University of Rhode Island (URI)
DHS CoE in Explosives Detection, Mitigation, Response & Characterization

The DHS Center of Excellence in Explosives Detection, Mitigation, Response and Characterization at URI continues to develop its strengths: 1) characterization of energetic materials; 2) chemical detection; and 3) blast mitigation. Our goal is to perform fundamental research in keeping with the homeland security mission. Thus, we will be able to respond quickly and effectively and, even, counter the next improvised explosive attacks. The field of homeland defense is broad; even when narrowed to defense only against attacks involving explosives, there is too wide a range for us to cover with available funding. Enclosed is a brief overview of what we are doing and what we wish to cover. We have added potential new starts in a separate section. We are requesting a few of these be funded in 2009.

Characterization of commercial and military explosives involves analyses for purity and identification of its crystal structure(s), performance properties, hazards, and reactivity. The review of each identified explosive and its properties allows extrapolation to structural configurations which might produce better explosives. Characterization, from a counterterrorism viewpoint, consists of many of the same activities. However, we do not ask how to make a better explosive, but what can terrorists do next in terms of making homemade explosives (HME). The Precursor Identification (C1) project pursues identification of chemicals and formulations that can potentially be exploited by terrorists to make new HMEs. The approach is focusing the detonation wave from the detonation of a high explosive into the target insensitive or non-detonable material. This configuration gives the material optimal conditions to respond, be it detonable.

Given that a number common materials can be formulated into explosives, the question is "Can we prevent this? Should these materials be replaced or banned? or can the chemicals be denatured without destroying their application in society?" Denaturing two of the more prevalent precursors—urea and hydrogen peroxide—is another thrust of characterization (C2). If these materials only need to be denatured for certain markets, then rapid success is anticipated.

Both the Characterization and the Mitigation research areas cannot be adequately covered by experimentation, alone. Extensive modeling is required. Israeli researchers are presently modeling destruction/digestion protocols and are beginning to model modes of explosive sample collection in a fundamental study coupling modeling with atomic force microscopy (AFM) results (C3 and D1). Modeling of the explosion/detonation is also necessary to properly design a small-scale test to probe potential explosivity (C1). Furthermore, it is essential to understanding the insult that structures must withstand (CN1). A new start in this area is proposed as well as one looking for explosive metabolites in hair (CN2).

The **Trace Detection** group is developing new tools for the detection of explosives. All the research activities are focused on the fundamental science of detecting explosives so that more sensitive, selective, and adaptable sensors can be developed. The limiting aspect of any sensor is the sample collection method; therefore, we examine systems that detect explosives using direct sample collection, nearby vapors, and remote sampling. Trace residue analysis by physical collection of a sample (typically by swiping) is normally done by mass spectrometry, which is exquisitely sensitive. Work in the past year has focused on understanding the detailed chemistry of gas phase ions. This is expected to lead to development of the thermodynamic and kinetic properties of the interaction of the gas phase ions of explosives with the ambient environment. The ultimate goal in the next few years is to build a mass spectrometer system that can work in a noncontact mode (D1, D2).

Direct detection of vapors using polymer transducers are being studied from two different approaches. All currently available explosive vapor sensors suffer from selectivity problems, i.e., is the sensor response really from an explosive? One solution to this problem is to build an array of sensors that have a slightly different signal at each array point. Thus, the analyte is detected by the pattern of responses across the array. The simple way to do this is with resistance measurements of a conducting polymer sample. The polymer absorbs the analyte and changes the electrical signal. Work is continuing to build polymers that are chemically specific to explosives, which will improve sensor selectivity. A second approach to the selectivity problem is to build in orthogonality to the sensing system, i.e., multiple detection methods from a single sensor. In work supported by the Center, high surface area porous systems containing polymers that will absorb explosives used in a multidetection system: fluorescent emission quenching, polymer swelling (as monitored by a Distributed Bragg Reflector), and the quenching time constant. Again, pattern recognition is used to uniquely identify the analyte (D3).

An avenue to persistent surveillance is to use many sensors distributed throughout the volume of a target area. A unique sensor system supported by the Center uses a MEMS design to produce a simple detector: a catalyst that can decompose the explosive is added to a micro heat detection module on a silicon chip. When the analyte encounters the sensor, the heat released by the decomposition is detected. This sensor system is inexpensive; thus, it can be distributed over a large area. If multiple sensors show positive responses, then it is likely that a threat exists (D4).

In a number of scenarios stand-off sensing systems are essential. Center researchers have developed a system using multiple light sources: a laser to desorb and decompose the target area, followed by illumination with ultraviolet light to induce fluorescence of the products. The fluorescence emission is collected using a telescope and signatures unique to explosives can be identified. Detection from as far as 30 m has been demonstrated and research for fundamental understanding of the physics and chemistry is being explored (D5).

The research focus of the **Mitigation** group is on preparing new materials and understanding present-day structural materials so that the blast response of bridges, tunnels, dams, and other critical structures can be anticipated,,fortified, and modified. Much of our present infrastructure is built of structural steel or steel re-enforcement, as in concrete. It is essential to understand how our present structures may respond at combined high strain rate/thermal exposure loadings resulting from severe blast conditions. To affect this we must determine constitutive laws accounting for damage accumulation and providing a criterion for deformation instability (M1). [The blast characteristics also must be characterized; hence, proposed new start CN1.] The outcome of research on response of present-day materials is to anticipate and predict failure and to access the potential for mitigation of failure. In addition to examining present day structural materials, Center researchers seek for better materials. Established stress waves due to explosive events are used to impose dynamic loading upon diminutive specimens for study of local and microstructure response. Such studies aid determination of material microstructure better suited for stress wave attenuation. Materials identified as promising at the microstructural level are scrutinized for global structural response using scaled explosions, simulated shock, and solid fragments impelling at varying temperatures. Satisfactorily tested materials will be identified for potential barricades or for structural components (M3). Laboratory and field-scale experiments will be conducted to understand explosion coupling to structural systems. Proper knowledge of this interaction provides relevant input parameters to fluid-to-rigid body coupled numerical models (M4). Results aimed at the application of blasts internal to a structure and also will provide input for task M3.

A number of white papers, both solicited and unsolicited, have been sent to us. We believe the Mitigation group could benefit from starting one or two of these and would welcome a discussion on that subject at your convenience. We plan to host a one-day workshop at the end of April to review what is being done and could be done in the field of blast mitigation. Such a workshop should aid our selection of “new starts” in the mitigation area.

Education: An advertisement will be issued next week for an administrator to assist with management of this program and the Center as a whole. Our work in this field to date is as follows. Each University project in the Center supports one or more graduate students. This is their best learning experience. Undergraduates also are supported on the projects as their class schedules permit. Since Spring we have performed five magic shows for elementary and junior high students; we paid for three teachers to attend the Lego Robotics workshop and purchased a dozen robot kits for two schools. We supported two teachers in the summer of 2008 for research experience in a University lab, and in 2009 we plan to accommodate 8 to 10 teachers. We have hosted the Massachusetts’s bomb squad for an educational day workshop about improvised explosive laboratories, and we have scheduled a similar exercise February 3rd with the Rhode Island bomb squad. The National Bomb Squad Commanders Advisory Board (NBSCAB) will visit URI February 10th to discuss how we can assist in their educational program. We provided a one-day workshop in explosives to the U.S. Marines at 29 Palms, CA on December 15th and have another session scheduled February 12th. We are currently discussing similar workshops with an Army group at White Sands (NM) and Japan and the NYPD CBRNE group.

If you have any questions, please contact me—Dr. Jimmie C. Oxley 401-874-2103 joxley@chm.uri.edu

Determining Detonability and Potential Explosive Threat of Energetic Chemicals
Profs Jimmie C. Oxley; James L. Smith, U. of Rhode Island, Chemistry
Dr. James E. Kennedy, Kennex; Prof. D. Scott Stewart, U of Illinois,

Potential scientific impact: Recently, law enforcement and counter-terrorism agencies have emphasized the threat of homemade explosives (HME), but the HME of concern are those which terrorists have already attempted to employ: ammonium nitrate (AN), urea nitrate (UN), hydrogen peroxide, and chlorates. However, there are other energetic chemicals with which it may be possible to fashion explosives. How can these be identified? Being energetic, i.e. releasing heat upon decomposition, is a simple property to measure, but not sufficient to guarantee detonability. It is important to identify potential threat materials, and equally important not to label merely hazardous materials as detonable. Identifying potentially detonable materials does not lend itself to small-scale rapid screening of numerous mixtures because most HME are relatively poor-performing explosives, compared to military explosives, and require large volumes of material (large critical diameters) to support detonation. Thus, they will not appear to be detonable until tested on very large scale.

The goal of this research is to identify the relative explosivity of energetic chemicals. To date it is impossible to say with absolute certainty that an energetic material is not an explosive. The only easily determined fact is that it does not detonate on the scale tested. For example, after the use of ammonium nitrate (AN) in the Oklahoma City bombing of 1995, there were various claims of ways to "inert" AN. Many of the modified AN formulations appeared "inert" on the small scale, but those that received rigorous testing, failed at larger volumes. Determining explosivity definitively on the lab-scale would save weeks of formulating and testing and tens of thousands of dollars for each mixture evaluated. For example, the number of test used to determine the explosivity of a variety of hydrogen peroxide (HP)/ fuel mixtures could have been drastically curtailed.

Technical Approach: This groundbreaking research will not only pioneer an intermediate scale shock-focusing test, but it will attempt to correlate explosive to routine laboratory-scale test[1] so that laboratory researchers may have warning of explosive hazard at the scale of a few milligrams, typical of initial syntheses. The shock-focusing test is anticipated to require only a few kilograms, which would mean pilot-scale production would be unnecessary for explosivity testing. It will focus a strong shock into an insensitive, potentially explosive material to definitively demonstrate the detonability or lack thereof. As funding permits, tests will be benchmarked to full-scale tests and modeled with Detonation Shock Dynamics (DSD) to permit simulation and extrapolation.[2]

Task 1: DSC Correlation: A definitive characteristic of explosives is its rapid release of heat and gas. Heats of decomposition and thermal hazard are routinely analyzed by differential scanning calorimetry (DSC); thus, this instrument is found in many labs. Recently, we have explored an empirical correlation between DSC data (heat release and temperature of the exotherm) and explosive hazard[1] and found that known explosives, e.g. TNT, RDX, PETN, could be plotted in the extreme upper left quadrant, while less energetic materials, e.g. oxidizer/fuel mixes, plotted close to a line. This correlation will be further explored.

Tasks 2/3 Enhanced Detonability: Detonability can be enhanced by the following: (1) adjusting fuel and oxidizer ratio or diluent; (2) seeding the material with high explosive; (3) using heavy confinement (our novel approach is explosive confinement, termed "shock-focusing").

Task 4: Validation Studies: The correlations developed will require validation. Our initial test material, hydrogen peroxide, has been chosen not only for its ease of adjustment from detonable to non-detonable but also because large-scale results are already available.

Task 5: Modeling: Modeling is required to optimize the shock-focusing test. As funding permits, modeling and simulation using DSD[2] will be used to extrapolate to a threat quantity.

Work to date:

1. DSC correlation to detonability plotted
2. test mix chosen—hydrogen peroxide (HP) and ethanol—due to ease of adjustment from detonable to non-detonable & availability of large-scale test results to "check" our tests.
3. CHEETAH calculation on HP formulations have been run
4. test protocol are written and submitted to National Labs & RI Bomb Squad for review.

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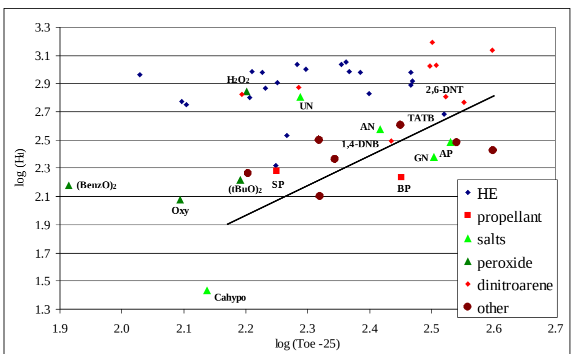

Fig.1 DSC data vs. Detonability--high explosives (HE) in top left quadrant.

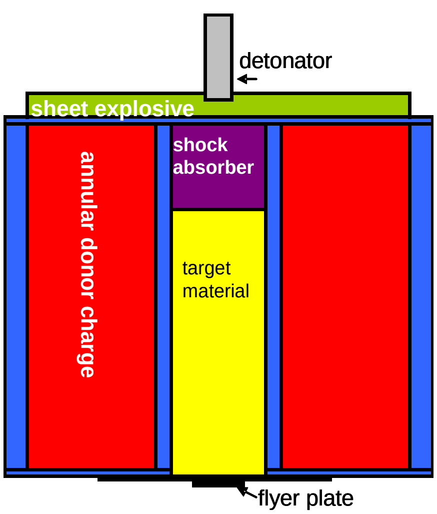

Fig.2.Shock-focusing test configuration.

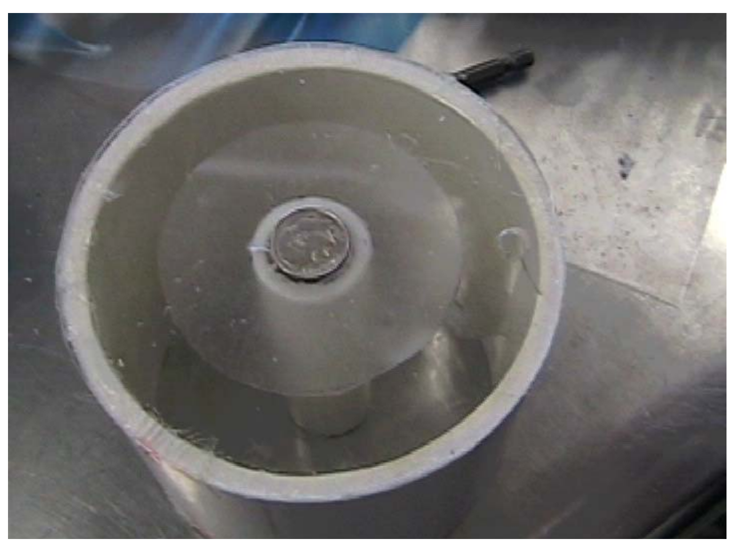

Fig. 3 Photo of PVC mockup setup

Denaturing of Explosive Precursors
Jimmie C. Oxley; James L. Smith, U. of Rhode Island, Chemistry

Potential scientific impact: A number of explosive precursors are in common commerce for legitimate uses and do not readily lend themselves to replacement. The goal of this project is to find means to adulterate such chemicals so that they cannot be used as explosive precursors. This will be a challenging task since the chemical reactivity and uses of each precursor must be thoroughly understood before choosing the appropriate denaturing reagent which does not interfere with the intended use of the precursor. Understanding the normal uses of a precursor is essential to limiting the denaturing agents to those which will not have a deleterious effect. Understanding chemical reactivity of precursors allows selection of potentially effective denaturing agents. Selection and screening of potential denaturing agents require both a systematic approach and a detailed mechanistic study. One can envision two grades of the chemical--that denatured and available to the public and that sold to legitimate industries without adulterants.

Two precursors have been targeted urea and hydrogen peroxide. Urea is the precursor of urea nitrate (UN), and both urea and nitric acid are made in large quantities. We believe urea, rather than nitric acid, is a better candidate for denaturation because nitric acid can be made in an improvise fashion from nitrate salts. The illicit use of hydrogen peroxide (HP) is difficult to manage because any concentration can be used to make explosives. HP in the concentration range of 60% to 90% can be combined with a number of miscible fuels to make a detonable mixture. HP sold in pharmacies at the 3wt% level for disinfectant use, in beauty supply shops at 12wt% for hair bleaching, and at 28wt% for spa treatment. These lower concentrations can be concentrated on a stove or used directly for synthesis of TATP or HMTD. Two approaches to denaturating HP can be taken: a miscible chemical which forms an azotrope to prevent HP concentration or a chemical which causes rapid decomposition at elevated peroxide concentrations.

