aligned well with Sandia's national security mission and experience in developing physical protection systems for nuclear facilities. The ACC has adopted a Responsible Care Security Code as an element of their responsible care program. Thus, the Sandia physical protection self-assessment tool might serve to compliment the ACC’s activities as well as the International Council of Chemical Associations’ (ICCA) responsible care initiatives.

2. APPROACH

In FY2009 the project team set a goal to generate a comprehensive characterization of the Southeast Asia chemical industry. Southeast Asia was selected as an appropriate model because this region is showing a growth in chemical industrialization as well as terrorism. The approach was later modified, on the basis of an LDRD review team concern that the methodology would only be applicable to a limited geographical region. Therefore, the project team developed a new set of milestones, the first of which was to identify potential target categories.

There are two approaches commonly utilized in the US for identifying chemical targets that are considered a security risk. The first is a list-based approach. For example, the Sandia RAM-CF product uses a list of chemicals that have been identified in the US CFATS regulation as chemicals of interest. Chemicals of interest pose a security risk under conditions of release, theft, or sabotage. However, this approach may not identify all chemicals in a facility which might be the target of a malicious attack. Alternatively, targets may be identified by a comprehensive facility safety and security analysis. This latter approach requires time and resources that are untenable for small to medium size chemical facilities in underdeveloped regions. Moreover, in many of these regions, there is no regulatory driver requiring either a list-based or the comprehensive facility analysis approach for identifying potential targets.

To bridge the gap between the list-based and comprehensive safety analysis approaches to target identification, the Sandia team developed a logic tree diagram to illustrate the means by which theft and/or sabotage of general classes of chemicals might occur, and thereby lead to an unacceptable consequence. This logic diagram can be used to systematically analyze a facility for potential chemical targets. Figure 1 illustrates this approach.