Technical Approach: Task 1: Perform a literature search to understand chemical synthesis and reactivity of the targeted precursors and review of commercial practices and markets. Task 2: Determine a way to analytically distinguish UN from commingled urea and a nitrate salt. Satisfactory analysis for HP already exist. Task 3: Use additives appropriate for fertilizers and perform analysis to determine if UN synthesis is curtailed. Task 4: Use potential catalysts for HP decomposition and examine whether HP is stable at room temperature while decomposing at high.

Work to Date:

- Ways to distinguish between UN and commingled urea and nitrate salts have been examined. A combination of thermal gravimetric analysis, recrystalization, and melting point have been used.
- The reaction below has been examined. Addition of 10% of certain phosphines or phosphates reduced UN formation dramatically, from 60% to 6-9%.

$$\text{Urea} + KNO_3 + H_2SO_4 \rightarrow \text{UreaNO}_3 + KHSO_4$$

# samples averaged	Preparation with additve 10wt% of urea	Crude Yield (%):	Crude mp (deg C):	Rec. Yield (%)	Rec mp (deg C):
2	HNO3	86%	153 - 155	60%	143 - 147
2	KN/HCl	98%	129 - 132	23%	131 - 136
5	KN/H_5SO_7	89%	133 - 137	21%	142 - 145
4	KN/H_5SO_7/TKPP	62%	134 - 140	9%	133-140
3	KN/H_5SO_7/DAP	85%	131-137	6%	139-150
2	KN/H_5SO_7/MKP	77%	132-138	9%	144-154

- 3% HP was treated with a variety of additives at the 10% level. Some decomposed the HP at room temperature. These could not be used without destroying the commercial value of HP
- Some of the additives which do not catalyze room temperature decomposition of HP are also commonly used as food additives. These will be tested further.

Figure: UN production using various concentrations of nitric acid (Almog)

Further Work:

- Urea and HP markets will be researched to determine if denaturing agents are compatible with those markets
- Analytical protocols for UN will be improved
- Concentrations of denaturing agents will be optimized
- Teaming with those producing UN on field-scale reduction of detonability will be determined.
- Potential HP denaturing agents will be examined at high temperature.
- Ways that room temperature destabilizing agents can be employed will be investigated
- Long-term stability studies of HP with best denaturing agents will be performed.

Theoretical Calulations

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Theoretical exploration of explosive sensitivity and detonatabiliy.

In recent years there has been a proliferation of the threat of improvised explosives. For example, until recently the list of peroxide based explosives was small and included mainly TATP and HMTD. The preparation simplicity of peroxide-based improvised explosives, together with the ease of H_2O_2 purchase, led to the development and use of a large family of H_2O_2 /fuel explosives. The challenge is to develop theoretical methods to assess the sensitivity of potential improvised explosive on the molecular level. The goal is to establish and apply theoretical methods that will allow reliable prediction of the sensitivity and detonatability of energetic materials. The theoretical modeling will be applied to a number of peroxide based explosives as well as improvised explosives including ionic salts (e.g. ammonium nitride and urea nitride).

The first step in the theoretical approach is to determine, using quantum chemistry calculations, the structure of the potential molecule and its energy in the ground state. An expected input to experiments is a list of final detonation products. If such a list is not available, we can perform further calculations to compute such a list by computation of the thermal decomposition route of the parent molecule into final, thermodynamically stable products. The next step is to perform thermo-chemical calculation to determine the energy and entropy difference between the reactants and products. We have found that the criterion of energy release during the decomposition/detonation is not sufficient to determine if a potential candidate high energy molecule is an explosive. Many of the peroxide improvised explosives have a relatively small energy release and entropy increase is a major source to their detonatability. Thus, we intend to calculate the free energy of reaction which is directly related to the power output of the detonation. These studies will be based on our experience with similar calculations for TNT [1].

An elaborate set of calculations is required to determine the sensitivity of candidate explosive molecules. We intend to perform this task by locating the transition state that corresponds to the initial step in the molecule decomposition. For peroxides, this transition state is usually associated with the cleavage of one of the O-O bonds. An example calculation for such a transition state for complex of Zn with TATP is shown in Fig. 1. The transition state is lowered from 31 Kcal from its value for pure TATP to 14.2 Kcal. This is an example that shows how the sensitivity of a detonable molecule can be altered by a small amount of additional impurity.

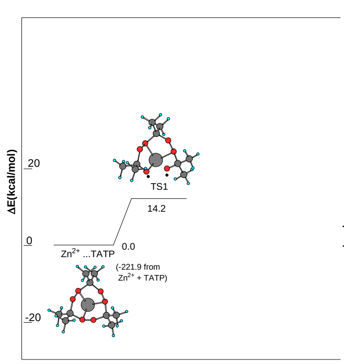
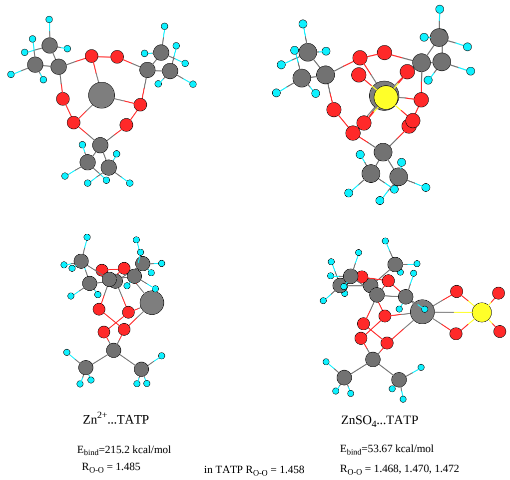


Fig. 1: Transition state for decomposition of Zn^{2+}-TATP complex.

To advance from calculations on a single molecule to bulk, molecular dynamics simulations are necessary. [2] We intend to model the sensitivity of different materials to potential shock. The idea is to generate a large bulk of either solid or liquid phase composed of a few thousand molecules and to equilibrate it at ambient temperature and pressure. We will simulate detonation by hitting this slab of molecules with a well-defined velocity. The results will be compared and calibrated to standard impact experiments (falling hummer).

Benign disposal of peroxide-based explosives

To avoid “blow-in-place” techniques, chemical disposal methods are desired. We have examined, using electronic structure calculations, the stability and thermochemistry of ion-TATP complexes. We propose to extend this investigation to include solvent effects and the possible use of surfactants to enhance explosive dissolution. The ring structure of TATP and DADP enable very strong complexation with metal ions similar to the case of crown-ethers. The consequences of this complexation are very important for peroxide explosive destruction. We can speculate on two routes backed by our calculations. The first is based on catalyzing the ring opening reaction. The second is the creation of stable metal complexes. Calculations of “one side” and “sandwich”/or "two sided" type complexes of TATP, DADP and HMTD with metal ions will be performed. The purpose is to determine the thermodynamic stability of these complexes. We will also determine, computationally, the catalytic ability of such metals ions as $ZnSO_4$ and Zn, $CuCl_2$ and Cu to open the rings. Initially, we found that interaction of TATP with Zn^{2+} reduces the barrier of the first stage of TATP decomposition from ~ 31 to ~14 kcal/mol. We will attempt to find barrier of the first O-O bond breaking in the above mentioned complexes.



Interaction of Explosive Particles with Solid Surfaces

We have examined the interaction between explosive molecules and hair surface in attempt to identify where and how binding occurs. We intend to use techniques developed in that study, both experimental and theoretical methods, to determine the adsorption sites of explosive micro- and nano-particles on hair surface. In addition, we plan to develop theoretical models that will enable the prediction of adhesion forces of explosive particle to the hair surface. The obvious application of such an investigation is improvement of sample collection techniques.

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The Need for Advanced Modeling Capability for Understanding the Hazard Potential from Novel and Unknown Energetic Materials and Explosives

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Energetic materials and explosives which in quantity pose significant or catastrophic potential for damage to sensitive infrastructure or high value assets are comprised of composite energetic materials and mixtures of the same. In potential terrorist threat scenarios the explosive can be manufactured from non-standard or uncommon source materials, whose explosive or violent reaction properties may not be characterized at all, or poorly at best. Energetic material reaction rates and materials properties are notoriously nonlinear and sometimes have extreme and unanticipated state sensitivity. Manufactured materials, including ad hoc materials have huge material, reaction rate, and mixture properties variations. Understanding ignition and explosivity potential requires consideration of some well-known material being subjected to a huge range of physical and thermal insult. Thus the combined parameter space that represents explosive material composition and a macroscopic threat sized charge reaction to mechanical and thermal insult is extremely large. Experiments that are formulated to test the explosion and reaction hazards, are very expensive and in light of the extraordinarily wide range and unknown behaviors possible, especially for uncharacterized materials it is essential that experiments be designed using the best available modeling and simulation methods. Integrated experimental design and simulation maximizes the ability of researchers to profitably and efficiently to verify key concepts that mitigate explosive hazards. All national programs in the U.S. use this approach.

State of the art predictive simulation capability for explosive characterization experiments and explosive systems has been established over the past numbers of year by a long-term collaboration between Prof. D. Scott Stewart at the University of Illinois, Los Alamos National Laboratory. Stewart's group at University of Illinios has developed a very powerful and predictive suite of modeling and simulation tools (collectively dubbed DSD-TOOLS) that have been successful in making blind predictions of tests that characterize explosives over a very wide range states, [WSD-JAP], [LSYW-JFM], [DSS-AF-FinalREport], [DSS-MULTIMAT]. Importantly with Dr. John Bdzil (LANL retired Fellow), Stewart is the creator of the theory of Detonation Shock Dynamics (DSD), [AnnualRev]. The DSD-based models have shown remarkable agreement with multi-material (hydrocode) simulation, asymptotic theory predictions and experiment and have made blind, non-calibrated predictions of explosive behaviors; such as 1D gas gun initiation transients and 2D axi-symmetric, quasi-steady rate stick, critical diameter experiments and prediction of complex multi-dimensional transient detonation behavior for both sensitive and insensitive, non-ideal explosives. This predictive capability is unprecedented and unlike other models previously developed.

Work on Shock Focusing and Explosivity Characterization

Specifically, the modeling and predictive simulation capability of the Stewart-group at Illinois will be used in the design of the Shock Focusing Explosivity Test, that is a key diagnostic and hazard screening experiment that is being developed in the Center. Stewart will work closely with Dr. James Kennedy and Prof. Oxley to verify experimental design concepts and validate experimental results. Adding predictive simulation and modeling to key experiments is key to rapid and sustained progress.

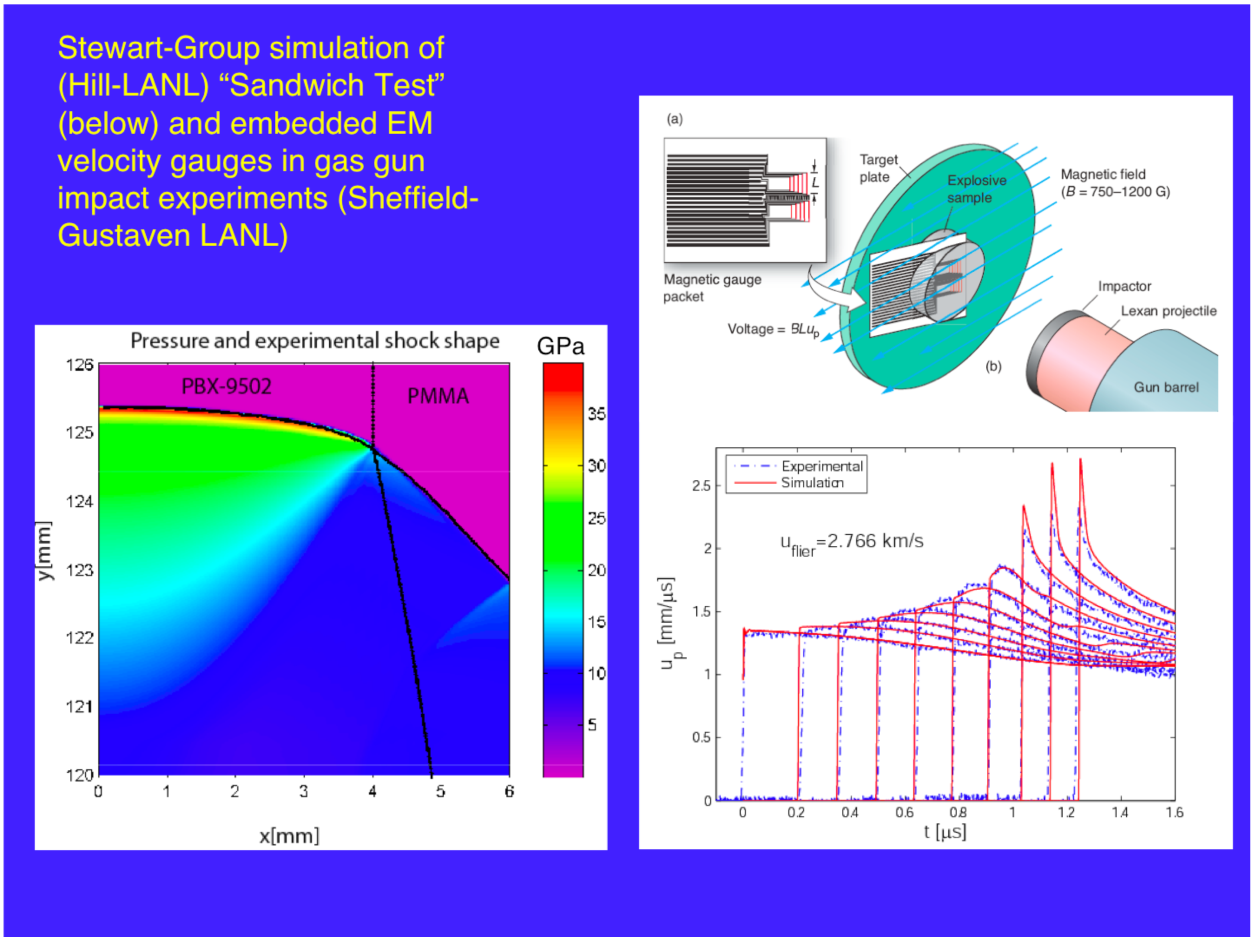

Figure 1. Shows typical prediction of the Stewart-Group model simulations with detonation propagation ("Sandwich Test") and ignition ("Impact"), with a DSD-derived model.

Work on Characterization of Unconventional Explosive for Predictive Simulation

The Stewart-Group at the University of Illinois will carry out systematic investigations to generate suitable models that can be used to describe unconventional and homemade explosive, such as Peroxide mixtures and other similar unconventional explosives. They will use proven methods of analysis to generate reactive flow models that can in turn be used to generate detonation velocity curvature data, shock to ignition transients and other standard explosive characterization experiments and data sets that are used to inform predictive simulation. By working closely with the DHS center, the Stewart group will generate a common data set for targeted materials of interest. The tools include access to state-of-the-art thermo-mechanical equilibrium codes such as Cheetah 4.0, ALE3D and the Stewart Group DSD-Tools Code Suite at the University of Illinois.

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Hair as Forensic Evidence of Explosive Handling: Are there Metabolites?

J.C. Oxley; J.L Smith; Chemistry; University of Rhode Island

Potential Scientific Impact: Persons who handle or use explosives become contaminated with traces. Traces recovered from a person's hands may be exploited to identify his involvement in the criminal use of explosives. However, as criminals become aware of trace contamination, they will make every effort to reduce the available forensic evidence, such as wearing disposable gloves. Hair captures evidence of explosive handling that cannot easily be hidden.

In previous studies, we have shown that exposure of hair to explosives results in particulate transfer onto the surface. Vapor transfer, being proportional to the vapor pressure of the explosive, was insignificant compared to particulate transfer. The persistence of the explosive in hair depends on the type of explosive and the subsequent treatment of hair. We have demonstrated that it can survive up to a week with or without washing.[1-5] Explosives may persist even longer; field studies are presently under way. Collecting evidence of explosives is not arduous; the explosive can be detected by combing the hair (see figure) or by insertion of locks of hair in an IMS inlet.[3]

Hair reflects its chemical environment. It acts to pick up substrates from environmental exposure and as a result of ingestion and metabolic activity. Detection of drugs in hair has been accepted as a confirmatory technique by the Society for Forensic Toxicology (SOFT). Hair is not only a good record of an individual's chemical exposure, read along its length, it is a historical record that cannot easily be hidden or disguised.

Hair analysis has the potential of becoming a powerful technique for providing evidence of explosive handling. However, a number of questions must be answered. One question is whether during exposure to explosive particulate and vapor, there is some degree of internal incorporation/metabolism of the explosives into the hair. Hair growth is one of the fastest cellular functions known.[8] As a result, drugs, such as heroin, can be found in the hair root bulb un-metabolized. Markers introduced into hair from metabolized explosives would be more confirming than explosives due to surface exposure.

Figs (left) collection of surface residue; **(**right) comb with clean substrate for collection

Technical Approach:

Task 1: Perform literature search of explosive metabolites. There have been numerous studies on the fate of TNT and other military explosives in soil and even plants. Furthermore, there are recent endeavors to determined explosive signatures in breathe. We will specifically look for studies of the expression of explosives in hair. A search for chemical exposure studies involving rats (i.e. LD_{50}) will be undertaken. Specifically, we will seek any studies where hair analysis was included with mortality data.

Task 2: If studies identifying metabolites from explosives are unavailable in animal studies, (e.g. rats), then we will initiate such studies in collaboration with faculty in the biology department, which houses, raises and sacrifices rats.

Task 3: Simultaneous with task 2 samples of hair will be collected from those who work with explosives. It may be that some of the explosives are so quickly incorporated, that like heroin, the un-metabilized explosive can be found in hair. Satisfying IRB[7] issues, we will ask for voluntary collection of hair. Sample collection bags would be provided for regular barbershop visits. Initially, we will examine employees of explosive production facilities who have daily exposure. However, questions of how long exposure is required will be considered, and those who handle explosives intermittently for short periods of time, such as EOD personnel and explosive researchers, will also be included. (Some of these questions can also be answered by parallel rat studies.) Hair will be examined using procedures established for analysis of hair for drugs, i.e. hair will be rinsed to remove external explosive contamination and then digested to look for targeted explosives.

Task 4: If no explosive is found in the digested hair of workers, then explosive metabolites must be sought. At this point the fruits of Task 1 and/or 2 will be employed. To aid the search for explosive metabolites the initial focus will be on analyzing for military explosives. The markers they produce are more likely to be recognized than those resulting from ammonium nitrate explosives or urea nitrate.

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Explosive particle – substrate adhesion force measurement

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Bio-Medical Engineering, Ben-Gurion University, Beer-Sheva, Israel

Adhesion force measurements – AFM

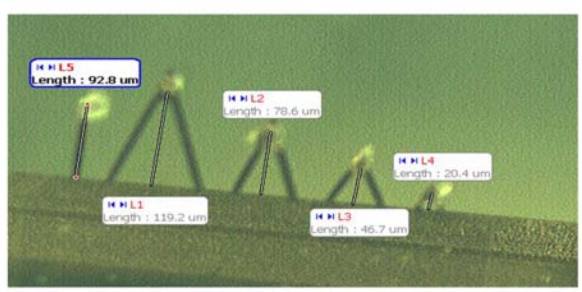
The ability to detect explosives depends on two interconnected issues: the collection of the sample and its analysis and identification as explosive. To fulfill the second part, high accurate analytical methods have been developed and utilized. The detection limit in many of these methods is well below the one required for explosive detection in most situations and environments. The most frequently used method is Ion Mobility Spectrometry (IMS). Many thousands of these types of measurements are carried out routinely every day in airports over the world. On the other hand, the sample collection is limited to quite old and simple methods. The scientific community did not devote to this issue enough effort to bring it to a high enough level that meets the detection limit of the IMS approach. Hence, in order to advance the detection limit of explosives one should first increase the sample collection efficiency.

Most of the explosives have low or very low vapor pressure. The result is that their detection is based on solid samples in a wide range of particle sizes. The size distribution of explosive particle is expected to depend on the environment they were created and the routes of their distribution. The best estimates for size distribution claim that the average size is about a few micrometers with a width of the distribution that is not well established. The explosive particles have to be collected from various substrates to which they are attached. Hence, any increase in the efficiency of their collection is expected to depend on our knowledge about their interaction with the substrate to which they are connected. This raise the need to understand the nature of adhesion forces among explosive particles and the substrates they may encounter.

In recent years Atomic Force Microscopy (AFM) became an important tool to study adhesion force between particles and various substrates [1]. The method is based on the attachment of a particle to the cantilever, usually by glue, and using this cantilever to study the force involved in the interaction between the particle and the substrate under investigation. The apparatus we built to glue explosive particles to cantilevers is shown in Fig. 1 while Fig. 2 shows RDX particles glued to a cantilever. In the force measurement the cantilever approaches the substrate until the particle is at a distance where the strong repulsion forces dominate. From this point the cantilever is retracted from the substrate and its bending at the point where it is released from the substrate is recorded. The bending of the cantilever at this point is proportional to the adhesion force. Typical measurements are shown in Fig. 3 for a 20 μm RDX particle.

Fig. 1: system used to glue particles to cantilevers.

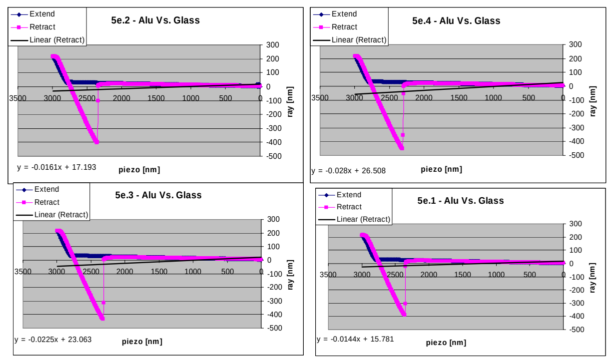
Fig. 2: Five RDX particles 15-20 mm in diameter, glued to tips of cantilever



Study in 2009

Both URI and the BGU research teams are interested in the interaction of explosives with biological tissue. Both groups published studies related to the adsorption of explosive molecules onto hair surface. We propose to extend during the present year this study to include adhesion of explosive particles onto hair. Such an investigation will constitute a natural extension of previous studies. In addition, it is important by its own merit since this might be an efficient way to collect explosive samples from suspects, due to the relatively strong chemical interaction between most explosive and the hair surface. We plan to use different color hair that will be pretreated. One group of samples will contain hair after rinsing, the second rinsed hair that was also treated by KOH+Ethanol solution to remove the fatty acids from the surface of the hair. The last group will constitute of hair that was treated by hydrogen peroxide. The adhesion forces between TNT, RDX and PETN particles and the hair samples will be examined

Adhesion measurement by Atomic Force Microscope (AFM):



Tip deflections obtained for 20 micron RDX particle over four different locations on a glass surface. The forces obtained are: 67.5, 66.0, 70.5 and 75.0 nN.

Fig. 3: Force measurement at 4 random sites on glass of 20 micron RDX particle

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GAS PHASE ION CHEMISTRY AND NON-CONTACT SAMPLING OF EXPLOSIVES

G.A. Eiceman, Department of Chemistry & Biochemistry

Potential scientific impact: In additional to physical properties of explosives such as vapor pressure and melting points, the chemical properties of explosives as gas phase ions govern both existing approaches and future possible innovations in detection technology. Moreover, knowledge of basic properties of explosives has intrinsic value to complete fundamental behavior of explosives and one goal of this work is the preparation, from laboratory measurement, of a table of lifetimes of explosive ions in air at ambient pressure. No such table exists and only in recent years have the capabilities been developed to permit such measurements (1). The impact of this work is understood to be broadly based including those interested in ion-molecule interactions with explosive molecules. The table is planned to include a range of explosives from nitro-aromatic compounds to those used in liquid and improved explosives. A second component of this work was the exploration of non-contact removal of explosives from surfaces and measures of surface interactions between explosives and materials. These studies will disclose trends in persistence of explosives and will have significance for material scientists, engineers, and those interested in trace residue analysis.

Technical Approach: There is today only one method to measure kinetics of ion decomposition and ion lifetimes and these were developed in our laboratory at NMSU (1). The methods developed resemble flow tube mass spectrometry but involve drift tubes at ambient pressure. The first step in this program was to redesign the drift tube mass spectrometer to allow a range of temperatures. We have tested the materials and designs for this and a new drift tube has been build. In addition, the mass spectrometer inlet has been rebuilt to allow precise ion kinetic measurements in air at ambient pressure.

Work to date: In the first year of work, construction of the instrument was expected to consume much of the year and this has occurred. To date, these are the accomplishments:

a. Construction of a new gas phase ion kinetic drift tube to allow precise determination of ion lifetimes. To our knowledge, this is the only instrument in the world that can make such determinations.
b. Redesign of the inlet of an API triple quadrupole mass spectrometer to accept the drift tube.
c. Study of some analog compounds to determine temperature dependence of ion lifetimes.

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Detection of Explosives Based on Optical Chemosensors Using Nanocomposites from Porous Silicon Photonic Crystals and Sensory Polymers

William B. Euler, URI
Igor A. Levitsky, Emitech, Inc.

Technical Need: New sensor array systems for explosives are being developed that meet the critical requirements of *sensitivity*, *selectivity*, and *adaptability* with dwell times on the order of seconds, giving fast detector response. The new idea in this sensor is the use of an optical resonator, a porous Si (PSi) microcavity (MC) between Distributed Bragg Reflectors (DBR), filled with sensory emissive polymers or nonemissive polymers blended with emissive dyes. A PSi-MC resonator is composed of alternating Si layers with high and low porosities (thickness of $\lambda/4$, where λ is the spectral position of the resonance peak) that forms the DBR. The MC (layer thickness of $\lambda/2$) is placed between two DBRs to provide a resonator structure (photonic crystal) tuned to the desired resonance (λ) wavelength. Photon confinement inside an optical resonator provides very narrow fluorescence peaks or a spectral "hole" in a broad fluorescent band, either of which can increase both the *sensitivity* and the *selectivity* of the sensor. An array of optical resonators filled with different sorbent polymers/dyes will provide a multiple response set for each analyte. The emission signal (fluorescent resonance peak or spectral "hole") has intensity, wavelength, lifetime, and bandshape components that will be modulated in the presence of explosive vapors. This multiplexed response provides multiple monitoring parameters, enabling the development of an optical sensor array, for the detection of target explosives vapor. The *adaptability* requirement is achieved through the signal processing algorithms used to interpret the array of information obtained from the detector. A new analyte molecule will provide a different set of responses across all of the array elements.

Technical Approach: Figure 1 shows a scanning electron micrograph of a typical PSi sensor, which has a low porosity layer at the surface. One of the issues in understanding the properties of these sensors is determining the depth of filling of the pores and the structure of the polymer in the pores. Further, we have found that samples with high porosity top layers behave differently than samples with low porosity top layers: the fluorescent emission intensity for either type of sample is similar, but the quenching by the TNT analyte is different. In particular, samples with low porosity top layers have faster quenching than samples with high porosity top layers. This is counterintuitive because simple diffusion arguments would suggest that larger top-layer pores would allow more analyte access to the polymers.

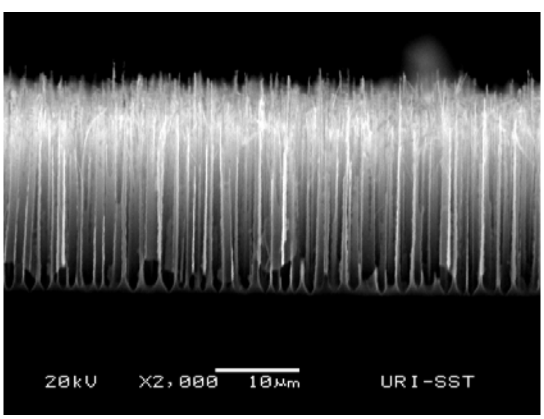

Figure 1: Cross-sectional SEM image of a DBR/MC/DBR structure.

Direct detection of the filling by elemental analysis of the pores as a function of depth is shown in Figure 2. The amount of carbon (arising from the polymer) abruptly decreases at about 3 µm while the silicon and oxygen increase (both from silicon oxide) at the same depth. This indicates that the polymer is filling through 3 µm of pore structure, which is then the limiting amount of transducing agent in the sensor.

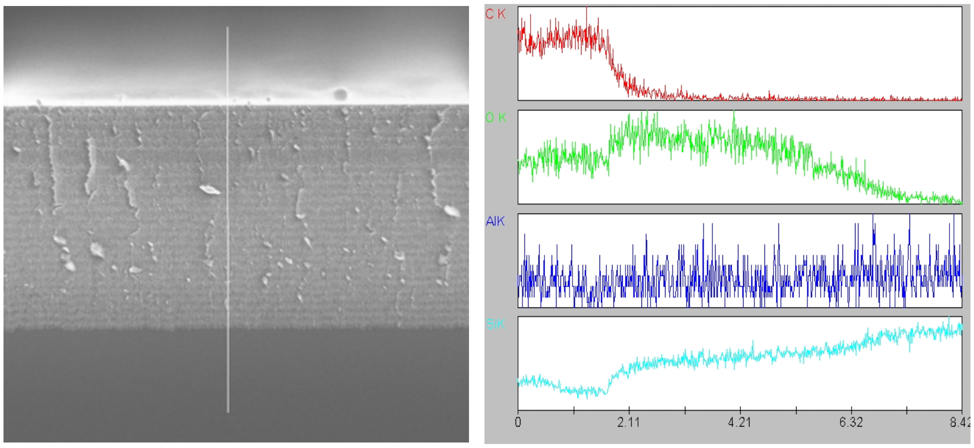

Figure 2: Left: SEM image of a porous layer, with the projected path of the line test. Right: EDS measurement of relative concentrations of each element as a function of depth into porous layer. The red line is C, the green line is O, the blue line is Al (as a control), and the cyan line is Si.

The sensor mechanism of action relies on two properties: the amount of polymer available to interact with the analyte (TNT in this case) and the refractive index changes found across the pore. Figure 3 shows an analysis of the refractive index as a function of depth and pore size. The striping in the figure shows the effect of layering of the sensor.

New Tasks:

1) Determine the photostability of the active polymer in the porous silicon structure.

2) Add agents that improve fluorescent energy transfer between the analyte and the polymer. One reagent identified is 7,8,10-triphenylfluoranthene.

3) Find new porous substrates to build sensor platforms. Work has begun on using nafion (which has porous pockets in hydrophilic regions of the polymer) and sol-gels (which can be designed with defined pore structures).

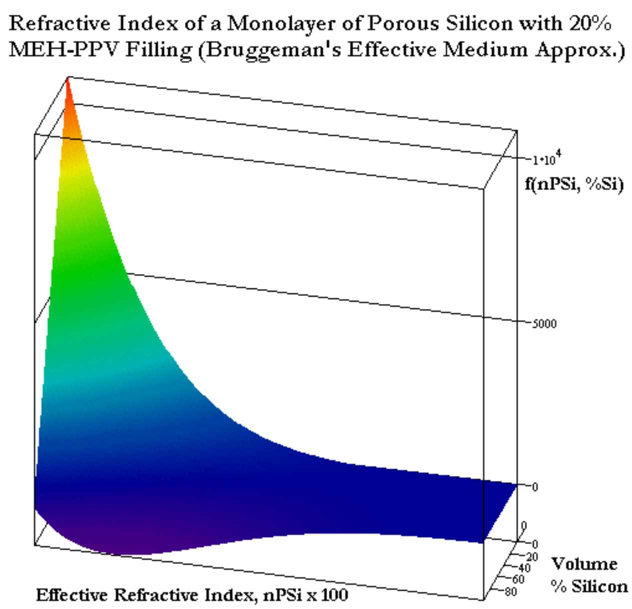

Figure 3: Refractive index profile as a function of pore size and filling.