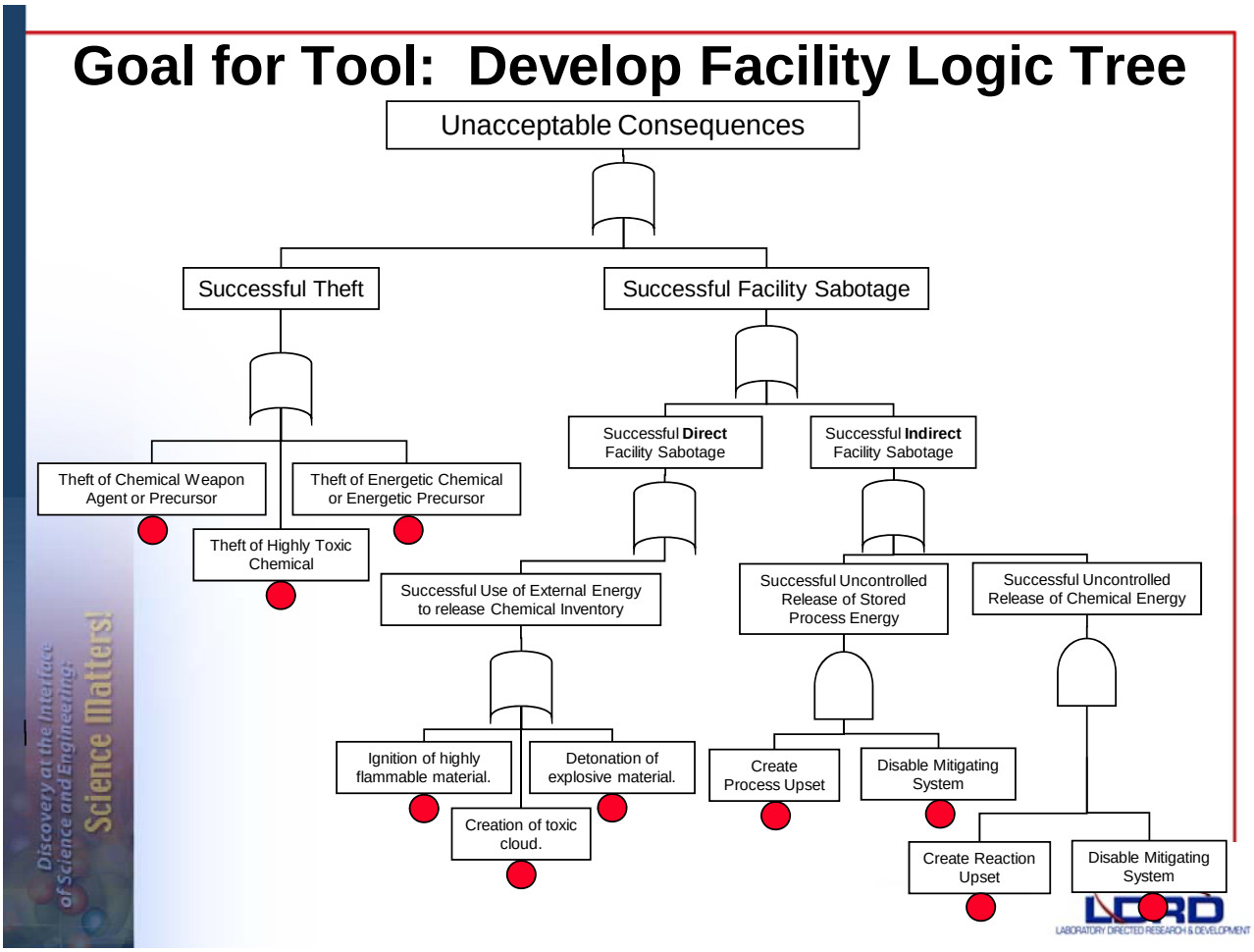

Figure 1. Develop Facility Logic Tree of Potential Target Categories

The top level event in the fault tree is an "undesired event" resulting from a malicious attack. Malicious attacks can be categorized by the adversary's goal—theft or sabotage. The act of theft is removing something from its authorized location, which is the outermost protected facility boundary. Furthermore a theft target is any chemical that has the potential to directly or indirectly endanger the health and safety of the public or environment. Sabotage is any deliberate act directed against a chemical facility or chemical in use or storage, which could directly or indirectly endanger the health and safety of personnel, the public, and the environment (adapted from INFCIRC/225/Rev. 4). Sabotage can be either direct or indirect. In a direct sabotage, the adversary uses external energy to accomplish the attack. A direct attack requires physical access to the chemical target. In an indirect attack, the adversary uses energy stored in the chemical inventory or process to accomplish the attack. Indirect sabotage may not require physical access to the chemical target. We identified three categories of direct sabotage acts: ignition of highly flammable material, creation of a toxic cloud, and detonation of explosive material. For indirect sabotage an additional subdivision is useful—the use of stored process energy (pressure) and the use of chemical energy (chemical potential or reaction). Both of these indirect sabotage categories may be accomplished by altering the process conditions, thereby exceeding any existing safety system's capacity. Alternatively, these indirect sabotage events could be accomplished by disabling an existing safety system.

Following are descriptions of the algorithms developed for identifying the theft and sabotage target categories. The team identified three categories of theft targets; chemical weapon agents or precursors, energetic chemicals or precursors, and toxic chemicals; and two categories of sabotage chemical targets.

Theft Target Categories

- **Chemical Weapon Agent or Precursor**
  A list of chemicals is found in the Annex of Chemicals, Schedules 1, 2, and 3 of the CWC. The Sandia target identification methodology requires cross-referencing a facility's inventory against these Schedule lists. Arguably this category does not need to be a separate category from toxic chemicals since the peaceful use of some of these chemicals is not prohibited by the CWC. However, keeping the list of chemical weapon agents and precursors as a distinct category recognizes the increased international scrutiny that would occur if a large-scale theft of a listed chemical occurs. Note that the Schedules are a limited resource since they do not identify all potential chemical targets.

- **Explosive Chemicals**
  The determination of which chemicals belong to this category of theft targets can also be determined by comparison to lists. Alternatively, the explosive hazard of some chemicals may be categorized on the basis of their molecular formula. This method of categorization is accomplished by the so-called oxygen balance, which is the difference between the oxygen content of the molecule and the oxygen required to fully oxidize the elements comprising the compound. This analysis is only valid for organic molecules and simple organometallic compounds. The advantage of this approach is that a large chemical inventory could be screened automatically as long as the molecular formula is known.

  The atomic oxygen balance is calculated from balancing the stoichiometric reaction of the compound with oxygen. Thus, the method requires the molecular formula of each chemical in the inventory. A chemical is potentially explosive if the oxygen balance is greater than minus (-) 200.