Detection of Explosive Precursors using Transition Metal Oxide Catalysts

Prof. Otto Gregory, URI, Chemical Engineering
Michael Platek, URI Electrical Engineering

Potential Scientific Impact: The detection of explosive precursors in suspected "bomb labs" and other enclosed areas that terrorists may target for the deployment of improvised explosives is the overall goal of this project. In such scenarios, the early detection of specific gas molecules without interference effects from background gases is essential. The sensor system must be sensitive enough to detect minute concentrations of these target gases yet not generate false positives in environments such as subways, train stations and other confined spaces where the public may be targeted. The initial focus of our work is on the class of explosives based on ammonium nitrate compounds and related compounds containing inorganic nitrates that are used in improvised explosives. Specifically, inexpensive, portable sensors tuned for ammonia and NO_2 under pre-blast conditions are currently being developed. Many gas detectors in the field suffer from marginal specificity, where background gases can confuse the output of the sensor yielding false positive and/or negative indications. We have been developing a sensor platform using transition metal-oxides as catalysts to unambiguously detect minute concentrations of specific gas molecules. This sensing capability is retained in the presence of both high concentrations of background gases and high concentrations of closely related gas molecules; e.g., ethanol vs. isopropanol. Originally, these sensors were envisioned for deployment where deliberate or accidental release of toxic gases could affect public health and safety.

Catalyst development and characterization of the sensor platform is currently being done in the Sensors and Surface Technology Laboratories at URI and the signal conditioning protocols are being developed by SensorTech (Savana, GA). To date we have explored V_2O_5, $AgCoO_2$, CuO and FeO and TiO_2 as catalysts for the detection of ammonia with promising results (see Figure 1). The current and proposed research will utilize combinatorial chemistry techniques to develop novel combinations of transition metal oxide catalysts for the existing sensor platform. The sensor platform consists of an array of small microheaters deposited directly onto alumina or other substrate along with small thin film thermocouples (Figure 2) for temperature monitoring. The sensors are thermally scanned (using controlled input power) and the power difference between a reference microheater and a catalyst-coated microheater is detected and the response recorded as a function of temperature. Thus, the technique measures the differential power response (thermodynamic response) and not a response based on the electrical conductivity changes or associated electrical resistance changes of the catalyst upon exposure.

Technical Approach: We have been employing combinatorial chemistry techniques as part of the development strategy to prepare new catalysts based on transition metal oxides. Combinatorial libraries are typically prepared onto arrays of nickel microheaters formed on individual alumina plates using microlithography techniques (Figure 2). The sensor elements can be snapped from the perforated alumina plate and mounted in connectors for insertion into a multi-sensor configuration and then exposed to gas flow (Figures 3 and 4). The responses of up to nine individual sensors representing various material combinations achieved by co-sputtering are then compared to each other. This configuration is extremely useful for screening catalysts and identifying catalyst activity. However, since the sensitivity and response are somewhat limited by the available surface area of the microheater elements, carbon nanotubes are now being applied to the surfaces of the microheaters prior to the deposition of the catalysts to enhance the sensitivity and response. To date we have explored V_2O_5, $AgCoO_2$, CuO and FeO and TiO_2 [5] with some success without the use of carbon nanotubes. Thus, we are now investigating the use of these same catalysts by depositing the catalysts onto the nanotubes. In addition, ZnO has considerable promise as a catalyst for ammonia [1-4]. Thus, aluminum and alumina doped ZnO as well as ZnO combinations with FeO and other transition metal oxides will be prepared by co-sputtering to form combinatorial libraries. In addition, palladium will be deposited underneath the ZnO catalyst to enhance the response via the release and subsequent adsorption of hydrogen. These approaches will be tested with the apparatus shown in Figures 3 and 4. In this way, a range of catalytic compositions (i.e., transition metal oxides) will be developed for ammonia and NO_2 for the purpose of improving the sensitivity and response of the existing sensor platform.

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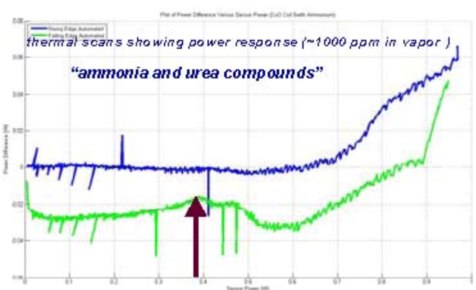


Fig 1. Response of CuO catalyst to 1000 ppm NH_3

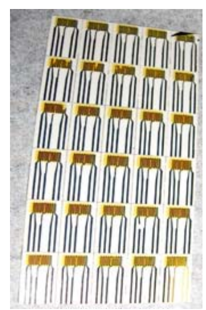
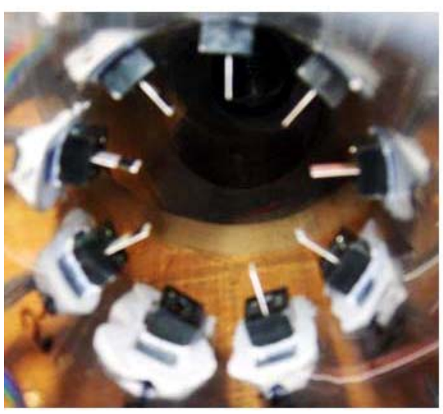
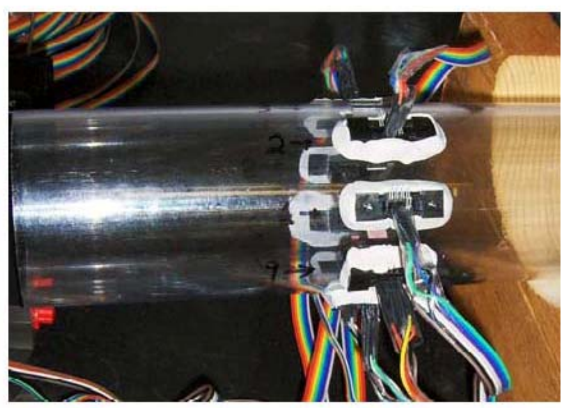


Fig 2. Array of thin film microheaters





Figs 3 and 4. Testing apparatus for the screening of potential catalysts for NH_3 detection.

Note: perforated alumina plates are snapped into individual sensor elements and mounted in connectors for insertion into a multi-sensor configuration and exposed to gas flow.

Remote detection by direct illumination

Dr. Talya Arusi-Parpar, and Dr. Shlomo Fastig, NRC Soreq, Israel.

Potential scientific impact:

The detection of Improvised Explosive Devices (IED) is a major Homeland Security challenge. Two most common detection approaches include penetrating radiation (Gamma or Neutron) and detection of explosive traces found on the device due to contamination during the preparation process.

Irradiation of explosives by laser can produce a variety of interactions that can give an indication about the irradiated material. Remote detection of explosive traces by laser photo dissociation holds promise for effective and fast identification of suspected objects, since it can reveal the presence of trace amounts of nitro containing explosives.

We used the PF (Photodissociation Fluorescence) method to detect explosives in the vapor phase. This method can detect nitrogen-based explosives and does not need any database such as Raman and LIBS. The development of Enhanced PF made it possible to detect 100 microgram/cm^2 explosive mixed in soil from a distance of 30 meters. This capability was demonstrated at Soreq, January 2008, in open environment. Recently we applied the PF method on explosive traces, by illumination of the explosive solid.

The main goals of our proposal include the understanding and optimizing the direct irradiation detection method. We propose to investigate the physics behind the process and the detection sensitivity as a function of irradiation intensity, trace material and the contaminated substrate. Various issues ranging from basic physics to dependence on various targets have to be addressed, while dedicated experimental tools have to be developed.

Technical Approach:

In a preliminary experiment, we detected two microgram/cm^2 of RDX. Although experimentally demonstrated, this mechanism is still not well understood. Therefore we propose to focus our research on the investigation of the use of PF by direct illumination of solid traces.

We will use the experimental system that we have built while developing the PF method. A tripled Nd:YAG laser that pumps a narrow-linewidth OPO system will be used as the laser source. A custom-made laboratory detection telescope will be used as the receiver coupled to a signal processing unit. Different explosives will be investigated by this system.

The first phase of the program will deal with theoretical and experimental investigations of the ablation mechanism relevant to our context. This phase will contain also the assembly of a dedicated experimental setup. We will use the existing infrastructure in Soreq for diagnostics and chemical analysis.

The second phase will study in more detail the strength of the effect as a function of different material parameters, such as influence of various substrates, different target materials (standard explosives, home-made), different distribution of the explosive material on the contaminated objects.

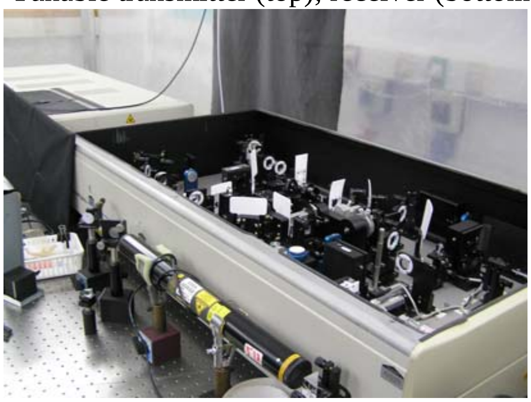
Task 1: *Development of experimental tools:* Irradiation by UV source: understanding of the physics behind the ablation process. Dependence on the flux of the irradiation and the way/geometry the target is irradiated.

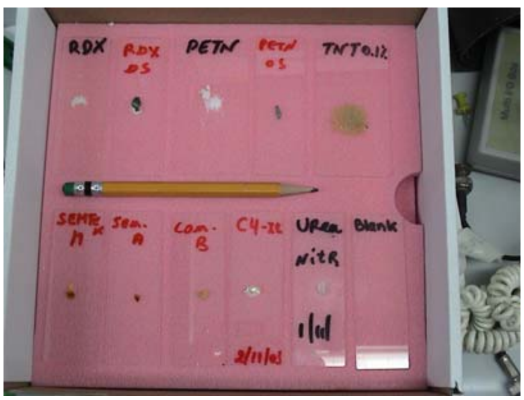
Task 2: *Target and substrates compatibility:* Evaluation of the contribution of numerous parameters to the PF detection sensitivity such as the kind of material, its physical and chemical properties, its distribution on a specific substrate, the influence of the substrate itself, the footprint of the explosive material, the effect of evaporation when irradiating a non-pure material such as explosives with plasticizer, or the presence of explosive material mixed in sand, etc

Task 3: *Sensitivity study:* Evaluation of detection thresholds as a function of concentration for different kinds of explosives and different substrates.

Work to date: Literature survey.

Tunable transmitter (top); receiver (bottom right); explosive samples (bottom left)





Terahertz spectroscopy for explosive detection
Prof. Martin Koch, Terahertz Consulting, Germany

Potential scientific Impact: The fortunately disrupted terrorist plot of bombing an aircraft with liquid explosives in London, August of 2006, exposed again breaches in the existing security systems for passengers and luggage control: While metallic items are reliably detected by portable and stationary metal detectors, other sources of danger like explosives can not be as easily found. Especially the strong restrictions which apply on equipment employed in passenger scans to protect the traveler's health make security scanning a very challenging task. For example, x-ray scans on persons, which would visualize hidden objects, are prohibited by law for security scanning purposes as they would impose a risk on the traveler's health. Thus only manual control is used nowadays to find hidden hazardous substances on the body or in the clothing of passengers. Terahertz waves are able to penetrate clothing, but are absorbed by the water content of the human skin, so that sensors based on non-ionizing, innocuous terahertz technology will provide the means of filling this security gap in the near future.

However, even very small amounts of a liquid explosive would be sufficient to inflict fatal damage on a plane. This group of materials is very hard to detect with existing devices installed in airports. In order to close this significant security breach, new mobile detection schemes, which provide sensitive, non-destructive, contact-free and innocuous security scanning, have to be developed.

Terahertz spectroscopy is a promising candidate for the detection of hazardous materials. It uses the interaction of electromagnetic fields with matter in the terahertz frequency range between 300 GHz and 10 THz to obtain a spectroscopic footprint of materials. The generation and detection of sub-millimeter waves have been very complicated for a long time. In recent years, researchers managed to conquer this frequency range between optics and electronics with efficient optoelectronic transmitter and receiver devices. The advantages of employing THz radiation result from its innocuousness for humans and the transparency of clothing and packaging materials (e.g. plastics and paper). With terahertz spectroscopy, explosives should be detectable even if they are kept in a closed bottle, a closed suitcase or hidden beneath the clothing.

Technical Approach: Terahertz consulting will provide a written report which will evaluate the potential of terahertz spectroscopy for detecting explosives and explosive devices. The report will also address the needs, data gaps, and the players in the field of terahertz technology. To this end terahertz consulting will continuously screen the scientific literature on spectroscopic investigations on explosives and on system improvements as well as observe the market for terahertz systems. It will discuss its findings with other partners of the Center of Excellence, especially those working in the field of terahertz systems.

Work to data:

Literature survey

Read several papers on THz spectroscopy on explosive chemicals

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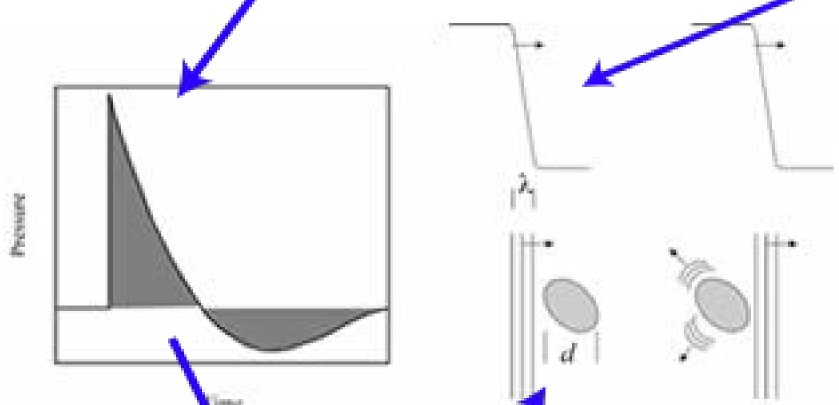
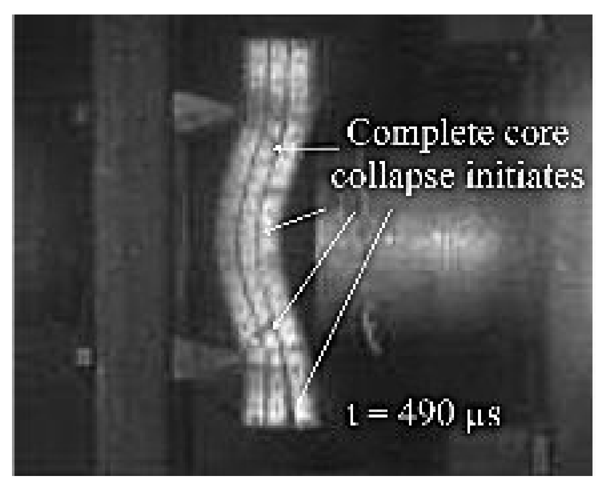
MITIGATION: Forestalling the Inevitable

Laboratory & field-scale experiments conducted to understand explosion propagation to structural systems coupling. Proper knowledge of this interaction provides relevant input parameters to fluid-to-rigid body coupled numerical models.
Shepherd (Caltech)

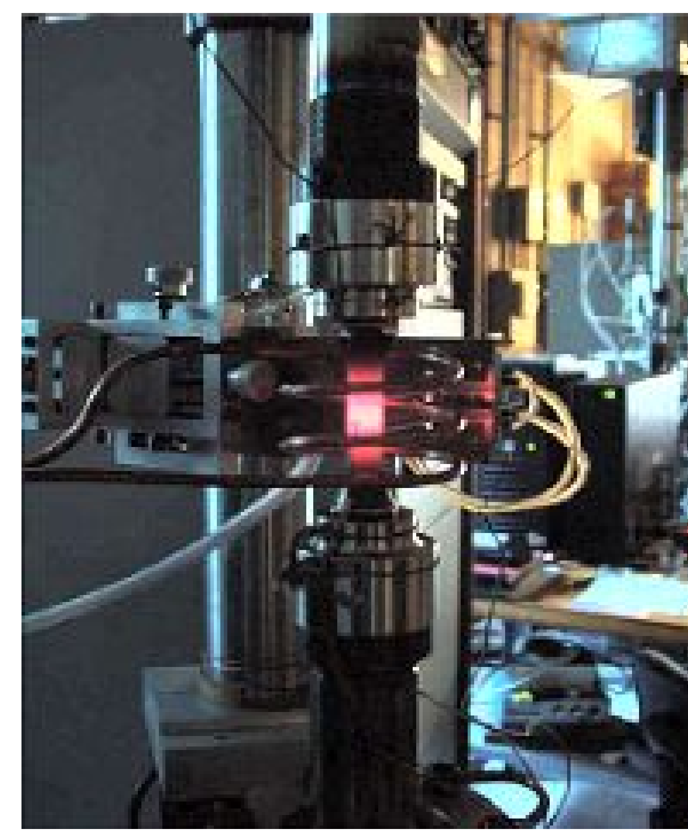


Established stress waves due to explosive events are used to impose dynamic loading upon diminutive specimen for study of local & microstructure response. Determination of material microstructure better suited for stress wave attenuation.
Rousseau (URI)

Materials identified as promising at the microstructural level are scrutinized for global response using scaled explosions, fluid, & solid dynamic impelling at varying temperatures. Satisfactorily tested materials will be identified as potential shields or for structural components.
Shukla (URI)



Structural steel response at combined high strain rate/thermal exposure loadings resulting from sever blast conditions. Determination of constitutive laws accounting for damage accumulation and providing a criterion for deformation instability.
Ghonem, Gregory (URI)



Mechanical and Material Performance of Reinforcing Phase of Civil Structures under Blast Loadings

Prof. Hamouda Ghonem* and Prof. Otto Gregory**
***Mechanical and **Chemical Engineering, University of Rhode Island**

Potential Scientific Impact: Structure design requirements to resist extreme environment associated with blast loadings are established on the basis of life safety and not in terms of life-cycle performance. On the other hand, post-blast performance criteria for critical structures, such as, bridges, tunnels, nuclear reactors, refinery complexes and explosive storage facilities, require serviceability and reuse. Under this condition, designs for post-blast survivability rely on the load transfer to the reinforcing phase of the structure and its ability to provide resistance to the combined dynamic/thermal loadings associated with a severe blast. This resistance can be achieved through the utilization of the plastic and viscoplastic response of the material in a manner that absorbs damage locally, so as to not compromise the integrity of the entire structure. The performance of the reinforcing phase must then be examined under the assumption that the blast damage has resulted in the compromise of the concrete/reinforcing phase interface and thus a full load transfer to the reinforcing phase has occurred. Assessment of this performance can, generally, be made through the use of non-linear analytical or numerical simulation techniques (1-3) which require as a key input to their formulations, the knowledge of the evolution characteristics of the material and mechanical properties of the reinforcing phase as a function of blast loading parameters. This type of simulation is essential in efforts aiming at both defining the global and local damage resistance of a structure and for the design of blast mitigation approaches being extrinsic (shock waves' attenuation designs and/or redundant load carrying phase) or intrinsic (modified or new reinforcing phase).

In almost all existing critical facilities, structural low carbon steel is the prime reinforcing material. As such, the goal of this research is to develop a fundamental understanding of the mechanics and mechanisms of deformation of structural steel subjected to shock wave/thermal shock loadings. Results of this experimental/numerical study will provide the basis to establish a criterion for the collapse of steel reinforced structure under blast conditions. This criterion is an essential component in the design of blast mitigation approaches. The research tasks to achieve the goal of the currant study can be summarized as follows.

Task I: Dynamic/Thermal Response: Loadings of reinforced concrete structures subjected to blast consist of coupled (or sequential) high strain rate and thermal shock. High strain rates which could reach up to 1000 s^{-1} can alter the hardening characteristics of the reinforcing bars with the potential that yield can increase by 100% or more, while available ductility is reduced significantly. In addition, thermal exposure (shock) can reach temperature levels capable of introducing microstructure phase transformation impacting the mechanical properties. The thermal shock could also introduce thermal strain gradients across the steel bars/concrete interface thus causing interface de-cohesion and consequently a full load transfer to the steel bars. The purpose of this task is to quantify the plastic exhaustion in structural steel as a function of explosion energy and determine the influence of combined explosion/thermal exposure on the material creep and fracture toughness. In addition, work will be carried out to determine damage initiation defined in terms of rate of accumulation of progressive inelastic deformation and failure criterion associated with strain instability. The shock wave loading will be achieved using a steel vessel subjected to controlled explosion or by subjecting steel coupons to dynamic high strain loading. Reference data line will be obtained from microstructures of test specimens subjected to thermal exposures alone. A facility capable of delivering thermal shock of 30 KW in a very short period of time is shown in Fig. 1.

Task II: Modeling and Validation: In order to model the structural material response to blast loading, a visco-plastic constitutive law that takes into consideration the evolution of time dependent kinematic and isotropic hardening properties will be developed (4). The material parameters required for the validation of the constitutive law will be generated using steel specimens subjected to a set of measured shock waves energies coupled with and without thermal exposure. These equations which currently do not exist will be examined by comparing their simulation outputs with those experimentally obtained. The reliability of the viscous flow equations will be examined using optimization techniques and comparisons with steel members subjected to controlled blast conditions.

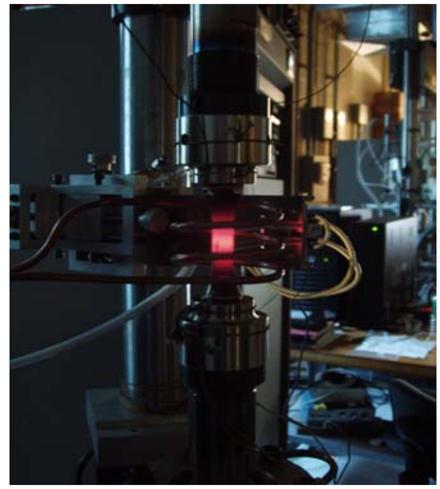


Fig. 1: Thermal shock of structural steel bar (30 KW)

Task III. Blast Survivability Criterion: Simulation of failure events will focus on two structures; bridges and tunnels, subjected to combined dynamic/thermal blast loadings. The former structure represents a mixed steel frame and reinforced concrete while the latter is a fully reinforced concrete structure. The FE simulation will be performed as a sequential process employing material parameters and constitutive laws being developed in Tasks I and II described

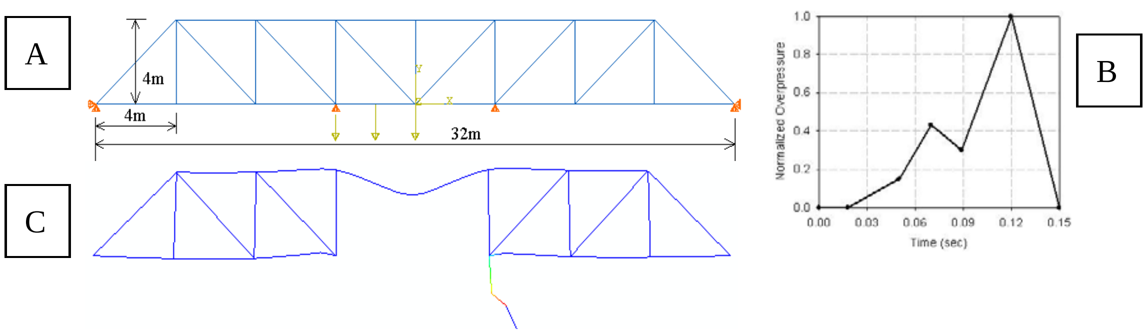


Fig. 2: A) Pre-blast bridge geometry and support BCs; B) Shock wave profile and C) Post-blast geometry

above. A preliminary result of a simulation of a bridge structure under dynamic load only is shown in Fig. 2.

Work to Date

1. Microstructure characterization of steel structure under thermal exposures is being performed.
2. Deformation response under different thermal exposures levels has been completed
3. Development of a FE simulation of coupled shock wave/thermal loadings is underway.

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Integrated Approach for Blast Mitigation of Critical Civil Structures

A subtask in the mitigation research efforts is to focus on blast mitigation of critical civil structures. Work in this task is based on linking two components pertaining to explosions: energy analysis; and material and mechanical resistance of reinforcing phase of concrete structures. The first component deals with a novel solution accounting for the total energy associated with a blast. This will involve high-strain-rate fragmentation analysis, materials characterization, numerical simulation of pressure wave propagation, and energy of impact calculations. The damage signature left in structural materials following a blast will be correlated with the intensity of the event. Signatures are expected to be manifest in work hardening, residual ductility and toughness measurements. In this, all the energies associated with a blast will be accounted for and boundary conditions for shock loadings and thermal excursions would be mapped as a function of the yield of weapon. The second component of this task deals with effects of blast dynamic/thermal loadings on the reinforcing phase of the affected structure. This is examined from the point of view that blast loadings are capable of delivering horizontal and lateral impacts in addition to uplift pressure with a severity that can cause concrete separation from the reinforcing phase. A criterion for the collapse of a structure will be defined in terms of the rate of accumulation of progressive inelastic deformation and strain instability of the reinforcing phase. These laws will be determined through novel experimental/numerical methods that take into consideration the evolution of time dependent kinematic and isotropic hardening properties of the reinforcing phase. This criterion while represents the limit of the survivability of a structure, provides the guidelines for blast-protection designs. Therefore, this integrated approach for blast mitigation investigates the complete cycle starting with calculation of explosion energies which provide input loading boundary conditions to assess the structure reinforcing phase deformation and damage criteria as well as establishing parameters for blast resistance protection designs. These two interactive research topics are:

- Total energy analysis of model IED devices (Otto Gregory (Chemical Engineering), Hamouda Ghonem (Mechanical Engineering), Jimmie Oxley (Chemistry))
- Mechanical and material performance of reinforcing phase of civil structures under blast loadings (Hamouda Ghonem (Mechanical Engineering) and Otto Gregory (Chemical Engineering))

Details of each of theses topics outlining potential scientific impact and planned experimental/analytical and numerical work are reported below.

Mitigation by Erection of Efficient Barriers
Carl-Ernst Rousseau, URI

Potential Scientific Impact: One of the primary focal points of security agencies resides in their endeavor to find means of diverting the effects of ballistic or explosive events. Furthermore, structural constraints related to weight and volume call for the innovative use of material combinations such as composite heterogeneous materials that will provide appropriate shielding while maintaining structural integrity. Such materials typically would include various types of particulate reinforced phases, as well as hollow phases. The behavior of such multi-phase materials under dynamic conditions is complex since considerable wave interaction and local failure will exist within the material microstructure. Attempting to optimize dynamic material properties for protection, therefore, necessarily calls for thoroughly understanding micromechanical behaviors and how to create particular material fabric that will provide desirable response. We intend to investigate and quantify such behaviors, primarily, in model materials. Attention will focus on the behavior of the microstructural components as a function of particle size, shape, and layout within the material system and thereby explore how local microstructural interactions or failure can be related to the macroscopic response. Better foundational understanding of the dynamic response of existing, as well as new material systems, either under current consideration by other agencies or of our own design, will have wide range of direct applications to body armor, building, and infrastructure protection, as well as weight lightening of armored and military vehicles.

Technical Approach: Various means of dissipation of the energy imparted by a bullet, projectile, shrapnel strike, or by an explosion will be sought. In all these various cases, the stress wave generated will propagate within the material, conveying damage along its path. Our goal is to minimize such damage, thereby, the focus on attempting to control both the magnitude and the breadth of the propagating stress. In addition to particulate and other types of composites, as well as biomimetic inspired material systems, certain methodologies such as purposeful induction of areas of local collapse, may constitute natural energy sinks, or diverting means by which we may achieve our mitigation goals.

Task 1 - Stress Attenuation: The effectiveness of each material system will be determined primarily through a stress wave propagation method, where stress attenuation over a specific distance within the material will be recorded by means of embedded piezoresistive stress gages.

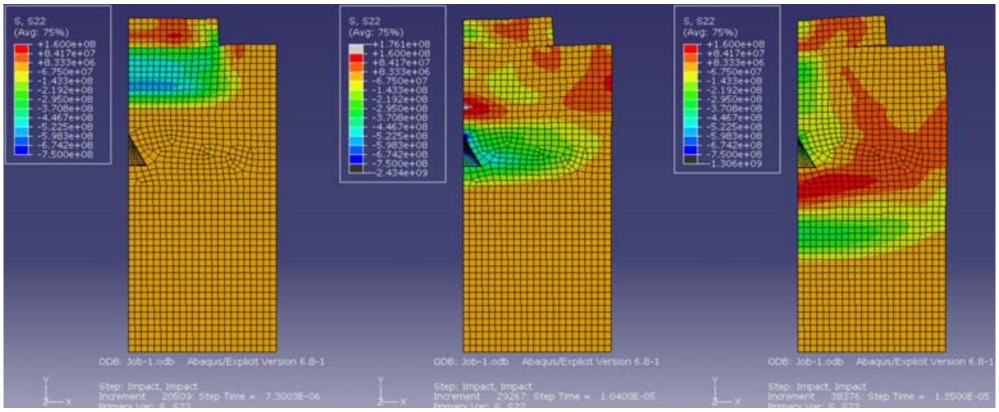
Tasks 2 - Internal Friction: Inherent internal friction within the material will be sought as this effect will dampen the influence nefarious external effects.

Task 3 - Stress Wave Scattering: At least as important in heterogeneous material, is the scattering or dispersion across grain boundaries, and at particle or material interfaces. This mechanism generates complex stress wave interactions that can greatly diminish stress propagation-induced failure. Thus, our goals here is to enhance the scattering mechanisms though manipulation of the microstructure.

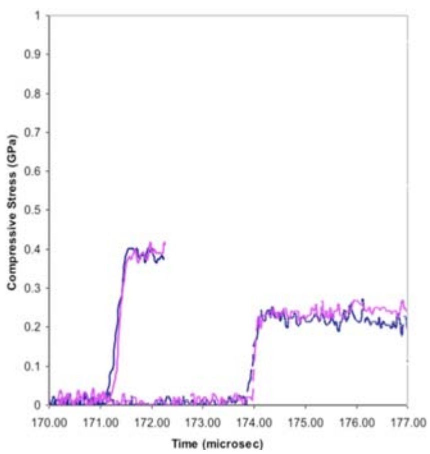
Task 4 - Numerical Modeling: We will perform finite element simulations aimed at guiding the direction of the experiments. Conversely, each experiment will be simulated numerically in an attempt to establish better simulations techniques. Upon correlation of specific empirical and numerical data, the latter can then be used to obtain full-field, detailed information about the material behavior.

Work to date:

1. Development of in vacuo chamber for increased testing reliability.
2. Preliminary experiments illustrating the overall influence of material gradation, and most importantly the directionality of the gradation, on an impact event.
3. Preparatory finite element computations aimed at guiding upcoming experiments, focusing primarily on the influence of particle geometry.



Finite element simulation illustrating the effects of inclusion geometry. Impact from a projectile, at the top, results in stress propagation, which is locally amplified at the asperities of the inclusion.



Stress signature from the impact of a homogeneous specimen, showing stress wave attenuation due to internal friction within the material. Two consecutive experiments result in identical levels of attenuation. The optimal injection of inclusions, with varying volume, size, or geometry, as well as voids, will result in ideal level of stress decline.