  The analysis is based on the following oxidation reaction:

$$C_xH_yM_zO_d + (x + \frac{y}{4} + \frac{z}{2} - \frac{d}{2})O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O + zMO$$

  where C represents carbon, H represents hydrogen, M represents a divalent metal, and O represents oxygen. The atomic oxygen balance is calculated from the balanced stoichiometry of this reaction. For 100 g of the organic compound, the oxygen balance is calculated as follows:

$$OxygenBalance\% = \frac{-100 * (2x + \frac{y}{2} + z - d) * 16}{MW}$$

  where MW is the compound molecular weight and 16 is the atomic weight of oxygen.

- **Toxic Chemicals**
  A chemical substance's toxicity is estimated from acute and chronic exposure studies involving different animal species and/or cell lines, or from evidence obtained through human epidemiological studies. The concentration of a chemical substance that results in a toxic effect is expressed in parts per million (ppm) or milligrams per kilogram (mg/kg) of body weight, and by route of exposure, length of exposure, and animal species. Lethal Dose 50 (LD50) or Lethal Concentration (LC50) are generally the best metrics for describing acute toxicity. However, not every chemical has been tested and those that have been tested typically offer a range of results for a range of different animal species by different investigators. For many chemicals there are summary tables that list the various studies, test animal used, and the result, but one must still sort through these results and determine a number that best represents all the studies. There are international organizations and regulatory agencies that have categorized chemicals by level of acute toxicity. For example, the World Health Organization (WHO) has established a classification scheme for pesticides on the basis of LD50 data (rat), chemical state, and route of exposure. The four classes range from extremely hazardous to slightly hazardous.

Class		LD50 Rat (mg/kg body weight)			
		Oral		Dermal	
		Solids[a]	Liquids[a]	Solids[a]	Liquids[a]
Ia	Extremely hazardous	<5	<20	<10	<40
Ib	Highly hazardous	5 to 50	20 to 200	10 to 100	40 to 400
II	Moderately hazardous	50 to 500	200 to 2000	100 to 1000	400 to 4000
III	Slightly hazardous[b]	>500	>2000	> 1000	>4000

a The terms "solids" and "liquids" refer to the physical state of the active ingredient being classified.

Table 1.WHO Pesticide Classification

The United Nations Committee on Experts on the Transport of Dangerous Goods (UNCETDG) has approved a document entitled "The Globally Harmonized System (GHS) of Classification and Labelling of Chemicals." GHS classification and labeling is based, as in the WHO classification, on acute toxicity, but adds gases, vapors, and dusts/mists as additional sources of inhalation exposure. Unfortunately, while the methodology is well documented and referenced around the world, no examples or lists of categorized chemicals have yet been identified.

	Hazard Statement	Oral (mg/kg)	Dermal (mg/kg)	Gases (ppm)	Vapours (mg/liter)	Dusts and Mists (mg/liter)
Category 1	Danger Fatal	<5	<50	<100	<0.5	<0.05
Category 2	Danger Fatal	50	200	500	2.0	0.5
Category 3	Danger Toxic	300	1000	2500	10	1.0
Category 4	Warning Harmful	2000	2000	20000	20	5
Category 5	Warning May be Harmful	5000	5000			

Table 2. UNCETDG/GHS Acute Toxicity Hazard Categories

The US Occupational Safety and Health Administration (OSHA) and the National Institute of Occupational Safety and Health (NIOSH) have also established LD50 and LC50 concentrations which designate a chemical as “highly toxic” or “toxic.” Nevertheless, in order to categorize potential toxic chemicals for the Sandia tool, experimentally determined toxicity concentrations must be obtained for each chemical substance in a facility inventory. This approach has two challenges—the tedious effort required for evaluating a large chemical inventory and the numerous different measures of toxicity. In general, the Sandia methodology proposed to use either LD50 or LC50 values to estimate potential toxic consequences for any particular facility inventory. Thus, given the current state of toxicological science, the only approach for identifying this class of target will be by comparison to lists or obtaining data for each chemical in a facility inventory.

Sabotage Target Categories

The general methodology for identifying targets may be used for identifying some, but not all sabotage targets. All of the theft targets are also evaluated as direct sabotage targets. One additional class of direct sabotage targets is flammable substances.