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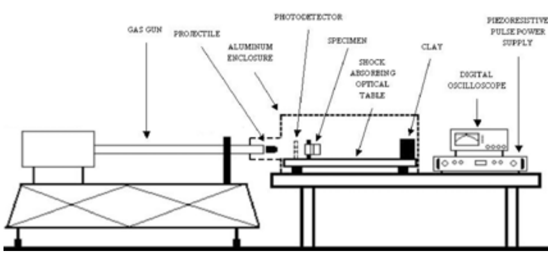

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Novel Composite Materials and Structures for Blast Mitigation

Arun Shukla, Mechanical Engineering, University of Rhode Island

Potential Scientific Impact: Composite materials have replaced metals in various engineering applications due to their numerous advantages, such as high strength/weight ratio, low cost, better stealth properties, etc. They are widely used in the defense industry (applications like naval ships, warplanes, and armored vehicles), aerospace industry (applications like wing construction, tail construction, fiber composite bodies) and transportation industry (lightweight bodies for buses and trains, composite truck bodies). In recent times, threats to such defense (USS Cole and Army Vehicles) and civilian structures (Oklahoma City bombing in 1995) in the form of terrorist attacks have added to the significance of comprehensive understanding of material and structural damage behavior under blast loading, in order to design and fabricate these structures to withstand such loadings. Difficulties with measurements associated with blast loadings have limited the extent of applied research in this area. But with growing concerns on safety and human lives involved, the significance of such a research cannot be understated.

The goal of this research is to investigate the blast resistance and the dynamic failure behavior of novel composite materials and structures subjected to extreme environmental conditions associated with blast and fragment loading. The results will help to understand the performance and the mechanisms of the dynamic failure of those structures. It will also provide a guideline for an optimal materials and structures system design for blast mitigation.

Technical Approach: The dynamic response of the materials used in novel composite structures will be experimentally studied by Split Hopkinson Pressure Bar apparatus. Composite structures will be subjected to a highly controlled simulated blast loading, which is generated by a Shock Tube (Fig. 1). The blast pressure profiles will be recorded by the high-frequency-response pressure transducers mounted on the shock tube. The real time deformation (Fig. 2) will be captured by three high speed digital cameras. The failure mechanisms will be analyzed by Digital Image Correlation and post mortem examinations. Also, the energy absorption capacity of the materials and structures will be estimated from the experimental data.

Task 1: Dynamic Response of Soft Core Materials: The performances of the sandwich structure under blast loading are highly controlled by the properties of the core materials. The dynamic response of different core materials will be studied by Split Hopkinson Pressure Bar apparatus. The related parameters such as the dynamic stress-strain curves, dynamic energy absorption abilities and strain rate effects on mechanical properties will be obtained and compared.

Task 2: Blast Loading Response of Sandwich Panels: Blast mitigation property of the sandwich panels can be improved by having different core designs. Composite materials having different core designs will be studied for its energy absorbing capacity and an optimized core design for better blast mitigation will be worked upon.

Task 3: Blast Response of Coated Panels: There are various existing structures which are already there and it's hard and costly to replace them with new novel materials. For these types of structures, the coated panels having blast absorption capabilities would be a good solution as they can be coated to impart blast mitigation properties.

Task 4: Blast Response of Panels at High Temperature: Buildings are exposed to varying temperature from low temperature (~-40^{o}F) in Alaska to high temperature (~120^{o}F) in Arizona. The behavior of sandwich panels and coated panels at these varying conditions should be studied as these structures are to be used under these conditions.

Task 5: Energy Absorptions in Panels: The properties of blast mitigation of the panels are main focus of the homeland security. The theoretical analysis to calculate the energies absorbed and reflected by the panels will be proposed based on the experimental data. These calculated energies will be used to estimate the performances of blast mitigation of the panels.

Work to Date:

1. The dynamic constitutive behaviors of some foam core materials have been obtained.
2. The blast loading experiments of the sandwich structures with stepwise graded foam core materials have been conducted.
3. The theoretical methods to calculate the energy of the incident shock wave, the reflected shock wave and the energy that deforms the specimen have been proposed based on experimental data. The performances of the sandwich structures are being analyzed using these data.

Figure 1: Shock tube facility.

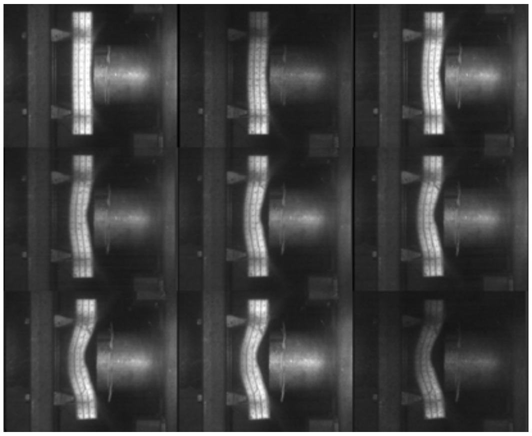

Figure 2: High Speed Images.

Structural Response to Internal Explosions

Joseph E Shepherd
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January 24, 2009

This subproject addresses fuel-vapor cloud explosions inside typical residential and commercial buildings. The focus is on developing an understanding interaction of flames in a yielding structure and developing quantitative models to predict damage.

Importance to DHS

Exploding vapor clouds inside structures result in a wide range of damage that is difficult to predict. Our goal is to improve the understanding and predictions of these events. This is important to DHS and other agencies for both evaluating threats and explosion hazards (predicting damage) and developing mitigation methods (strengthening structures).

Approach

The research will use a combination of subscale experimentation and numerical simulations to study the development of explosions and response of model structures with known failure modes to internal deflagrations and detonations. The educational component will be teaching explosion dynamics and structural response to graduate students, postdoctoral researchers, and professionals through seminars and workshops, class room teaching, laboratory, and field experiments.

Progress to date

The mode of combustion, deflagration vs. detonation, and the peak pressures and impulses depend crucially on the extent of motion of the structure during the explosion event. We are designing a model structure which consists of a box with panels that will fail at predetermined pressure. Deflagration experiments will be carried out inside of our blast room using these models. Diagnostics will include high-speed photography, pressure, and strain measurements.

Next Year

Based on the lab testing from this year, next year we will develop approximate methods for describing the development of the explosion and extent of damage to the structure. Our goal is to develop methods that are useful for analyzing potential explosive hazards or investigating accidental or deliberate non-ideal explosions inside a structure.

Self-Healing Materials for Autonomic Mitigation of Blast Damage

Nancy R. Sottos and Scott R. White
Beckman Institute for Advanced Science and Technology
University of Illinois Urbana-Champaign

Summary

Self-healing composite structures will be developed to mitigate blast damage. A two-phase research program is proposed to incorporate self-healing technology in a variety of platforms including civil based structures and vehicles. The first phase of the project will involve the integration of microencapsulated healing agents into polymers and polymer composites. Short-term objectives will focus on the healing of larger scale damage through the use of expanding healing chemistries and novel autonomic crack closure mechanisms. The second phase of the research will expand the investigation to the use of novel composites with internal microvascular systems to heal and potentially regenerate damaged regions.

Technical Approach

For autonomic mitigation of incoming threats, four domains of strategies can be defined based on the relative timing: obscurance, interception, energy absorption, self-healing. *Obscurance*, protects the object (e.g. vehicle, structure) before the projectile is fired either by reducing its detectability or by changing its apparent location or identity. *Interception* places a protective barrier at some distance from the object before the projectile impacts to reduce or eliminate damage. *Energy absorption* reduces the damage after impact through deformation of some non-functionally critical material. Finally, *healing* allows damage to occur to the object, but the material can repair itself. Adaptive materials and structures have the potential to provide solutions to each of these strategy domains.

We propose to develop self-healing polymer composites capable of mitigating blast damage. While external armor is designed to absorb the primary energy from a blast, significant damage also occurs deep within a structure. This secondary damage can impair function and lead to failure even if the structure survives the initial explosion. Autonomic healing this of secondary damage can significantly improve reliability and safety by providing recovery of structural integrity.

Background

Self-healing materials are inspired by living systems, in which minor damage (*e.g.*, a bump or bruise) triggers an autonomic healing response. In biological systems, chemical signals released at the site of fracture initiate a systemic response that transports repair agents to the site of injury and promotes healing. The general concept for autonomic healing is illustrated in Fig. 1. Successful self-healing has been demonstrated in polymers and polymer composites using microencapsulated healing agents (Fig. 1a,b) [1-3] and more recently via microvascular networks (Fig. 1c) [4]. When damage occurs a crack will form and eventually propagate until it ruptures a microcapsule that contains a healing agent. The healing agent is then transported to the crack plane where it encounters a second phase that initiates polymerization and rebonding of the crack faces. Recovery of mechanical properties occurs without manual intervention (Fig. 1d). High levels of healing efficiency have been achieved under both static and dynamic loading conditions. Self-healing technology has significant potential to mitigate damage induced by a detonation and enable recovery of structural properties, thereby increasing protection of vehicles, base structures and personnel.

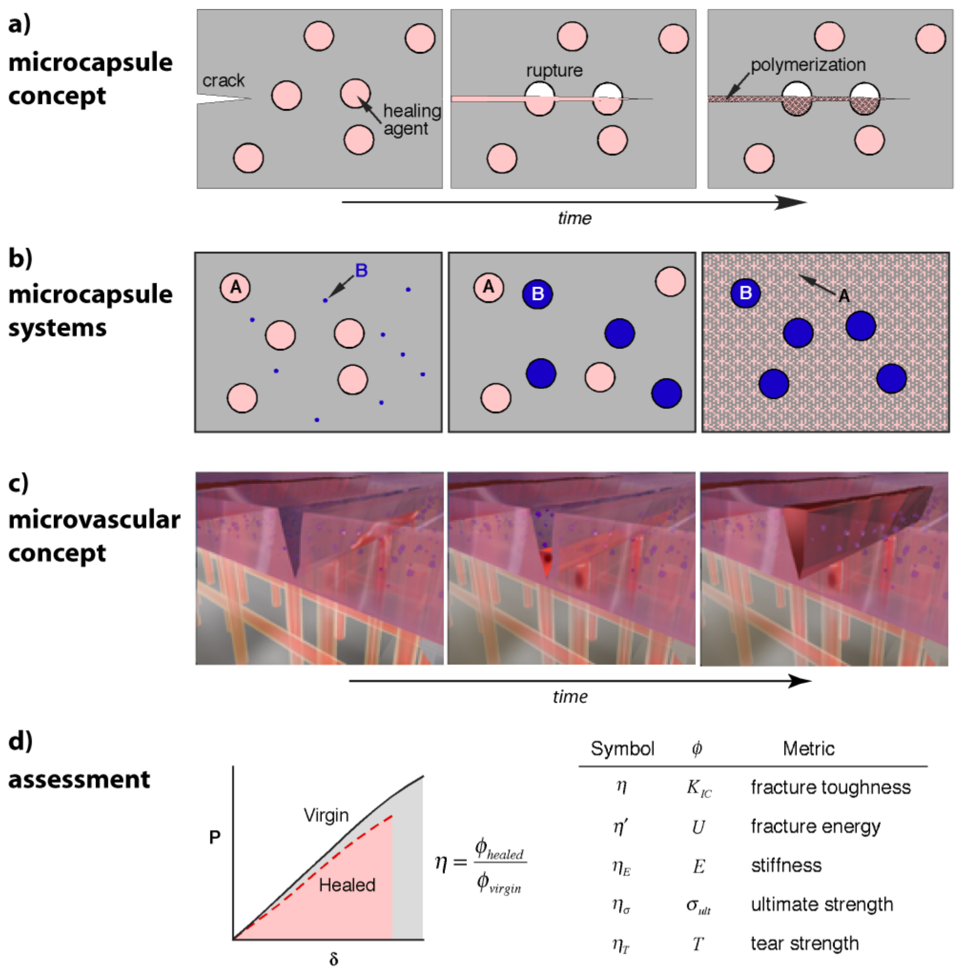

Fig. 1. Autonomic healing of mechanical damage in polymers. a) Underlying concept in which damage (crack) triggers the healing response by rupturing embedded microcapsules that contain a healing agent which polymerizes in the crack plane rebonding crack faces. b) Types of autonomic healing systems: left – healing agent (A) is encapsulated and catalyst (B) is dispersed in the polymer matrix, center – both the healing agent and catalyst phases are microencapsulated and dispersed in the matrix, right – the healing agent is phase separated in the matrix and the catalyst phase is microencapsulated. c) Microvascular based self-healing- healing agents are replenished via a circulatory network. d) Assessment of healing efficiency is based on the recovery of properties. For structural materials, properties of interest including fracture toughness, fracture energy, stiffness, ultimate strength, and tear strength.

Research Plan

Phase I - Microcapsule Based Self-Healing: The first part of the proposed research effort will focus on development of microencapsulated materials for self-healing of composite sub-structure damage due to blast loading. In preliminary work, we have studied the low velocity impact of self-healing composite panels (Fig. 2). Impact damage ruptures the microcapsules, releasing healing agent into the cracked regions. The large-scale damage induced by high-speed detonation presents several new technical challenges that we will need to address. As the size scale of damage increases, the volume of available healing agent needs to increase, but there are practical limits to the size and concentration of the capsules. We will screen and select new

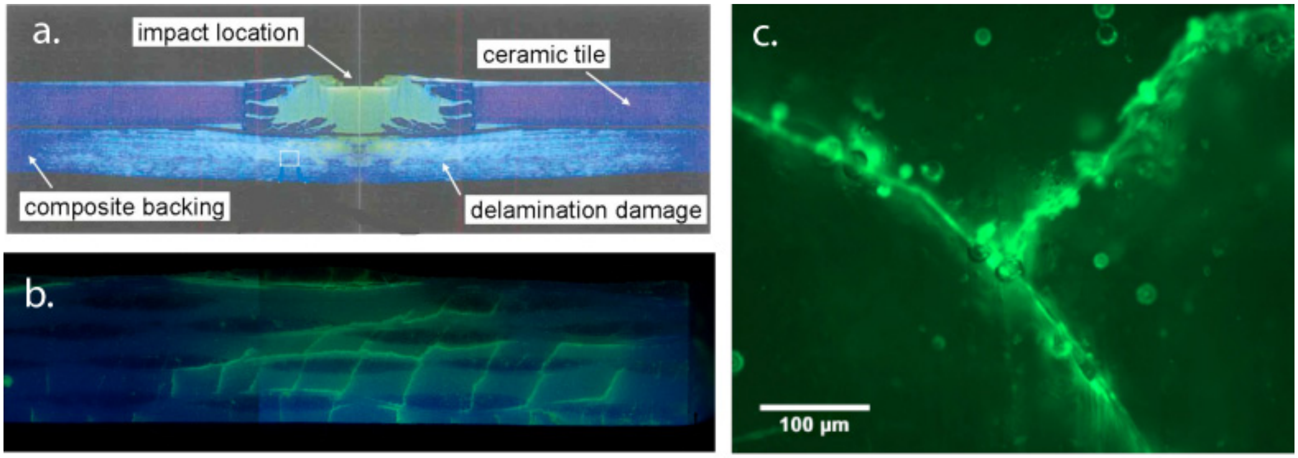

Fig. 2. Release of microencapsulated healing agent triggered by impact damage. a) Impact damage to composite substrate in ballistic armor. b) Fluorescently highlighted delamination damage in composite. c) Magnified image showing rupture and release from microcapsules.

microencapsulated polymer systems that are capable of expanding and filling open crack volumes, delaminations and punctures. Preliminary work shows polyurethanes are excellent candidate materials. Seamless integration of the self-healing functionality into the structural platforms of interest for damage mitigation will be critical. The focus of the next stage of the project will be to determine the mechanical recovery of the composite after healing. Although fluorescent imaging of crack patterns can tell us the space filling ability of the self-healed material, it does not provide information on the mechanical recovery. We will develop an experimental protocol based on compression after impact (CAI) to obtain quantitative data on the mechanical healing of impact damage.

<u>Phase II- Self-Healing via Microvascular Networks:</u> Longer-term research will explore the use of composites with internal circulatory networks to provide continuous healing of large-scale structural damage (Fig. 3). In contrast to the microencapsulated approach, this strategy allows the supply of healing agent to be replenished indefinitely in a vascular network. Hence, a much larger volume of healing agents can be delivered to the damage sight, which should enable healing of larger damage regions. In addition, the microvascular approach allows for multiple healing cycles in the same location. We propose to design and integrate microvascular networks with a composite substructure. We will screen different healing chemistries and identify combinations that provide the most efficient delivery and healing of large-scale impact damage.

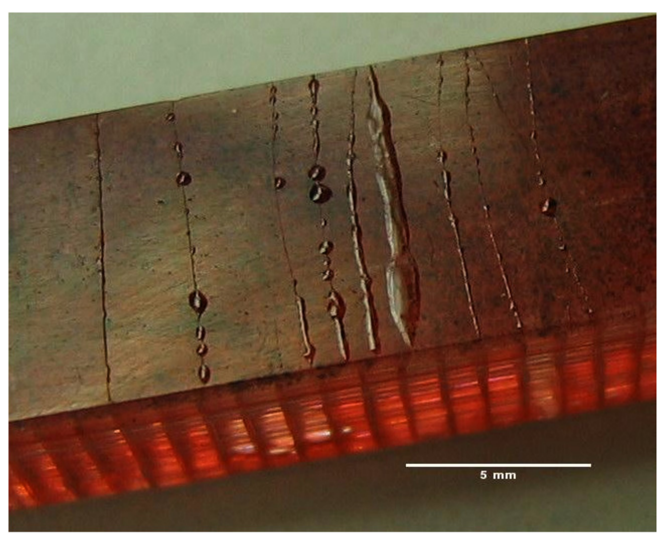

Fig. 3 Self-healing coating on a substrate with a three-dimensional microvascular network.

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Budget Estimate –year 1

A $110,000 budget is requested to complete the tasks described above. Individual costs are estimated in Table 1. The largest portion of this money will be utilized to support a postdoctoral research associate at the Beckman Institute. Additional funds are allocated for PI summer salary, travel, consumable materials, supplies, and microscopy services.

Table 1. Budget Summary

Item	Cost
PERSONNEL	
a. Postdoctoral Research Associate, 12.0 months @100%	40,000
b. PI (Sottos), 0.25 month @100%	3,883
c. Benefits (33.06% of a+b)	14,508
Total Salaries and Benefits (a+b+c)	58,391
MATERIALS, SUPPLIES & SERVICES	
d. Raw materials, chemicals, consumables, lab supplies	8,000
e. Beckman Microscopy Suite ($45/hr user fee)	2,000
TRAVEL	
f. Travel for one scientific meeting	2,000
TOTAL DIRECT COSTS (a+b+c+d+e+f)	70,391
INDIRECT COSTS (56% of Direct Costs)	39,414
TOTAL BUDGET REQUEST	**109,810**

Synthesis and Evaluation of Self-healing Concrete Under Blast Loading Conditions

Arijit Bose
Department of Chemical Engineering
University of Rhode Island
Kingston, RI 02881

PROBLEM: Concrete used in, buildings, bridges and highways are expected to last for decades without damage or loss of structural strength. However, because of environmental exposure and repeated cyclic loadings, defects and cracks develop in these materials. If these cracks are allowed to stay after they have been initiated, the mechanical properties of the concrete get degraded substantially. Moisture migration through these cracks also provides a pathway for corrosion of rebars. There is a substantial need to produce 'smart' concrete materials that have a capacity to self-repair cracks, thus leading to materials that can withstand blast loading conditions without catastrophic or premature failure.

RESEARCH STRATEGY: The key concept is that the concrete will have hollow, closed fillers that contain liquid that interacts with the concrete either physically or chemically. When a crack moves through the concrete, it will break the filler wall, release its contents, and allow it to flow into the crack by capillary action. The liquid in the filler is chosen to interact with the concrete surface, and solidify either by evaporation of solvent, or by chemical reaction. This will permit the crack to get at least partially filled by a solid, allowing rapid recovery of the mechanical properties as well as blockage of moisture diffusion pathways of the concrete. These concepts are illustrated in Figure 1.

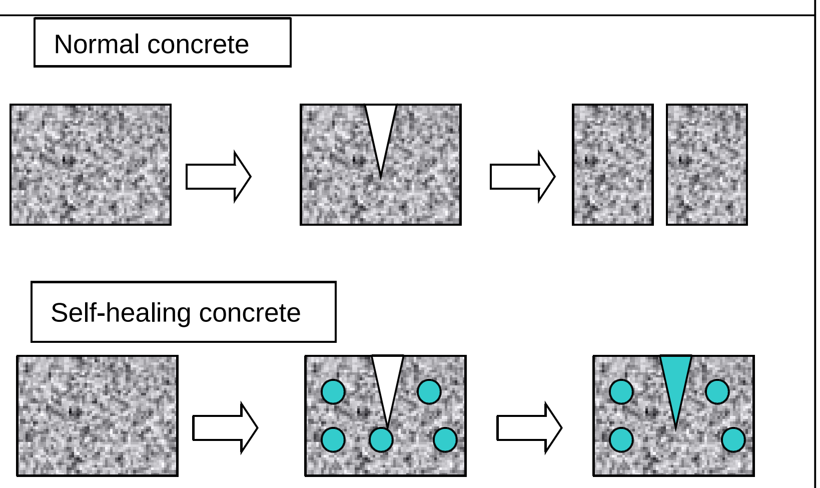

Figure 1: Illustration of difference in expected response between normal and self-healing concrete when a crack impinges on the sample.

Through RIDOT funding, our laboratory has already initiated a comprehensive program, beginning in the summer of 2007, for the preparation and characterization of self-healing concrete. The new funds will permit us to characterize our samples under blast loading conditions that are characteristic of explosions. These dynamic loading experiments will be conducted in the Shukla laboratory at URI. Michelle Pelletier, a graduate student in the Chemical Engineering department will work on this project.

BUDGET – 1 year

Item	Budget
Stipend, Level 1 graduate student	22350
Tuition, in-state	7238
Fringe	2044
Materials and supplies (includes microscope time, costs for modifications to equipment, machining)	5000
Indirect costs (49% of all costs except tuition)	10559
Total	**51035**

Total Energy Analysis of Model IED Devices

Profs Otto J. Gregory, Hamouda Ghonem, Jimmie C. Oxley,
URI, Chemical Engineering, Mechanical Engineering & Chemistry Departments

Potential Scientific Impact: One of the first questions bomb scene investigators are asked are "How big was the bomb? What was it?" While the general public is simply curious, investigators need this information to attempt to find the perpetrators. Who had access to the material? What type of sales records should be sought? Where was the material stored or made pre-blast? Such questions are just now being asked of the bombing of the Pakistan Marriot. Analysis of the energy signature suggests a certain size and such a size suggests a homemade explosive. The project will involve high-strain-rate fragmentation analysis, materials characterization, numerical simulation of pressure wave propagation, and energy of impact calculations [1-4]. It will leverage already established fragmentation and characterization of small IED's, pipe bombs ("Microstructural Characterization of Pipe Bomb Fragments", <u>Materials Characterization</u> in press, 2009). The damage signature left in structural materials following a blast will be correlated with the intensity of the event. Signatures are expected to be manifest in work hardening, residual ductility and toughness using well-established techniques such as microhardness, quantitative metallography, uniaxial tensile tests, etc. In the short term, such characterization of blast signatures will provide pervasive field gauges for terrorist events. On the basic science level, all the energies associated with the IED blast will be accounted for in order to develop constitutive equations accurately describing static as well as dynamic extreme loadings (temperature, strain) on structural materials. Boundary conditions for shock loadings (pressure) and thermal excursions must be mapped as a function of various threat materials (military versus HME). Energy and pressure wave spreads and methods of explosion energy absorption will be identified from small-scale tests. Scaling effects will be examined. The constitutive equations and boundary conditions derived from this study are essential in the development of 2D and 3D models for simulation of structural performance before and after proposed mitigation solutions. These characterizations will also permit post-blast assessment of structural integrity of large-scale engineering systems (bridges, tunnels, dams, etc.) critical to the U.S. infrastructure.

Technical Approach: Initially, commercially available, steel pipes with standard end caps will be initiated in a vertical orientation, with the detonator threaded through holes drilled in the top end cap. Contained and uncontained experiments will be done to determine the energies for the constitutive equations and boundary conditions. Initially, the fragments, pipes will be initiated in 55-gallon drums, either filled with sand or ground cornhusks. Pipes will be filled to volume with black powder, WC 870 (DB); IMR-PB (SB); Red Dot (DB); Winchester Action Pistol (DB); Bullseye (DB); where SB and DB indicate single (nitrocellulose) or double-base (nitrocellulose and nitroglycerin) powder. Improvised formulations made of sodium chlorate and aluminum paint will also be tested. Nitromethane will be used as a reference material. Efforts will be made to collect as many of the fragments as possible and the number and weight of the fragments will be recorded. Recovered pipe fragments will also be examined by scanning electron microscopy (SEM) and optical microscopy using standard metallographic preparation techniques [5]. The threshold energy levels associated with the different propellants and levels of deformation of the phases (microconstituents present) is shown in Figure 1. Low-power propellant fillers, released only enough energy to deform both the α-ferrite and pearlite colonies whereas higher-power fillers showed twin formation. In the devices employing very high energies, the pearlite colonies were severely distorted and formed continuous bands extending beyond a single ferrite grain or pearlite colony. Fragment analysis from the pipe bomb detonated with very high-energy explosives showed the generation of a significant number of slip bands. The extent of plastic deformation prior to fracture will be determined by measuring the wall thickness of the fragments in the radial direction. By comparing the ratio of the fragment wall thickness to that of the wall thickness of an unexploded pipe the engineering radial strain, or plastic strain, prior to fracture will be estimated (Fig. 2). Microhardness measurements will be made across the through-thickness of the wall of as-received fragments. This will provide considerable insight into the extent of work hardening in the individual fragments as a function of radial position (Fig 3).

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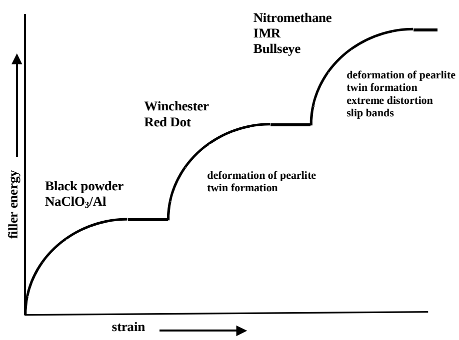

Fig1. Microstructural changes observed in pipe bomb fragments

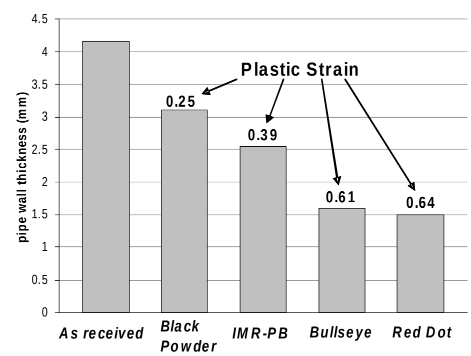

Fig 2 Changes in pipe bomb wall thickness as a function of propellant energy.

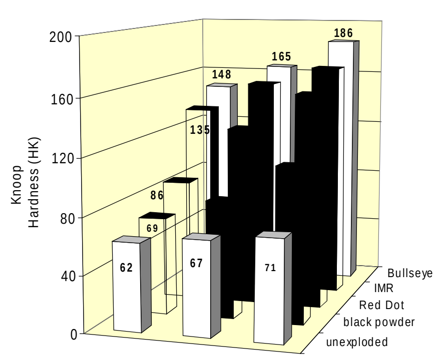

Fig 3. Microhardness variations of pipe fragments as a function of radial position, i.e. microhardness variations within wall of exploded pipes.

POTENTIAL NEW START MITIGATION 4

Modeling Heterogeneous, Graded and Microstructural Materials
Under Severe Dynamic Loadings

Martin H. Sadd
Mechanical Engineering Department
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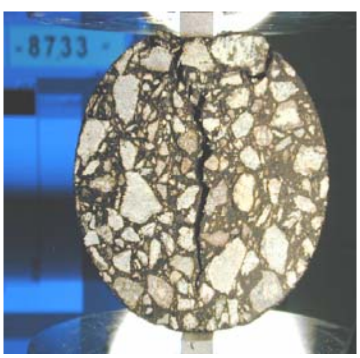
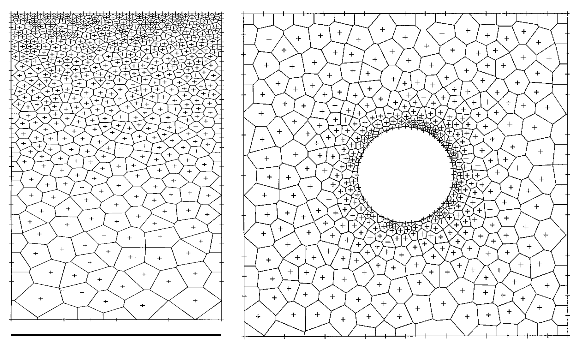
I wish to propose a computational modeling project that will simulate the dynamic response of materials that contain heterogeneity with microstructures that provide improved failure response. Based on past studies, materials that have shown promise in absorbing high mechanical/thermal energy have commonly involved particulate, fiber or layered reinforced materials and porous and cellular solids. By using computational methods, such materials can be numerically generated with varying degrees of microstructure: e.g. particle size, shape, and distribution; porosity fabric; cellular geometry; gradation; etc. Employing computational finite and discrete element methods enables determination of relationships between applied dynamic loadings and local failure mechanisms associated with the material's microstructure. Such micromechanical failure mechanisms will lead to the establishment of damage mechanics models that would be typically connected to: particle/matrix debonding, particle and/or matrix cracking, layer debonding, cellular collapse, etc. Of particular interest is to determine new information on how internal microstructure can be best created to provide better macro dynamic response under extreme loadings. Through a detail series of simulations, useful material designs can be established that will lead to improved overall structural designs for mitigation. It is expected that such modeling efforts would be done in combination with current experimental studies (Shukla and Rousseau) thereby providing a more comprehensive investigation into the mitigation problem. Observed data will provide guidance and characterization information for the modeling efforts and theoretical concepts will provide input as to what experiments to conduct.
The figures shown below illustrate some of my past modeling work dealing with particulate composites (asphalt concrete failure) and graded cellular solids.



Asphalt Sample Failure

Computational Model Prediction



Graded Cellular Materials

Mechanically Stabilized Earth (MSE) Geosynthetic Systems: Blast-Protective Construction Design and Shock Mitigation for Infrastructure Applications

George Veyera
URI, Civil Engineering

Introduction

The events of 9-11 and other recent terrorist activities have led to the formation of the Department of Homeland Security, and a very clear recognition of the need for appropriate technology to prepare for and respond to potential terrorist threats directed at the U.S. In particular, the vulnerability of our nation's infrastructure elements (transportation systems, water distribution systems, communications, systems, web, etc.) underscores the need for comprehensive, creative solutions to protect, repair, and stabilize these systems as necessary, while considering an ever-changing potential threat matrix. Terrorist attacks could severely cripple the U.S. infrastructure and our ability to effectively meet the needs of our population. Clearly there is a need to have available appropriate technology to maintain and restore operational stability of our nation's infrastructure in the event of an attack. The proposed work described herein is directed at applying just such technology *(geosynthetics)* to one specific aspect of our infrastructure: the transportation systems component (embankments, slopes, bridges, bridge abutments, foundations, retention structures, piers, columns, etc.) with an extension to buildings, airports, and roadways.

Background

Conventional military applications of blast-resistant protective construction design traditionally have relied on heavily reinforced, thickened concrete structures, with redundant rigid concrete reinforcement systems. In addition, in the civilian sector work has been conducted to experimentally study the resistance of traditional reinforced concrete and steel structural elements such as bridge decks, bridge piers, buildings, etc., to intentional or accidental blast loadings.

Extensive practical experience exists worldwide with mechanically stabilized earth (MSE) systems for various static applications as alternatives to traditional designs. However, experience with the dynamic loadings, especially those due to explosions, with MSE systems has been far more limited to date. The military has been incorporating MSE construction as a part of protective measures for storage facilities containing ammunition and ordnance, which has proven to be a successful alternative. The private sector has been primarily interested in the dynamic resistance and behavior of MSE systems subjected to earthquake loadings; however, a clear need exists to extend this research to include blast loading effects.