- **Flammables**
  The National Fire Protection Agency (NFPA) has established a categorization scheme for flammable liquids based on the normal boiling point and flash point of a substance. The scheme is as follows: T_f = flash point temperature and T_b = boiling point temperature (Figure2).

Hazard Rank	U.S. NFPA Flammability criteria
4	$T_f < 22.8^oC$ AND $T_b < 37.8^oC$
3	($T_f < 22.8^oC$ AND $T_b \geq 37.8^oC$) OR ($T_f \geq 22.8^oC$ AND $T_f < 37.8^oC$)
2	$37.8^oC \leq T_f < 93.4^oC$
1	$T_f > 93.4^oC$
0	Only if indicated by US NFPA assignment

Table 3. NFPA Criteria for Flammable Liquids

The normal boiling point of organic liquids is easily found in reference texts and vendor catalogs. The flash point is less commonly available, although it may be listed on safety data sheets. Safety data sheets are required for all chemicals manufactured or imported in the United States and European Union. In addition, many flash point estimation models exist, but these models require the molecular formula and the normal boiling point. One model that worked well when evaluated against a Sandia building inventory is Prugh, *J. Chem. Educ.*, **50** (1973), p. A85 (Figure 3), where X_{st} = the stochiometric concentration of the vapor in air; C, S, H, X, and O are respectively the number of carbon, sulfur, hydrogen, halogen, and oxygen atoms in the substance; T_f = the flashpoint; and T_b = the boiling point temperature.

$$X_{st} = \frac{83.8\%}{4 \cdot C + 4 \cdot S + H - X - 2 \cdot O + .84} \text{ vol\%}$$

$$T_f = \frac{T_b}{1.3611 - 0.0697 \cdot \ln(X_{st})} \text{ (alcohols)}$$

$$T_f = \frac{T_b}{1.4420 - 0.08512 \cdot \ln(X_{st})} \text{ (all others)}$$

Figure 2. Prugh Model for Estimating Flash Point

- **Indirect Sabotage Targets**
  A successful indirect sabotage attack may not require physical access to the chemical inventory. Alterations in process conditions and/or the disabling of a process safety system may be possible from multiple locations. To identify potential runaway exothermic reactions, we have devised a parameter--the potential adiabatic temperature rise rate. This parameter can be used to rank the runaway potential of different chemical reaction processes within the facility. Calculation of this parameter requires knowledge of the chemical kinetics, heat of reaction, and overall process heat capacity. One key resource for understanding the function and location of process and safety systems is process safety analysis documentation, especially when that documentation is required by a country's regulations. Both the availability and quality of such analyses is likely to vary from non-existent to comprehensive depending upon a country's level of regulatory maturity.

3. CONCLUSIONS

The goal of this work was to develop an exportable, low-cost, computer-based risk assessment tool for small to medium size chemical facilities. In FY2009, the team completed an initial milestone which was to create an approach for identifying and prioritizing potential chemical targets. These targets, when used maliciously, can lead to unacceptable consequences such as death, injury, as well as impacting the environment and the chemical industry infrastructure. Algorithms for categorizing chemical weapon agents or precursors, energetic chemicals or precursors, toxic chemicals; and two categories of sabotage chemical targets were developed. In addition, work was initiated on methods to identify target categories from a facility chemical inventory using minimal information. Additional milestones proposed for FY2010 were not pursued and the LDRD funding therefore was redirected.

This work served to address a gap in the current list-based approach used by the regulatory community for identifying chemicals of interest. A prioritized list, on the other hand, is beneficial to small and medium-size chemical facilities with limited physical protection resources as their resources then can be applied to the targets with the highest conditional risk.

It is hoped that future work in this area will continue. Although a comprehensive evaluation of country-specific safety and security regulations was not completed, this information would be useful in understanding the range of information that may be available to support indirect sabotage target identification. A logical next step would be to calculate a semi-quantitative risk value for each target. This calculation will provide a ranking of each target to identify where resources should be applied to achieve the greatest improvement in physical protection. Such a calculation requires both the likelihood of success of a malicious attack on a particular target as well as the potential consequence of that attack. Extensive analysis of attack methods and chemical plant vulnerabilities would need to be conducted. Ideally, a computer based risk assessment tool would include all of these elements and be customized for the end-user.

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