MSE systems incorporate *geosynthetics*, a novel polymeric-based class of engineering construction materials, with abundantly available earth materials - soil and rock. Geosynthetics are manufactured engineering materials made of various polymers *(Polyethylene [PE], Polypropylene [PP], polyester [PET], polyamide [PA], polystyrene [PS; expanded-EPS, extruded-XPS) and polyvinyl chloride [PVC]*, and come in several forms, including two-dimensional grids, woven and nonwoven fabrics, randomly oriented discrete polymeric inclusions, and three-dimensional blocks. The combination of geosynthetics and earth materials produces a unique synergistic system that provides engineers with a proven alternative for static applications. The use of MSE for dynamic loading conditions has attracted considerable interest in recent years, and this application is on the cutting edge of technology with enormous potential benefits in both the military and civilian arenas.

MSE systems using geosynthetics have distinct advantages over traditional construction approaches because of the polymeric materials present, including:

- Geosynthetics are engineered (manufactured) construction materials; therefore desired properties can controlled;
- Geosynthetics can be produced that are lightweight and have high ultimate strengths:
    - Geotextiles – ~1000 kN/m (68 k/ft)
    - Geogrids – ~30 kN/m (2 k/ft)
- Variable stiffness (function of polymer type and product configuration);
- Flexible energy absorbing system especially for seismic and blast loading;
- Ability to absorb high amounts of energy before collapse (i.e. DOD ECM – Earth Covered Magazine and Ammunition Storage Structures);
- Ability to absorb shrapnel fragments from explosions;
- Can sustain large deformations and maintain system integrity;
- Large strains to failure for polymer materials (tens to hundreds of percent) compared to traditional construction materials (i.e. concrete, steel, wood, etc.);
- Provides a desirable ductile localized failure mode;
- Can accommodate large differential settlements;
- Works with most locally available soils, so specific fill materials do not need to be imported;
- Ease of construction and does not require highly skilled labor;
- Rapid construction using locally available earth materials with readily available geosynthetic polymeric materials; and
- A cost-effective economical alternative.

Several useful applications of MSE technology for blast-protective infrastructure design and shock wave mitigation can be identified, including:

- Protective construction for existing structural elements by MSE retrofit;
- Expedient repair of damaged structural elements after an explosion;
- Alternative advanced technology to be incorporated in new construction for blast protection;
- Shock wave attenuation barriers.

Clearly there is tremendous potential in developing an understanding of MSE systems subjected to high-energy explosive loadings as an important alternative to traditional construction methods for blast-protective design. Civilian applications include key elements of critical infrastructure protection such as bridge abutments, retention structures, foundations, embankments, structures, etc. MSE technology provides a new approach for these applications. The proposed research using MSE technology will provide a fundamental understanding of MSE technology under high strain rate loadings from explosive detonations.

Proposed Research

The overall approach is for a research program that will involve a number of integrated phases over several years, including various aspects of:

- Scaled explosive loading tests of specific MSE configurations and variations;
- Computer modeling of dynamically loaded MSE systems (FEM; FDM);
- Development of appropriate material (constitutive) models;
- Optimization of MSE system configuration for maximum effectiveness (may be specific application-dependent) for shock wave mitigation and performance;
- Extensions to other infrastructure system components involving transportation systems and structural design; and
- Applications to large-scale field explosive tests.

The proposed research program dovetails nicely with the research of Gregory and Ghonem for MSE-soil-structure-interaction modeling, and there will be direct integration of this research program with their work. The research proposed herein is directed at the first phase, which involves small-scale field explosive loading tests and is briefly described below.

Phase One – Small Scale Field Blast Tests of MSE Systems

The initial phase is designed to characterize and develop an understanding of specific MSE systems and variations subjected to explosive loadings and will probably require about 2 years of testing and analysis to complete. It is anticipated that tests will be conducted at the FM Global, Johnston, RI, explosives bunker test facilities. The FM global connection will also be useful in developing risk assessment models for the applications that this research is directed at. This phase will involve the design, construction, and instrumentation of select MSE systems subjected to blast loadings with variations as described below.

A detailed literature review will be conducted to assess current experience with blast protective construction approaches. The main body of experience has been with military application. There also has been some work done for civilian applications. However, nearly all investigations have examined traditional construction materials, with limited experience using earth reinforcing elements such as steel and polymeric materials.

The field work will examine the effects of a blast loading on specific MSE systems and configurations. The MSE system will consist of layers of compacted soil and geosynthetics (geotextiles, geogrids, and a mixture of soil and discrete randomly oriented polymeric materials). These are resilient and flexible composite systems that can be configured many different ways. Initial tests will be used to examine the basic blast attenuation behavior of the constructed reinforced systems, and gain insight into their response characteristics.

The MSE system configurations will be instrumented to obtain specific performance data and measurements before, during and after a blast loading. Measurements will include near field blast pressure, multi-axial acceleration and spatial variation of shock wave attenuation within each MSE system, ultimate strength, stress-strain behavior, deformation at failure, yield strain, failure strain. It is anticipated that real-time high speed photography will also be used during these events. Candidate field models will include reinforced embankments, retention structures, and a mitigation barrier structure to protect traditional materials (i.e. a bridge abutment, concrete pier, concrete wall, etc.).

With this understanding in hand, tests will progress to include refinements and improvements to the MSE structure such as variations in the specific geosynthetic polymer used, system configuration (layering, spacing, length, anchorage, etc.). Also variations in explosive charge parameters (yield, shaped, standoff distance, etc.) will be examined. Clearly the effect of a single blast is very much of interest; however, the influence of multiple blast loadings will provide an understanding cumulative damage to the system (CDA - cumulative damage assessment) and will also be examined. It will be of interest to also bring each of the reinforced systems to ultimate failure to develop an understanding of the mechanisms in involved.

The results of these tests will be available to develop constitutive modeling approaches that incorporate dynamic system response. Such relationships will be useful in FEM/FDM modeling efforts that involve MSE systems, shock wave mitigation characterization, failure prediction, and structural response. The combined efforts of this work along with that of Gregory and Ghonem will provide guidance that will advance the state-of the-art in protective construction design for blast loading of civilian infrastructure systems.

BUDGET REQUEST:

Budget request for the first year is $100,000; it will be used as follows:

- Instrumentation;
  - Electronics (accelerometers, transducers, pressure gauges, strain gauges)
  - Electronic data collection system
  - Non-electronic tell-tale units
- Geosynthetic materials
  - various polymers
  - various product configurations
- Real-time photography of explosive loading events with high speed photography
- Field construction of MSE system and test set-up;
- Explosive materials, certified personnel for set-up and detonation, required permits, etc.
- Graduate student (1-2 MS)
- Faculty summer support
- Miscellaneous supplies
- Miscellaneous equipment
- Publication costs
- Domestic travel

White Paper

Engineered Structures for Mitigation of Very High Energy Explosive Damage by an AIKIDO APPROACH

Conducted by:

PI Dr Vilem Petr,* Co-PI Dr. Dave L. Olson, P.E.*, Co-PI Dr. Stephan Liu*, Dr. Eric Rinehart**, Dr. Donald Linger**,

* Colorado School of Mines,** Defense Threat Reduction Agency,

Submitted to:

Dr. Mary Ellen Hynes

Director of Research, Infrastructure & Geophysical Division Science and Technology Directorate
U.S. Department of Homeland Security, Washington DC,

Time Duration: **3 Years**

Total Amount: **$950,000**

Date of Submission: **November 10, 2008**

Engineered Structures for Mitigation of Very High Energy Explosive Damage by an AIKIDO APPROACH

BACKGROUND

The Colorado School of Mines (CSM), Mining Engineering Department is propose research in the area of developing engineered structural modules to manage and reduce the effect of very large, high energy explosive pressure waves acting on large man-made civil projects. It is proposed to do this through the use of the combination of engineered (civil composites) materials and energy deflection through specifically designed structural components. The proposed concept is shown in Figure 1. This proposal addresses a mitigation practice for large civil engineered structures such earthen dams and strategic road structures being attacked by terrorist using large semi tractor truck containing up to 30,000 lb of high explosives. The primary defense technology use of energy absorption material with proven capability to interact with the explosive shock waves to maximize the energy absorption material properties to mitigate the shock effects; and to maximize this absorption property by the use of separated composite heterogeneous layers specifically designed and layered to absorb energy; and to maximize the energy absorbing material capability by utilizing a fracturing and fragmentation capability to also absorb energy. The second energy absorption technique will utilize the interaction which will be designed to be an integral part of the system and will be a specifically design pre-stress concrete module structure that will contain the mixture of composite layered modules. This shape pre-stressed concrete assembly will also physically deflect the remaining energy by directing the blast, fragments and energy about and around of the civil structure in non compromising directions.

This mitigating structure, made up of energy absorbing material that will be fragmented by the initial traveling explosive wave and then totally rejected by the reflected wave will be build on the top on the strategic structure. It will be either an integral part of a new design, or could be retrofitted.

TASKS and WORK STATEMENTS

The proposed research and development work will entail three primary tasks:

Task 1 Develop a summary of the physical testing data to date, utilizing the DNA/DTRA test data including the DNA experiments conducted at WES, for tests conducted with vehicles loaded with high explosives which were specifically planned to produce a large crater, to develop a data base of center size (emphasis on depth) for various amounts of explosive, heights-of-burst and type of geology.

Task 2 Develop a composite module section that achieves the best energy absorption and material fragmentation producing the best absorption of the explosively produced potentially damaging energy. The composite material layers will include the rubberized concrete, partially bonded granulated material, pumice loaded concrete and other potentially energy absorbing materials.

Task 3 Investigate and design a pre-stress concrete and optimum shape that will deflect the energy to non compromising directions. Very small scale explosive testing may be used to supplement the analyses and calculational program. Calculations will be used for the designs of experiments. The investigation will involve both computational and explosive laboratory tests to determine the effective shape and design of the pre-stress concrete reflector. The end of Task 2 will be a go no-go point to continue the project to a full scale design and demonstration.

Task 4 Develop design and demonstration of the modules of the composite section, the pre-stress concrete reflector section and the road at the 1/3 (150 lb size). This task will be large scale and components will be design and build to be easily and transported and assembled to the road section to be protected. The last task will require numerous subcontractors and will only be advance when Tasks 1 and 2 has demonstrated effectiveness.

DISCUSSION

Each component of the proposed integration has been tested at some scale and has proven to be effective in energy reduction. **CSM has experience in the effective use of composite energy absorbing materials, i.e., composite rubberized concrete CRC and the tubular rebar material. The use of natural highly porous material, i.e. pumice, is presently in use in ammunition storage containers and has proven to be highly effective. The proposed calculation tool is Autodyna, a well established FE code** having proven material models and explosive equations of state. The literature research has been done.

PROPOSED PERSONA

Dr Vilem Petr, Research Associate Professor, Department of Mining Engineering, Colorado School of Mines

Co-PI Dr. Dave L. Olson, P.E., Professor, Dist. Prof. of Physical Metallurgy, Department of Metallurgical and Material Engineering, Colorado School of Mines

Co-PI Dr. Stephan Liu, Professor, Department of Metallurgical and Material Engineering, Colorado School of Mines

Government Consultant: Dr. Eric Rinehart, Chief Scientist, Test Division, Defense Threat Reduction Agency.

Government Consultant: Dr. Donald Linger, Senior Scientific Advisor, Advance Systems Concepts Office and former Director for Test, R&D Enterprise, Defense Threat Reduction Agency.

ESTIMATED PROPOSED COSTS

Task 1: **$ 60,000** (First year)

Task 2: **$ 140,000** (First year)

Task3: **$ 250,000** (Second year)

Task 4: The proposed budget for this task will be submitted after successful demonstration of Tasks 1 and 2. It is expected that this demonstration, pretest predictions and analyses will be on the order of **$ 500,000**. It is also proposed that due to the size of the experiment (~150 lbs) that it be conducted at Kirtland AFB's CHESTNUT test site using DTRA Test Division.(Third year)

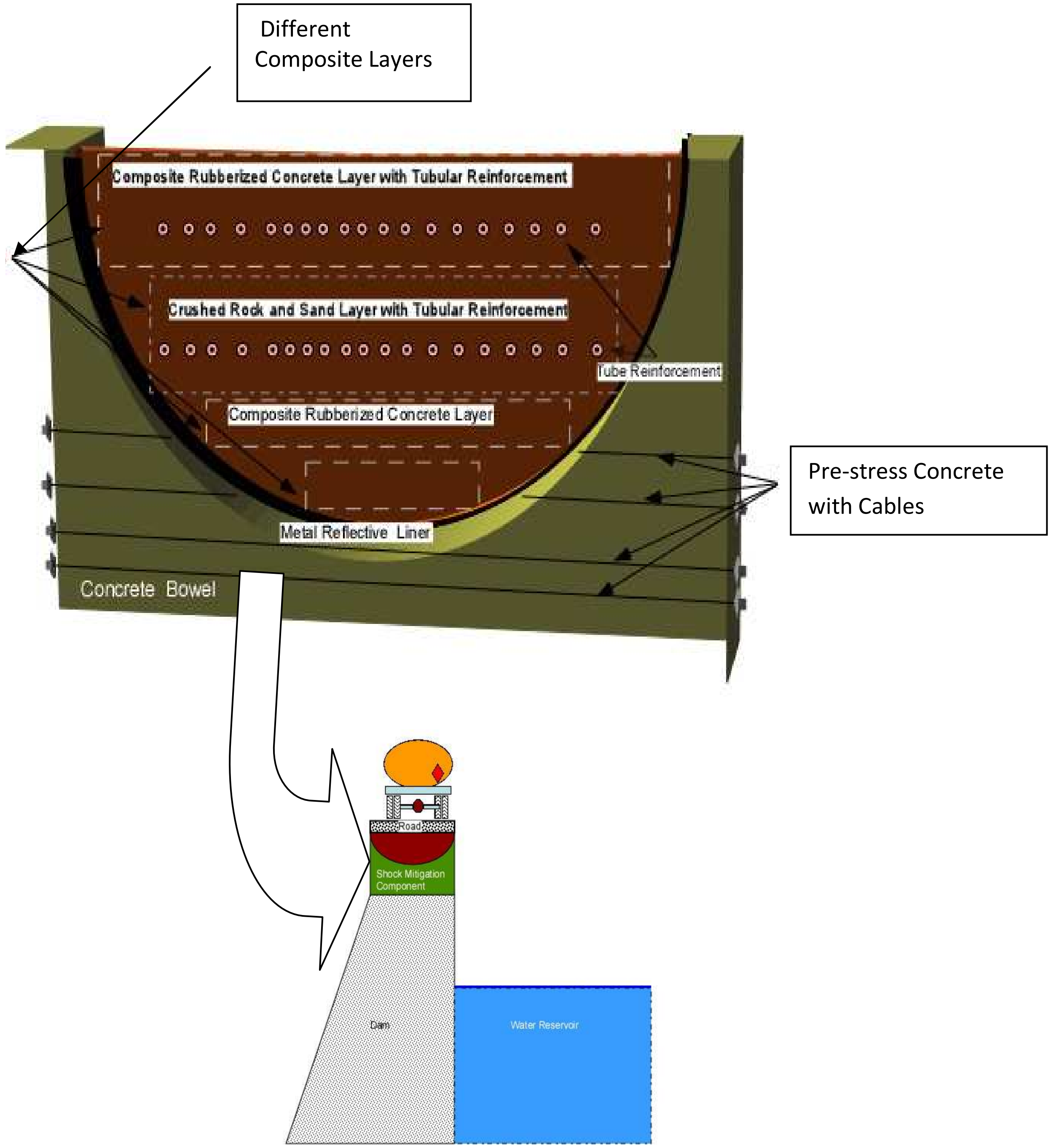


Figure 1. Concept overview of the Engineered Structures for Mitigation of Very High Energy Explosive Damage Reflector.